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RESEARCH ARTICLE

TRANSESTERIFICATION OF *JATROPHA CURCAS* L. SEED OIL TO BIODIESEL: AN UPDATE

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ABSTRACT

Jatropha curcas L. seed oil has been identified as one of the potential source of feedstock for biodiesel production which is a renewable energy. The oil cannot be used directly as fuel due to its high viscosity and therefore has to be processed to lower the viscosity. Transesterification is the best process adopted by many of the researchers for processing *jatropha* oil into biodiesel. The current review is intended to look at these different processes used by many of the researchers; considering the conditions that optimized the process used, comparing the yield and quality of the biodiesel produced with the standard properties prescribed by American Society of Testing and Materials (ASTM) standard. The use of subcritical hydrolysis or addition of micro amount of catalyst employed with supercritical transesterification has shown to reduce drastically the high reactant molar ratio, temperature and pressure associated with supercritical transesterification process. Heterogeneous transesterification of high free fatty acid (FFA) content jatropha oil assisted with ultrasonic irradiation reduces the reaction time and increase yield of biodiesel. All the transesterification processes used by many of the researchers gives high yield of biodiesel from *jatropha* oil or seed at various reaction conditions and the fuel properties falls within the ASTM standard specification. There is a need to carry out research on the economic analysis of the best processes that gives high yield at better reaction condition which can be employed in the production of biodiesel from *Jatropha curcas* L. seed oil at industrial scale.

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INTRODUCTION

The gradual depletion of the world petroleum reserves and the impact of environmental pollution as a result of using fossil fuels, the world attention have been shifted towards a source of renewable energy which will serves as an alternative to fossil fuels. Bio-fuels obtained from vegetable oils are promising alternative, because it has the following advantages; (a) it helps reduce carbon dioxide and other pollutants emission from engines and therefore environmental friendly (b) engine modification is not needed as it has similar properties to diesel fuel (c) it comes from renewable sources whereby people can grow their own fuel (d) diesel engines performs better on biodiesel due to its high cetane number (e) high purity of biodiesel would eliminate the use of lubricants (f) biodiesel production is more efficient as compared to fossil fuels as there will be no underwater plantation drilling and refinery (g) biodiesel would make an area become independent of its need for energy as it can easily be produced locally (Raphael *et al*., 2010).

Seeing the cost and edible oil consumption, threat to future food security, the use of non – edible oils for production of bio-fuels becomes significant. *Jatropha curcas* Linn is a small tree (shrubs) that practically grown under variety of agro – climatic conditions and is commonly found in most of the tropical and subtropical regions of the world (Singh and Saroj 2009). The oil obtained from *Jatropha curcas* Linn is non – edible oil and the oil content of the seed ranges from 30 to 35% by weight. Generally in all vegetable oils, the main constituent is triglyceride. The high viscosity and instability derived from triglycerides are the most challenging obstacles to the use of vegetable oil directly as diesel fuel. The high viscosity leads to unfavourable pumping; insufficient mixing of fuel with air contributes to incomplete combustion. Several processes have been developed to resolve the problems in recent years, such as transesterification, pyrolysis, blending with petrol diesel, micro-emulsification with alcohols and hydro-treatment (Shaofeng *et al.,* 2012). Transesterification is the most widely used process because the fatty acid alkyl esters (biodiesel) physical characteristics are similar to the existing diesel fuel. The vegetable oil is converted into fatty acid alkyl esters by the reaction of triglycerides with alcohol in the presence of

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catalyst. The yield of the esters depends on the reaction condition such as temperature, type and amount of catalyst, alcohol to oil ratio, agitation speed, reaction time, free fatty acid and moisture content of the oil (Endalew *et al*., 2011; Meher *et al*., 2013). Generally the composition and percentage free fatty acid contained in a vegetable oil depends on the plant species and on the growth condition of the tree (Meher *et al*., 2013). Therefore jatropha oil obtained from different places is bound to have different compositions and percentage of free fatty acid as shown by the works carried out by different researchers in Table 1. It can be seen that the different properties of the crude jatropha L. curcas oil varies with viscosity ranging from 8.72 cSt – 36.9 cSt, density 892 Kg/m^3 - 940 Kg/m^3, flash point 125^{o}C – 256^{o}C, moisture content 0.1 wt% - 6.2 wt%, free fatty acid (FFA) content 0.775% - 14%, oliec acid 12.8% - 44.7%, palmalic acid 4.2% - 18.97% and stearic acid 5.6% - 17%. Many researchers adopted different processes of transesterification of jatropha oil to biodiesel, all with the intention of lowering the cost of production, high yield of biodiesel and favourable reaction conditions. These processes includes, non catalytic transesterification using supercritical alcoholysis method, Catalytic transesterification, transesterification using enzymatic catalyst, and in situ esterification and transesterification of jatropha seed. The current review is intended to look at these different processes used by many of the researchers; considering the conditions that optimized the process used, comparing the yield and quality of the biodiesel produced with the standard properties prescribed by ASTM standard.

Transesterification without catalyst

Joon *et al*. (2011) carried out an overview of biodiesel production from jatropha oil by catalytic and non – catalytic approaches. The non catalytic transesterification reaction (without using any catalyst) requires high temperature (more than 250^{o}C) and pressure above the critical temperature of alcohol and is called supercritical method. At supercritical temperature and pressure the liquid alcohol will reach a critical point where liquid and gas becomes indistinguishable fluids, in which it would exihibits properties of both liquid and gas. It is able to penetrate to solid like gas and dissolve other materials into them as liquids, therefore a higher alcohol molar ratio is required to push the reaction forward (Leung *et al*., 2010). Joon *et al*. (2011) reviewed the works of Rathore and Madras (2007) who investigated the possibility of using the supercritical method on methanol and ethanol to produce biodiesel from crude jatropha oil containing 10% free fatty acid. An optimum condition of 50:1 alcohol to oil molar ratio under 20MPa at 300^{o}C was reported with maximum jatropha oil conversion of 70% and 85% after 10 and 40 minutes respectively. The conversion increased by 2.5% when ethanol was employed under the same optimum condition. When higher temperature of 400^{o}C was employed a higher conversion of 95% for both methyl and ethyl esters was reported. It was also reported that Hawash *et al*. (2009) used supercritical method to tranesterify jatropha oil with 2% free fatty acid under a mild condition of 320^{o}C, 8.4MPa pressure, 43:1 methanol to oil molar ratio and a 100% yield of methyl esters was reported within 4 minutes. The improvement of yield and conditions was due to the low free fatty acid content jatropha oil used, because high FFA content will generates more water via esterification reaction and thus hydrolyzing the esters produced from transesterification. It was noted that the major drawback of supercritical method or condition was that the methyl/ethyl esters are easily degraded in extremely high temperature (300^{o}C). Chen *et al*. (2010) extracted jatropha oil using supercritical carbon dioxide and then subjected to hydrolysis. The hydrolyzed fatty acid was further reacted with methanol under supercritical methylation (esterification), under 11MPa at 290^{o}C with 33% v/v of hydrolyzed oil to methanol and 99% of biodiesel was obtained in 15 minutes. In a similar work Ilham and Saka (2010) employed a two step process to produce biodiesel from jatropha oil but dimethyl carbonate was used instead of methanol in the second step. In the first step 217:1 molar ratio of water to triglycerides was used at sub-critical condition (270^{o}C/27 MPa) for the hydrolysis reaction for 25 minutes. They used excess water to ease the separation of the hydrolysed product from the water portion containing glycerol. The hydrolyzed oil portion in the form of fatty acid was esterified in supercritical dimethyl carbonate at 300^{o}C under 9 MPa for 15 minutes. A yield of 97% methyl esters was reported and more valuable glyoxal as a by-product instead of glycerol and water, the process is not affected by high FFA content of the oil. However the cost of dimethyl carbonate is more expensive compared to methanol/ethanol. The advantages of two steps supercritical method is that there is no purification step needed to remove catalyst, but the disadvantages of the process is the use of high temperature and pressure, and use of large amount of alcohol is required which increase the cost for large scale production. A schematic process diagram of a typical supercritical process is shown in Figure 1. The schematic process showed two parts; subcritical water (hydrolysis) treatment and supercritical methynation. Some of the researchers adopt both steps while others use only supercritical methynation; but it was observed that hydrolysis of the jatropha oil before supercritical methynation reduces the reactant to oil molar ratio and gives higher yield of biodiesel as reported in Table 2. Tang *et al*. (2007) carried out transesterification of jatropha oil containing 0.42% free fatty acid (FFA) under supercritical method, a yield of 20% methyl esters in 28 min was obtained, but the yield increase to 90.5% when micro – NaOH catalyst was introduced at the same condition. The best biodiesel was obtained using methanol to oil ratio of 24:1, micro – NaOH (0.8% w/w), temperature of 250^{o}C and pressure of 7.0 MPa. The introduction of micro-NaOH catalyst by Tang *et al*. (2007) improves the conversion, lowers the reaction temperature, and pressure, and lower reactant molar ratio compared to what other researchers reported in Table 2. Comparing the work carried out by Chen *et al*. (2010) and Ilham and Saka (2010) in Table 2 who both employed subcritical hydrolysis before supercritical methynation, the use of methanol by Chen *et al*. (2010) gives better reaction condition and yield compared to dimethyl carbonate used by Ilham and Saka (2010) with the exception of the pressure which was higher. It was observed that subcritical hydrolysis tends to lower the reactant to oil ratio in supercritical transesterification of jatropha oil. It can be seen from Table 2 that Hawash *et al*. (2009) reported the highest yield of 100% biodiesel in a short reaction time of 4 minutes at lower pressure, but used the highest temperature of 320^{o}C and high methanol to oil molar ratio of 42:1 which makes the process less economical based on the energy and materials employed.

Table 1. Properties of some jatropha oils used by researchers

Properties	Rahmath and Pogaku (2013)	Tiwari *et al.* (2007)	Olutoye and Hameed (2011)	Lu *et al.* (2009)	Sahoo and Das (2009)	Deng *et al.* (2011)	Antony *et al.* (2011)	Kumar *et al.* (2011)	Vyas *et al.* (2009)	Xin *et al.* (2010)	Org *et al.* (2013)
Density Kg/m^3	920	940	892	916	920	892	920	918	912	912	915.1
Viscosity cSt at 40°C	-	24.5	24.7	36.80	18.2	24.5	36.92	34.33	15	8.72	28.35
Flash point °C	236	225	-	164	174	225	256	186	125	125	190.5
Moisture content wt%	0.15	1.4	3.28	<0.1	-	5.2	6.2	-	-	0.135	-
Oleic acid %	33.90	12.8	44.7	35.28	43.5	41.17	43.1	-	-	42.1	44.5
Linoleic acid %	34.16	47.3	32.8	38.36	34.4	31.25	34.3	-	-	27.72	35.4
Palmalic acid %	14.07	11.3	14.2	18.97	16.0	15.18	4.2	-	-	16.09	13.0
Stearic acid %	6.39	17.0	7.0	5.60	6.5	6.25	6.9	-	-	6.44	5.8
Free fatty acid (FFA) %	-	14	7.23	5.5	1.9	5.25	14	0.775	5.25	5.235	1.01
Calorific value MJ/Kg	-	38.65	-	-	38.5	38.65	39.76	-	-	-	38.96

Table 2. Summary of supercritical transesterification of jatropha oil with optimized reaction Variables

Authors	Reactant	Initial FFA %	Molar ratio	Temperature °C	Pressure (MPa)	Time min)	X %	Comments
Hawash *et al.* (2009)	Methanol	2	43:1 (methanol to oil)	320	8.4	4	100	The use of high reaction temperature, lower pressure and oil with low FFA can give 100% conversion in shorter reaction time
Chen *et al.* (2010)	Methanol		3:1 (methanol to oil)	290	11	15	99	Subcritical hydrolysis of oil was employed before supercritical methynation, which lowers the reactant to oil ratio and gives high yield.
Tang *et al.* (2007)	Methanol	0.42	24:1 (methanol to oil)	250 (0.8 wt% micro-NaOH catalyst was added)	7.0	28	90.5	Operation with micro catalyst improves the conversion, lowers the reaction temperature, and pressure, and lower reactant molar ratio.
Rathore and Madras (2007)	Methanol	10	50:1 (methanol to oil)	300	20	10	70	High reactant mole ratio, increasing time of reaction increases the conversion of the oil to biodiesel
Rathore and Madras (2007)	Methanol	10	50:1 (methanol to oil)	300	20	40	85	
Rathore and Madras (2007)	Ethanol	10	50:1 (ethanol to oil)	300	20	10	72.5	High reactant mole ratio, increasing time of reaction increases the conversion of the oil to biodiesel. Ethanol is better than methanol
Rathore and Madras (2007)	Ethanol	10	50:1 (ethanol to oil)	300	20	40	87.5	
Rathore and Madras (2007)	Methanol or ethanol	10	50:1 (methanol or ethanol) to oil	400	20	40	95	Increase in reaction temperature increases the conversion of the oil into biodiesel
Ilham and Saka (2010)	Dimethyl carbonate	-	14:1 (dimethyl carbonate to oleic acid)	300	9	15	97	The use of dimethylcarbonate instead of methanol or ethanol and Subcritical hydrolysis of oil reduces the reactants to oil molar ratio, pressure and time of reaction and gives high yield.

X= fatty acid esters yield

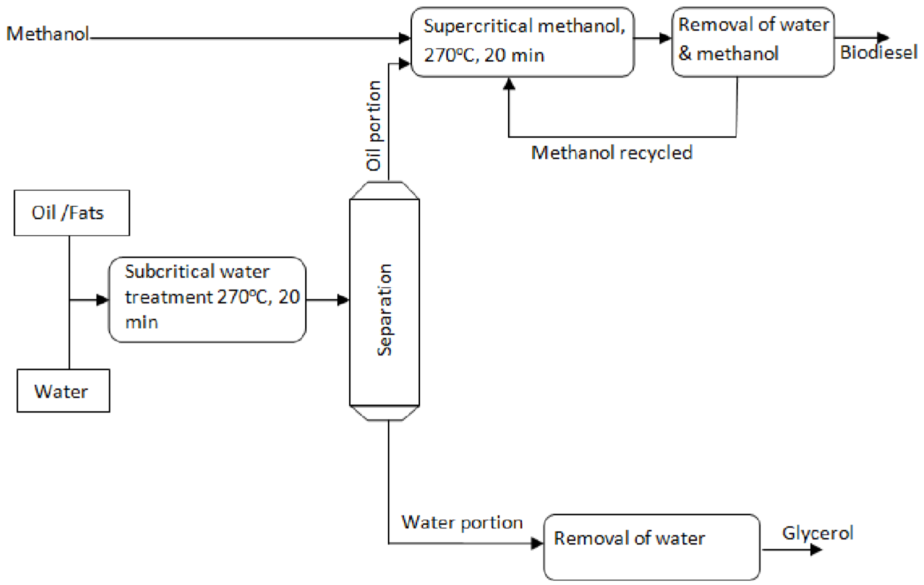

Figure 1. Schematic process of biodiesel production by supercritical Methynation

Alkaline catalyst transesterification

The most common method to produce biodiesel is alkaline or base catalyzed using alkaline such as sodium hydroxide (NaOH), potassium hydroxide (KOH) and sodium methoxide ($NaOCH_3$) (Kulkarni and Dabai, 2006). The base catalysed transesterification according to Schuchardt *et al.* (1998) and Tapane *et al.* (2008) follow three step reactions. In a pre-step the base catalyst reacts with the alcohol to produce alkoxides anions. The first step neucleophilic will attack the alkoxide anions on the carboxyl group of glyceride to form tetrahedral intermediate I, which will react with the second alcohol molecule to generate another alkoxide and form intermediate II. The two intermediates then rearrange to form acid esters as seen in Figure 2.

$$OH^- + CH_3OH \longrightarrow CH_3O^- + H_2O$$

Homogenous alkaline catalyst

Researchers (Helwani *et al.*, 2009, Kulkarni and Dalai, 2006) have found out that the use of homogeneous alkaline catalyst has the advantage of being cheap with high catalytic activity which produces high quality biodiesel in a short period of time. The homogenous alkaline catalyst has been proven to be faster than acid catalyst transesterification, but the only disadvantage is that the catalysts do not have the ability to convert free fatty acids (FFAs) into alkyl esters; hence oils that have FFA content > 1% transesterification would not be favourable using alkaline catalyst because the FFAs react with alkaline (saponification reaction) to form soap which prevent glycerol separation from biodiesel and therefore damage engines when used as fuel. The use of alkaline catalyst also produces more waste from purification, disposal and recovery of the catalyst is not possible.

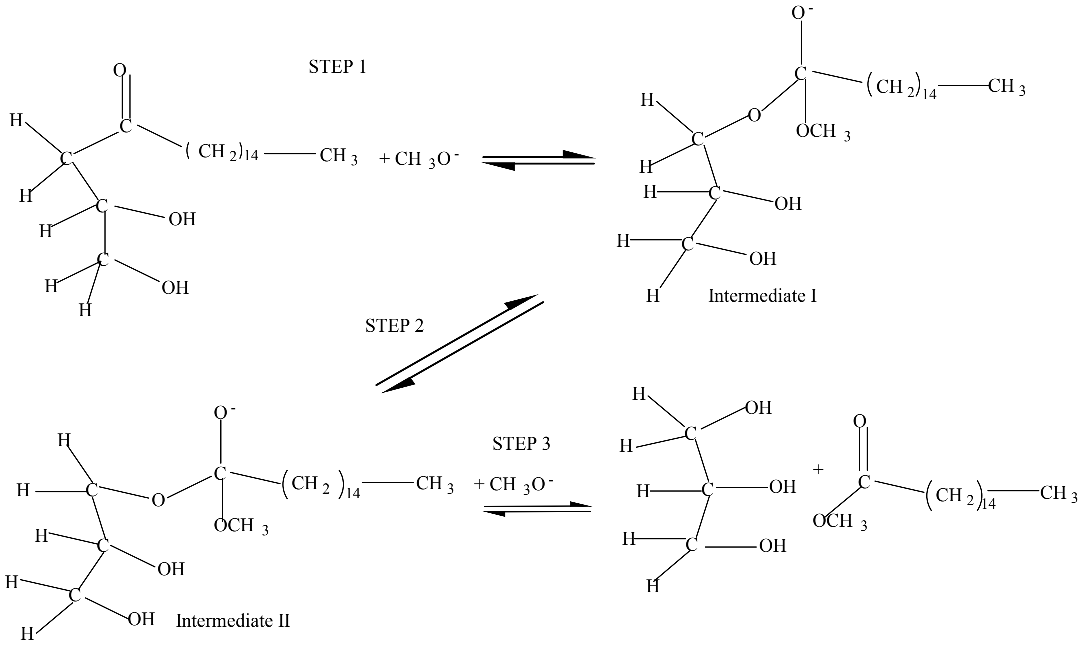

Figure 2. The mechanism of based catalyzed transesterification with the formation of two tetrahedral intermediates

Despite these problems associated with alkali catalyst, researchers (Chitra *et al*., 2005; Tang *et al*., 2007; Tapanes *et al*., 2008; Berchmans *et al*., 2013) and others reviewed by Silitonga *et al*. 2013 still uses alkaline such as NaOH and KOH as catalyst in the transesterification of jatropha oil with methanol and ethanol. The free fatty acids (FFA) contents of the jatropha oils used ranges from 3 to 19%. Chitra *et al.* (2005) used complete randomized design (CRD) method to optimize transesterification of jatropha oil with NaOH as catalyst and 98% yield was obtained at the optimum condition of 5.6:1 methanol to oil molar ratio, 1.0% w/w catalyst, at 60^{o}C temperature and in 90 minutes reaction time. The NaOH reduces the FFA content of the crude jatropha oil from 3% to 0.25%, but another step was added to remove the sodium salt after the reaction. Tapanes *et al*. (2008) mixed NaOH catalyst with methanol or ethanol to form methoxide/ethoxide, which was used for the transesterification of jatropha oil. The yield of methyl esters obtained was 96% which is lower than the yield obtained by Chitra *et al*. (2005), but the time of the reaction was 30 min three times faster and a lower temperature of 45^{o}C as shown in Table 4, while the methanol to oil ratio of 9:1 and 0.8% w/v of catalyst were used. When ethanol was used the yield dropped to 93% under the same condition with the rate constant lower than that of methanol. They concluded that it is more difficult to breakdown molecules of ethanol to form ethoxide anions as compared to breaking of methanol to form methaoxides anions. In contrast, Asakuma *et al*. (2009) pointed out that transesterification process occurs via transition state when the alkoxy group attacks the carbon of the group, an intermediate polygonal ring is form and predicted lower activation energy is acquired when a longer chain alcohol form larger polygonal ring; which means that longer chain alcohols are suitable to be used to produce alkyl esters of biodiesel. When the optimum conditions used by Chitra *et al*. (2005) was upgraded to pilot plant scale the average biodiesel yield is 96%, the production capacity was 250 litres per day.

Berchmans *et al*. (2013) investigated the transesterification of mixture of jatropha oil (5.5% of FFA content) and waste cooking oil (0.45% FFA content) using potassium hydroxide as catalyst. The FFA content of the mixture (1:9 of jatropha oil to waste food oil) was about 1% prior to transesterification. The process was carried out at 50^{o}C in 2 hrs using methanol to oil ratio of 6:1, a stirring speed of 900 rpm, 1% w/w of KOH to oil and a highest conversation of 97% was reported. Rathore and Mandras (2007) also carried out a synthesis biodiesel from edible (palm oil and groundnuts oil) and non-edible oils (pongmia pinnata and *Jatropha curcas*) in supercritical methanol and ethanol without using catalyst from 200 to 400^{o}C at 200bars, and enzymatic synthesis with Novozym-435 lipase in presence of supercritical carbon dioxide. The results showed that very high conversion (> 80%) were obtained within 10 minutes and nearly complete conversion were obtained within 40 min for synthesis of biodiesel in supercritical alcohols at 1:50 oil to methanol/ethanol molar ratio. However, conversion of only 60 – 70% was reported in the enzymatic synthesis after 480 minutes. Hailegiorgis *et al*. (2013) used *Jatropha curcas* seeds with base catalyzed methanol and ethanol to produce biodiesel using in – situ transesterification assisted by benzyltrimethylammonium hydroxide (BTMAOH) as a phase transfer catalyst (PTC). Phase transfer catalyst is a powerful technique to enhance reaction between two or more sparingly miscible phase. They reported that in – situ transesterification reaction rate was enhanced with the use of BTMAOH as a PTC and biodiesel was formed in relatively shorter time compared to the reaction in the absence of PTC. The reaction parameters were optimized using response surface methodology (RSM) and the optimum conditions were shown in Table. It can be seen from the results that at optimum reaction conditions, a good agreement between the yield of biodiesel obtained experimentally and that predicted by the model equation. Also the biodiesel yield obtained using in situ ethanolysis was higher as compared to the yield obtained using in situ methanolysis. From the studies carried out by Vyas *et al*. (2009) and Deng *et al*. (2011) as seen in Table 4, they used jatropha oil of the same free fatty acid content with different catalysts. Although Deng *et al*. (2011) used mild reaction conditions compared to those of Vyas *et al*. (2009), still recorded higher yield of biodiesel which shows that the Mg-Ag hydrotalcite catalyst has higher catalytic activity than the . KNO_3/Al_2O_3 used by Vyas *et al*. (2011). Also from Table 4, Yun *et al*. (2013) and Zanette *et al*. (2011) produce biodiesel from jatropha oil of comparable free fatty acid contents. Although Zanette *et al*. (2011) used severe conditions of higher reaction temperature, high methanol to oil molar ratio, longer reaction time and higher stirring speed but still reported a less biodiesel yield compared with Yun *et al* (2013). This shows that the catalyst (Na_2SiO_3) used by Yun *et al*. (2013) has higher catalytic activity compared to KSF Clay and Amberlyst 15 used by Zanette *et al*. (2011). Also the use of microwave irradiation employed help in overcoming the mass transfer problems leading to higher conversion of jatropha oil to biodiesel.

Comparing the process condition of Chitra *et al*. (2005) and Kian and Suhaimi (2012) in Table 4 which have almost the same yield of biodiesel, although the FFA content of the oil used by Chitra *et al*. (2005) is slightly higher than that used by Kian and Suhaimi (2012), the homogeneous catalyst (NaOH) used by Chitra *et al*. (2005) at milder conditions of temperature, reaction time, lower methanol to oil molar ratio and less amount of catalyst is better compared with the conditions employed by Kian and Suhaimi (2012) using heterogeneous catalyst Al_2SiO_3(zeolite). It can be concluded that the process adopted by Chitra *et al*. (2005) is more economical based on the energy, time, amount of alcohol and catalyst used. It can be seen from Table 4 that a biodiesel yield of 94% was reported by Umer *et al*. (2010) and Olutoye and Hammed (2011) both using heterogeneous catalyst. Although the FFA of the oil used by Umer *et al*. was not given, the transesterification conditions adopted by them are very mild compared with those of Olutoye and Hammed. This indicates that the catalyst ($NaOCH_3$) used by Umer *et al*. (2010) has higher catalytic activity than Mg-Zn/Al_2O_3 used by Olutoye and Hameed (2011). Therefore Umer *et al*. (2010) process is more economical compared to those of Olutoye and Hameed (2011) based on the energy, time and materials used in the process. Comparing the work of Endalew *et al*. (2011) with that of Kafuku *et al*. (2011) who used the same condition of reaction temperature, reaction time, stirring speed and methanol to oil molar ratio, also have comparable oil FFA of 9 and 8.14%, and amount of catalyst 5 and 3% respectively, but recorded different biodiesel yield as seen in Table 4.

Table 3. The optimum conditions for production of fatty acid methyl and ethyl esters

	Optimum value for FAME	Optimum value for FAEE
Mol of BTMAOH to NaOH	1.42	1.62
Mass of NaOH to jatropha seed (%)	1.52	1.38
Mass of methanol (ethanol) to jatropha seed	5.92	6.5
Reaction temperature °C	37.62	34.9
Reaction time (min)	103	92
Predicted optimum FAME yield (%)	91.75	-
Experimental optimum FAME yield (%)	89.8 ± 0.7	-
Predicted optimum FAEE yield (%)	-	99.74
Experimental optimum FAEE yield (%)	-	99.4 ± 0.4

FAME = fatty acid methyl esters FAEE = fatty acid ethyl esters

Table 4. Summary of alkaline catalyst transesterification of jatropha oil

Authors	Initial FFA %	Final FFA %	Alkaline catalyst	Time (min)	Reaction temp. (°C)	Stirring speed (rpm)	Methanol/oil molar ratio	Catalyst amount	X (%)
Tapanes *et al*. (2008)	-	-	Homo. NaOH	30	45	300	9:1	0.8% w/v	96
Chitra *et al*. (2005)	3	0.25	Homo. NaOH	90	60	yes	5.6:1	1.0% w/w	98
Berchmans *et al*. (2013)	5.5	< 1	Homo. KOH	120	50	900	6:1	1.0% w/w	97
Zhu *et al*. (2006)	0.5	-	Hete. CaO	180	70	yes	9:1	1.5 wt%	93
Vyas *et al*. (2009)	5.25	-	Hete. KNO_3/Al_2O_3	360	70	600	12:1	6 wt%	87
Umer *et al*. (2010)	-	-	Hete. $NaOCH_3$	120	65	600	6:1	1% Conc.	94
Olutoye and Hameed (2011)	7.23	-	Hete. Mg-Zn /Al_2O_3	360	182	yes	11:1	8.86 wt%	94
Kian and Suhaimi (2012)	2.04	-	Hete. Al_2SiO_3 (Zeolite)	360	70	yes	20:1	5 wt%	97.8
Yun *et al*. (2013)	6.4	0.55	Hete. Na_2SiO_3	5	400 W, microwave radiation	250	11:1	4 wt%	92.8
Liu *et al*. (2010)	-	-	Hete $Ca(OH)_2/Fe_3O_4$	80	70	-	15:1	2 wt%	95
Taufig *et al*. (2011)	-	-	Hete. CaMgO and CaZnO	360	65	yes	15:1	4wt%	> 80
Deng *et al*. (2011)	5.25	0.35	Hete. Mg-Al hydrotalcite	90	45		4:1	1 wt%	95.2
Yee *et al*. (2011)	11.35	-	Hete. $SO_4^{2-}/ZrO_2/Al_2O_3$	240	150	-	9.88:1	7.61 wt%	90.32
Endalew *et al*. (2011)	9	-	Hete. CaO:$Fe_2(SO_4)_3$ or	180	60	300	6:1	5 wt%	100
			Hete. Li-CaO: $Fe_2(SO_4)_3$	180	60	300	6:1	5 wt%	100
			Hete. La_2O-ZnO	180	60	300	6:1	5 wt%	30
Badday *et al*. (2013)	10.5	_	Hete. HPA/AC	40	65 (assisted with ultrasonic energy)	_	25:1	4.23% w/w	91
Zanette *et al*. (2011)	6.5	-	Hete. KSF clay and Amberlyst 15	360	160	300	12:1	5 wt%	70
Kafuku *et al*. (2011)	8.14	-	Hete. SO^{2-}/SnO_2-SiO_2	180	60	300	6:1	3 wt%	97

X = fatty acid esters yield

Table 5. Properties of biodiesel compared with ASTM D6751 and EN 1424 specifications

Property	Jatropha (Biodiesel)	ASTM D6751	EN 1424
Viscosity (mm^2/s; 40°C)	4.8 ± 0.17	1.9 – 6.0	3.5 – 5.0
Cloud point °C	10 ± 0.1	-	-
Pour point °C	6.0 ± 0.2	-	-
Flash point °C	188 ± 3.0	93 min	120 min
Sulphur content wt%	0.011 ± 0.001	0.05 max	-
Acid value mgKOH/g	0.40 ± 0.03	0.05 max	0.05 max
Density (15°C) $Kg.m^{-3}$	880 ± 14.2	-	860 – 900

This may be due to the amount and the catalyst used, which suggest that the catalyst $CaOFe_2(SO_4)_3$ and Li-CaO: $Fe_2(SO_4)_3$ have better catalytic activity than SO^{2-}/SnO_2-SiO_2 used by Kafuku *et al*. (2011). The Ca_2O-ZnO catalyst has the least catalytic activity.

Heterogeneous alkaline – catalyst

In heterogeneous catalytic transesterification the catalyst remains in different phase (i.e solid, immiscible liquid or gaseous) Helwati *et al*. 2009. The process was included under the Green Technology due to its attributes such as (1) the catalyst can be recycled (reused), (2) there is no or very less amount of waste water produced during the process and (3) separation of biodiesel from glycerol is much easier, and also because the heterogeneous solid catalyst does not mix with the alcohols (methanol or ethanol), it becomes relatively easy to separate the catalyst from biodiesel and glycerol (Lee and Saka 2010). Therefore many researchers tried to adopt the process for transesterification of jatropha oil. Zhu *et al*. (2006) used calcium oxide (CaO) as heterogeneous base catalyst for transesterification of jatropha oil of free fatty acid content of 0.5%. They increase the basicity of CaO by immersing into ammonium carbonate and calcined at 900°C for 90 minutes. The transesterification was performed at optimum reaction temperature of 70°C, catalyst loading of 1.5%, reaction time of 150 minutes and methanol to oil ratio of 9:1. A highest yield of 93% of biodiesel was reported. When the reaction was allowed for more than 3 hrs they observed formations of white gel in the product which increase the viscosity of the biodiesel. Vyas *et al*. (2009) studied the transesterification of jatropha oil containing 5.3% FFAs using potassium nitrate (KNO_3) supported on Al_2O_3 catalyst (KNO_3/Al_2O_3). A biodiesel yield up to 87% was obtained in 360 minutes at 70°C with 12:1 methanol to oil molar ratio using 6 wt% catalysts. They also tested the reusability of the catalyst and reported that the conversion continued to decrease with the number of times the catalyst is reused, 72% conversion was recorded after the third reaction, subsequent runs showed poor activity of the catalyst. Granados *et al*. (2007) (study transesterification of sunflower oil with activated calcium oxide) pointed out that the dissolution of CaO does occur, even if the catalyst can be reused for several times without significant deactivation. They observed that catalytic activity of CaO is both on heterogeneous active site and homogeneous active species due to dissolution of CaO in methanol.

Vyas *et al*. (2009) study biodiesel production by transesterification of jatropha oil with methanol in a heterogeneous system using alumina loaded with potassium nitrate as a solid .catalyst. The effects of catalyst loading, molar ratio of methanol to oil, reaction temperature, agitation speed and the reaction time were studied. It was reported that at optimum condition of 12:1 methanol to oil molar ratio, 600 rpm agitation speed, 6 wt% catalyst (catalyst/oil), 360 minutes reaction time and at 70°C, a maximum yield of 84% conversion was obtained. The catalyst can also be used three times and still give over 70% conversions. The overall rate of reaction was determined and the experimental data were fitted with an n^{th} order equation of the form of Arrhenius law. $-r_A = \left(-\frac{dC_A}{dt}\right) = KC_A^n$

Where K is the reaction rate constant and C_A is the triglycerides concentration in the oil phase and n is the reaction order. The reaction order was found to be 0.5239, rate constant 0.00309 $ml^{0.25}mol^{-0.25}h^{-1}$, activation energy was 26.957 cal and frequency factor is 4.67. Umer *et al*. (2010) studied the production of biodiesel from jatropha oil using 1 % sodium methoxide ($NaOCH_3$) catalyst, with methanol to oil ratio of 6:1, mixing intensity of 600 rpm at 65°C for 120 minutes. A maximum yield of 94% biodiesel was reported. Also the quality characteristics of the biodiesel were in agreement with ASTMD 6751 and EN 1424 specifications with the exception of acid value which is higher as seen in Table

Olutoye and Hameed (2011) produced biodiesel from crude jatropha oil using Aluminium oxide modified Mg – Zn heterogeneous catalyst. Their aim was to bypass the first step of pre-treatment because jatropha oil has high FFA and therefore it has to first be reduced through pre-treatment before transesterification. The FFA content of the jatropha oil used was 7.235% which is higher than the maximum of 3% above which transesterification cannot occur. The transesterification was carried out with 11:1 methanol to oil ratio, 8.86 wt% catalysts at 182°C for 360 minutes and a yield of 94% of methyl esters was obtained at these optimum condition, the catalyst remains stable even after 5 runs producing a yield of over 90% of methyl esters. The biodiesel properties are comparable to the standards according to ASTM. It was concluded that the catalyst is selective to production of methyl esters from oil with high fatty acid (FFA) and water content of 7.3% and 3.28% respectively in a single stage process. Endalew *et al*. (2011) used single step simultaneous esterification and transesterification of jatropha oil with heterogeneous catalyst. Mixture of solid base catalyst (CaO and Li-CaO) and solid acid catalyst ($Fe_2(SO_4)_3$) were found to give complete conversion with 100% biodiesel yield in a single step simultaneous esterification and transesterification without any trace of soap formed at optimum condition of 6:1 methanol to oil molar ratio, 5 wt% catalyst (CaO or Li-CaO: $Fe_2(SO_4)_3$ of 2:1), 300 rpm agitation, at 60°C reaction temperature for 180 minutes reaction time. Under the same condition the use of La. They concluded that the use of heterogeneous catalyst in single step simultaneous esterification and transesterification simplifies the biodiesel production process and decreases the cost of production.

Kian and Suhaimi (2012) studied the production of biodiesel from low – quality crude jatropha oil (acid value > 4 mg KOH/g and water content > 1000 ppm) using heterogeneous catalyst (modified natural zeolite). The effects of reaction time, molar ratio of methanol to oil, reaction temperature, mass ratio of catalyst to oil and catalyst reusability were investigated. It was reported that the modified natural zeolite catalyst had an excellent catalytic activity and stability in transesterification of low quality jatropha oil to biodiesel with methanol. An optimum condition of 20:1 molar ratio of methanol to oil, 5 wt% zeolite catalysts, at temperature of 70°C and reaction time of 360 minutes gives 97.8% optimum yield of biodiesel which is above the European standard EN14214 minimum of 96.5 wt% of ester content. Yun *et al*. (2013) carried out transesterification of rapeseed and jatropha oil to biodiesel under microwave radiation with calcined sodium silicate as catalyst. A biodiesel yield of 95.8% and 92.8% were achieved from rapeseed and jatropha oil respectively, at optimum operation where microwave power of 400 W, methanol to oil molar ratio of 11:1, 4 wt% catalysts and 5 minutes reaction time were used. The catalyst was recycled and biodiesel yield reduces to 83.6% at forth cycle for rapeseed oil. It was also reported that when crude jatropha oil of acid value 12.8 mg KOH/g was transesterified under the optimal condition only 11.6% biodiesel yield was obtained due to severe saponification. The researchers also combined the reused catalyst with Nickel catalyst to carryout hydrothermal gasification of the by – product glycerol to hydrogen. A maximum yield of 82.8% hydrogen was reported at 350^0C.

Badday *et al*. (2013) used activated carbon –supported tungstophosphoric acid catalyst (HPA/AC) assisted with ultrasonic irradiation for transesterification of jatropha oil. influence of the ultrasonic energy on the different process variables such as reactant's mole ratio, ultrasonic amplitude and catalyst amount were studied. A central composite design (CCD) was applied for the optimization of the process and an optimum yield of 91% was achieved in just 40 minutes at high molar ratio of 25:1, moderate ultrasonic amplitude of 60% and lower reaction temperature of 65^oC. Under conventional mixing process HPA as unsupported catalyst (Cao *et al*., 2008) or zirconia-supported HPA catalyst (Sunita *et al*. 2008) has reported a yield of 97% in about 300 minutes. The ultrasonication allow better accessibility of the reactant to the surface of the heterogeneous catalyst leading to intensified reaction rates and thus reducing drastically the reaction time.

*From the above review it could be concluded that homogeneous alkaline catalyst is very good in transesterification of jatropha oil when the free fatty acid content is less than 1%. Thus the yield of biodiesel from jatropha oil using homogeneous catalyst depends on the free fatty acid content of the jatropha oil.
*Homogeneous NaOH catalyst has the best yield of 98% biodiesel from the above review of jatropha oil transesterification using heterogeneous or homogeneous catalyst. However the process requires extra refining step to make the jatropha oil with high purity and low FFAs content which are more expensive process.
*Although using heterogeneous catalyst eliminates the pre-treatment stage and has the advantage of reusability of the catalyst, the yield of biodiesel is low compared with homogeneous catalyst. From Table 4 the homogeneous catalyst gave higher yield of biodiesel at mild temperature condition and shorter reaction time compared to heterogeneous catalyst. Although Endalew *et al*. (2011) reported 100% yield using heterogeneous catalyst, but it takes longer reaction time to achieve. The use of heterogeneous catalyst assisted with ultrasonic irradiation as seen in Table 4; drastically reduce the reaction time even lower than when using homogeneous catalyst because strong microwave irradiation accelerates transesterification process (Yun *et al*., 2013), but the yield is still lower than those of homogeneous catalyst.

Acid and alkaline, a two step transesterification

Considering the high free fatty acid content of jatropha oil which makes it difficult for direct transesterification using homogeneous alkaline catalyst; a two step transesterification using acid and alkaline catalyst have been adopted by researchers. The first step is the use of the acid catalyst to reduce the free fatty acid content before transesterification with alkaline catalyst. The two step transesterification process gain more popularity because of its effectiveness. The acid catalyst converts the free fatty acids in the jatropha oil into esters (esterification reaction), it is then followed by alkaline catalyst transesterification of the jatropha oil into biodiesel which is the second step.

Berchmans and Hirata (2008) applied two step transesterification on crude jatropha oil of 15% free fatty acid content. They first treated the jatropha oil with 1% w/w H_2SO_4 to oil, 0.6 wt% of methanol in oil at 50^oC for 60 minutes and the free fatty acid was reduced to less than 1%. The oil was then transesterified in the second step with 6.7:1 methanol to oil molar ratio, 1.4% w/w NaOH catalyst to oil at 65^oC and a yield of 90% was reported in 120 minutes. The yield dropped to 55% when the jatropha oil was only treated by the second step alkaline catalyst transesterification. In a similar study Jain and Sharma (2010 b,c) pre-treated jatropha oil of 21.5% free fatty acid content with 1% H_2SO_4 to oil, 0.6 wt% of methanol in oil at 50^oC for 180 minutes and the free fatty acid was reduced to less than 1%. They then transesterified the oil with 9.6:1 methanol to oil molar ratio, 1% w/w NaOH catalyst to oil at 50^oC for 180 minutes and a yield of 90% was obtained which is the same as the previous study, but used less catalyst, reaction temperature and high methanol to oil molar ratio. This suggest that the process conditions adopted by Jain and Sharma (2010 b,c) is more economical than that of Berchmans and Hirata (2008). In other studies researchers employed the potentials of alkaline KOH as catalyst in the second stage transesterification after pre-treatment with acid catalyst. Tiwari *et al*. (2007) treated jatropha oil having 14% free fatty acid content with H_2SO_4 as catalyst for 88 min and the FFAs was reduce to less than 1%. The pre-treated jatropha oil was then transesterified with 0.55% w/v KOH to oil; 4:1 methanol to oil molar ratio at 60^oC for 24 minute and an optimum yield of 99% was obtained based on response surface methodology (RSM) optimization. In a similar study a Patil and Deng (2009) treated jatropha oil with H_2SO_4 and reduce the FFAs from 14% to less than 1%. The treated jatropha oil was transesterified using 4.5% w/v of KOH to oil, 9:1 methanol to oil molar ratio at 60^oC for 120 minutes and 90 – 95% conversion was achieved. Despite low amount of catalyst and methanol to oil molar ratio used, Tiwari *et al*. (2007) was able to achieve high conversion in short time saving 80% of the time used by Patil and Deng (2009), because of the use of response surface methodology in optimizing the reaction conditions. Lu *et al*. (2009) tested the catalytic activity of homogeneous (H_2SO_4) and heterogeneous (SO_4^{2-}/TiO_2) acid catalyst in pre-treatment process of jatropha oil. The results suggested that the solid acid catalyst (SO_4^{2-}/TiO_2) gave more than 97% conversion of FFAs to methyl esters in 120 minutes. The optimum molar ratio of methanol to FFA and amount of SO_4^{2-}/TiO_2 were 20:1 and 4 wt% in oil respectively. Homogeneous H_2SO_4 was also used in the pre-treatment of the jatropha oil using optimum of 1% w/w H_2SO_4 to oil, 4:1 methanol to oil molar ratio at 70^oC for 120 minutes. Both the pre-treatment conditions using the two types of catalyst were able to reduce the jatropha oil FFAs content from

7.0% to less than 0.5%. A yield of more than 98% was obtained when the jatropha oil was further transesterified with 1.3% w/w KOH to oil, 6:1 methanol to oil molar ratio at 64°C for 20 minutes.

Corro *et al.* (2010) used solid catalyst SiO_2.HF to pre-treat jatropha oil before transesterification with alkaline catalyst (NaOH). The pre-treatment step reduces the FFAs of the jaropha oil from 7.9% to 0.3% in 180 minutes. Comparing with the pre treatment using (SO_4^{2-}/TiO_2) solid catalyst by Lu *et al.* (2009), it shows that the catalytic activity of (SO_4^{2-}/TiO_2) is better because of the short period time of 120 minutes as seen in Table 9. The reaction was conducted at 60°C using 10 wt% of catalyst to oil with 12:1 methanol to oil molar ratio. The second step transesterification was done with 6:1 methanol to oil molar ratio, 1% w/w NaOH to oil, at 60°C in 120 min; and a yield of 99.5% was reported; but the reaction time is longer compared to that of Lu *et al.* (2009).

Sahoo and Das (2009) carried out process optimization of biodiesel production from jatropha, karanja and polanga oils. A three stage process was adopted; zero catalyst transesterification, acid pre-treatment followed by main base transesterification reaction. Methanol was used as reagent, H_2SO_4 and KOH as catalyst for acid – base reaction respectively. It was reported that only two step transesterification was required for jatropha and karanja, but polanga requires three steps to convert the high free fatty acid of the oils to its esters. The zero transesterification (mixture of 1 litre crude oil, 250 ml methanol, 5 ml ortho-phosphoric acid and 5 ml toluene and stirred at constant speed of 450 rpm and at 66°C for 30 – 240 minutes. Toluene helps in dissolving organic matter with methanol separating it from the neat oil along with other impurities and reduces the free fatty acid content of jatropha and karanja oils to less than 2% while for polanga oil it was achieved after the second step acid transesterification. It was concluded that at optimum condition of volumetric ratio 11:1, 11.5:1 and 12:1 of alcohol to oil, for 120 minutes, the yield of jatropha methyl esters, karanja methyl esters and polanga methyl esters were 93%, 91% and 85% respectively. The properties of the biodiesel produced shows that the density and Calorific value are comparable with that of diesel, while the viscosity, flash point, pour point and cloud point are quite higher than that of diesel as shown in Table 6.

Table 6. Properties of biodiesel produced compared with that of Diesel

Property	Jatropha biodiesel	Karanja biodiesel	Polanga biodiesel	Deisel
Density (kg/m^3) at 40°C	873	883	869	850
Calorific value (KJ/Kg)	42.673	42.133	41.397	44.000
Viscosity (c.St) at 40°C	4.23	4.37	3.99	2.87
Flash point °C	148	163	140	76
Cloud point °C	10.2	14.6	13.2	6.5
Pour point °C	4.2	5.1	4.3	3.1

Kazi *et al.* (2010) produced and tested biodiesel from jatropha oil as an alternative fuel for diesel engines. They used two – step approach of acid – catalysed (H_2SO_4) esterification followed by base – catalysed (NaOH) transesterification to produce biodiesel from jatropha oil. It was reported that 900 ml of biodiesel was produced from 1 litre of jatropha oil. The fuel properties of the jatropha oil and the biodiesel produced were determined. The biodiesel was used to run a laboratory heat engine and the engine performance was reported. They observed that the properties of the biodiesel are comparable with that of diesel. The performance in laboratory engine showed that biodiesel has greater brake power and brake thermal efficiency than biodiesel or 50% to 50% biodiesel and diesel blends. It also has less fuel consumption, mass of air and air fuel ratio compared to diesel or the blend. The exhaust gas analysis also showed less CO_2, high O_2 and no CO emissions when biodiesel was used. It was concluded that jatropha oil is a better alternative in reducing the green house effect in our environment and thus environmental friendly. The density and calorific value of the biodiesel and the blend are lower than that of diesel while the viscosity and boiling points are higher than that of diesel as seen in Table 7.

Table 7. Properties of jatropha oil, biodiesel, blend and diesel

Property	Jatropha oil	Biodiesel	(50% biodiesel &50% diesel)	Diesel
Density (gm/cc)	-	0.62	0.58	0.84
Viscosity at 30°C (cst)	55	5.34	6.86	4.0
Calorific value (MJ/Kg)	39.5	41	42.7	45
Cetane number	43	-	-	47
Solidifying point °C	-10	-	-	- 14
Boiling point °C	286	255	-	248

Table 8. Properties of jatropha oil, biodiesel compared to the German standard

Property	Jatropha oil	Biodiesel	German Standard (DIN V 51606:1997)
Density (g/ml, 298K)	0.892	0.886	0.975 – 0.900
Flash point (K)	498	459	≥ 373
Viscosity (mm^2/s, 313K)	24.5	3.89	3.5 – 5.0
Acid value (mgKOH/g)	10.5	0.154	≤ 0.5
Sulphur content (wt %)	-	0.003	≤ 0.01
Cetane number	51	58	≥ 49
Water content/(mg/Kg)	5200	172	≤ 300
Ash content (wt %)	-	0.024	≤ 0.05
Pour point (K)	371	268	-
Carbon residue %	1.0	0.2	≤ 0.05
Calorific value (MJ/Kg)	38.65	41.72	-

From Table 9 Tiwari *et al.* (2007) and Patil and Deng (2009) using jatropha oil of the same FFA and catalyst reported different biodiesel yield. Although Tiwari *et al.* (2007) use lower methanol to oil molar ratio and amount of catalyst recorded higher yield at short reaction time. This may be due to the higher temperature used compared to that used by Patil and Deng (2009), despite the fact that they used higher methanol to oil molar ratio and amount of catalyst the yield was lower compared to those of Tiwari *et al.* (2007). Xin *et al.* (2011) employed two step transesterification to study the biodiesel production from jatropha oil using nanosized solid basic catalyst in the second step. In the first step 200 ml jatropha oil, 40 ml anhydrous methanol and 4 ml H_2SO_4 was vigorously stirred and reflux at 318 K in ultrasonic reactor for 90 minutes. The jatropha oil FFA content was reduced to 0.7 mg KOH/g.

Table 9. Summary of two step transesterification of jatropha oil

Authors	Initial FFA %	Final FFA %	Acid/Alkaline catalyst	Time (min) z/y	Reaction temp. (°C) z/y	Stirring speed (rpm)	Methanol/oil molar ratio	Catalyst amount	X (%)	Remarks
Berchmans and Hirata (2008)	15	< 1	H_2SO_4/NaOH	60/120	50/65	400	6.7:1	1.4% w/w	90	High FFA gives low yield and longer second step reaction time
Xin *et al*. (2010)	5.25	0.75	H_2SO_4/NaOH	60/30	45/60	600/ultrasonic power 210 w	24% (v/v)	1.4 wt%	96.4	Use of ultrasonic irradiation reduces reaction time and increase yield
Jain and Sharma (2010b,c)	21.5	< 1	H_2SO_4/NaOH	180/180	65/50	400	3:7	1.0% w/w	90.1	High FFA gives raise to low yield and longer reaction time
Ong *et al*. (2013)	6.4	-	H_2SO_4/NaOH	180/120	60/50	1200	10:1	1% w/w	98.75	High stirring speed and methanol to oil molar ratio gives high yield, but longer first reaction time as a result of high FFA value of the oil
Venkateswara and Srinivasa (2013)			H_2SO_4/NaOH	60/60	60/60	500 to 600	6:1	6.3g	-	
Anthony *et al*. (2011)	14	< 2	HCl/NaOH	20/60	-/60	yes	6:1	0.92%	-	Use of HCl as catalyst reduces the first step reaction time, which is better than H_2SO_4 using oil with the same FFA
Tiwari *et al*. (2007)	14	< 1	H_2SO_4/KOH	88/24	60/60	-	4:1	0.55% w/v	99	High yield with moderate reaction conditions
Patil and Deng (2009)	14	< 1	H_2SO_4/KOH	120/120	45/60	1000	9:1	4.5% w/v	90 - 95	Yield is lower than that of Tiwari *et al*, may be due to lower first step reaction time, despite higher amount of catalyst and methanol to oil molar ratio.
Worapun *et al*. (2012)	12.5	< 3	H_2SO_4/KOH	20/30	30/30	Ultrasonic irradiation	15% (w/w)	1% w/w	98	High yield with mild reaction condition, due to the use of ultrasonic irradiation and high methanol to oil molar ratio.
Lu *et al*. (2009)	7.0	0.5	[(SO_4^{2-}/TiO_2) or H_2SO_4] /KOH	120/20	70/64	1500	6:1	1.3 wt%	98	Heterogeneous catalyst SO_4^{2-}/TiO_2 has high catalytic activity compared to Si O_2.HF, since it gives shorter reaction time
Sahoo and Das (2009)	1.9	< 2	H_2SO_4/KOH	240/120	66/55	350	11:1	1.1% w/v	93	Longer first step reaction time, despite higher temperature used, may be due to lower stirring speed
Joshua (2013)	18.4	-	H_2SO_4/KOH	60/60	50/60	-	8:1	1.0%	90	High FFA gives raise to low yield
Corro *et al*. (2010)	7.9	0.3	Si O_2.HF /NaOH	180/120	60/60	400	6:1	1.0% w/w	99.5	High yield but longer reaction time, may be due to lower stirring speed

z = first step esterification reaction condition y = second step transesterification reaction condition X = conversion

Table 10. Properties of biodiesel produced compared with that of Diesel

Property	Jatropha oil	Biodiesel	Diesel
Flash point °C	214	128	65
Fire point °C	256	136	78
Pour point °C	6	-2	-6
Cloud point °C	11	8	5
Viscosity (c.s.t 40 °C)	36.92	4.82	2.86
Viscosity index	181	154	98
Specific gravity g/cm^3 (29 °C)	0.944	0.84	0.792
Refractive index (40 °C)	1.61	1.46	1.32
Calorific value (MJ/Kg)	39.76	42.80	44.34

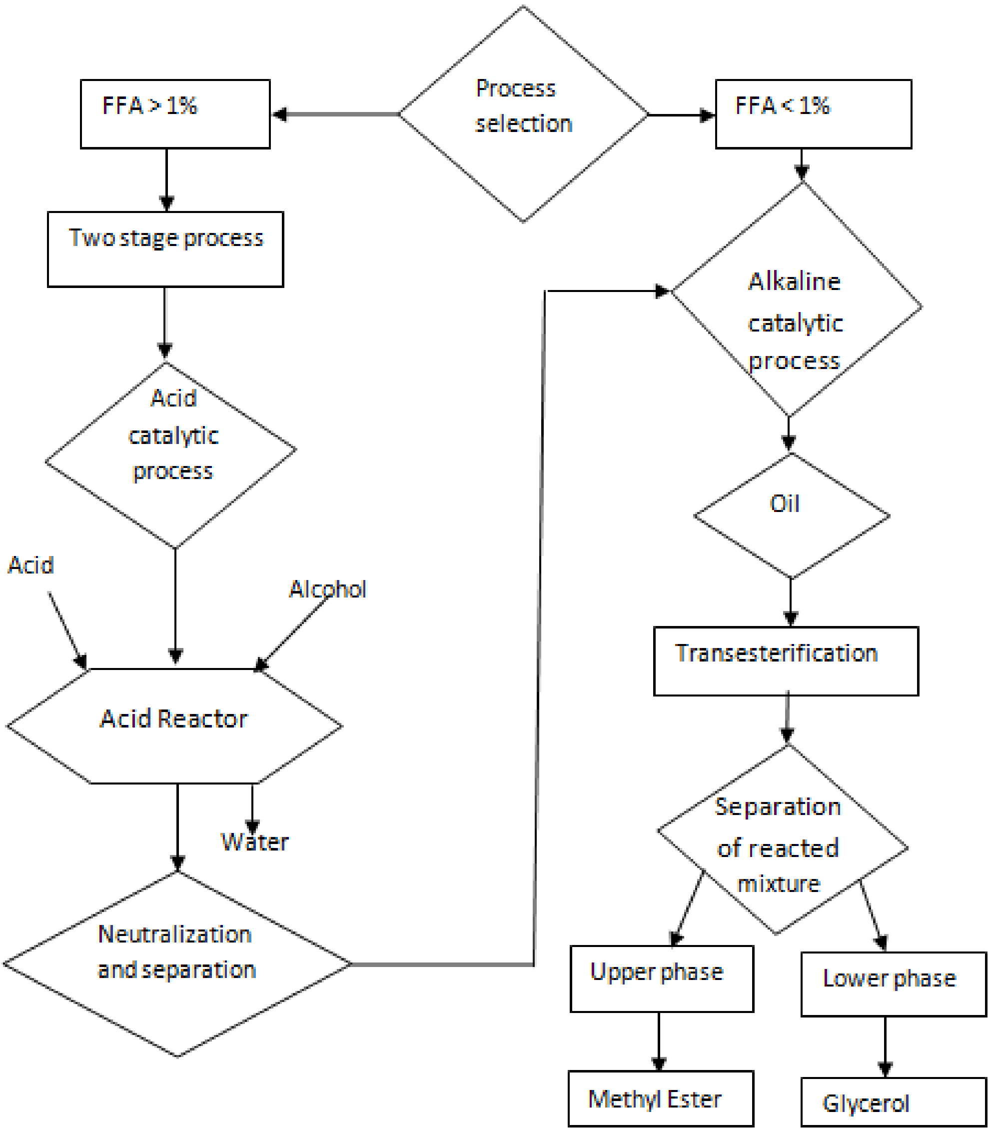

Figure 3. Process selection and steps for *Jatropha curcas* biodiesel production

The description of the process selection of biodiesel production from jatropha is shown in Figure 3. If the FFA content of the jatropha oil is less than 1% the process goes directly through alkaline catalyst transesterification, but when the FFA content is greater than 1% two step process is adopted. First step is the acid esterification of the jatropha oil to reduce the FFA content to less than 1% before second step transesterification with alkaline catalyst to produce biodiesel.

The second step transesterification was performed with 1 wt% hydrotalcite solid catalyst of Mg/Al (molar ratio of 3:1) to oil, using 210 W ultrasonic powers, 4:1 methanol to oil molar ratio, at 318 K for 90 minutes, and a biodiesel yield of 95.2% was obtained. It was also reported that the catalyst can be reuse for 8 times. The properties of jatropha oil and biodiesel produced were comparable with the German standard (DIN V 51606) as shown in Table 8. The description of the process selection of biodiesel production from jatropha is shown in Figure 3. If the FFA content of the jatropha oil is less than 1% the process goes directly through alkaline catalyst transesterification, but when the FFA content is greater than 1% two step process is adopted. First step is the acid esterification of the jatropha oil to reduce the FFA content to less than 1% before second step transesterification with alkaline catalyst to produce biodiesel.

Antony *et al.* (2011) carried out biodiesel production from jatropha oil and its characteristics. The oil was first agitated with 4% HCl solution for 25 minutes and 0.82g of NaOH was added per 100ml of oil to neutralize the free fatty acids to below 2% and to coagulate. Filtration was used to remove the coagulated free acid (soap). The second step transesterification was carried out at optimum condition of 6:1 methanol to oil molar ratio, 0.92% NaOH catalyst, at 60^{o}C reaction temperature for 60 minutes. The characteristics of the jatropha oil and the biodiesel produced was compared with the petroleum diesel, it was found that the jatropha oil and biodiesel characteristics are quite higher compared to the petroleum diesel as shown in Table 10

Worapun *et al.* (2012) used two – step process to produce biodiesel from *Jatropha curcas* L. oil assisted with ultrasonic irradiation. The high free acid of the oil 12.5% was treated with 15% w/w methanol to oil ratio, 3% w/w H_2SO_4 as catalyst and ultrasonic irradiation time of 20 minutes under reaction temperature of 30^{o}C, the free fatty acid was reduced to less than 3%. The second step alkaline catalyst transesterification was carried out, as methanol to oil 15% w/w, 1% w/w of KOH catalyst, reaction temperature of 30^{o}C and ultrasonic irradiation time of 30 minutes. A high percentage conversion to biodiesel of about 98% was obtained, comparing with Lu *et al.* (2009) who reported the same percentage yield using the same type of catalyst, but with jatropha oil having lower FFA contents as seen in Table 9. Despite the lower amount of catalyst and high FFA oil used by Worapun *et al.* (2012), the use of ultrasonic irradiation, reduced drastically the first reaction time and temperature, though the second step reaction time is higher than that used by Lu *et al.* (2009). Also higher stirring speed used by Lu *et al.* (2009) help in overcoming mass transfer among the phases leading to less reaction time in the second step transesterification. Comparing with the conventional method of stirring, ultrasonic irradiation technique significantly illustrated the higher efficiency more especially for high free fatty acid oils.

Joshua (2013) carried out two step process using acid and base catalyst to produce biodiesel from jatropha oil. The jatropha oil of 21.6% free fatty acid was treated with 1% concentrated H_2SO_4, 30% (v/v) methanol and heated to 50^{o}C to reduce the free fatty acid content of the oil. The second step transesterification was carried out using 10% KOH as catalyst, 8:1 methanol to oil mole ratio, at 60 ^{o}C reaction temperatures in 60 minutes reaction time. It was reported that the yield of biodiesel was 90% which is the same yield as reported by Berchmans and Hirata (2008), but the reaction conditions employed by Joshua is milder with the exception of methanol to oil molar ratio. Also the jatropha oil used by Joshua (2013) has higher FFA compared to that used by Berchmans and Hirata (2008). This suggest that the KOH catalyst used by Joshua has higher catalytic activity than NaOH catalyst used by Berchmans and Hirata (2008), because of the shorter time of transesterification as can be seen in Table 9. The properties of biodiesel produced are within the ASTM D6751 specifications as seen in Table 11.

Table 11. Properties of biodiesel produced compared with ASTM D6751 specifications

Property	Biodiesel	ASTMD 6751
Specific gravity Kg/L	0.90	0.95 max
Kinematic viscosity at 30^{o}C c.s.t	4.93	1.9 – 6.0
Cloud point ^{o}C	37	40 max
Flash point ^{o}C	137	130min
Cetane number	52	40 min
Free glycerine wt%	0.05	0.02 max
Ash content wt%	ND	0.1 max
Carbon residue wt%	ND	15 max

Venkateswara and Srinivasa (2013) studied the production and characterization of jatropha oil methyl esters. A two step acid – alkaline catalyst transesterification was used. In the first step 2 ml of 99% H_2SO_4 was used as a catalyst with 120ml of 99% methanol per litre of oil heated to 60^{o}C for 60 minutes to reduce the free fatty acid content of the jatropha oil. The second step was the transesterification of the oil with low free fatty acid content with NaOH as catalyst. It was concluded that the optimum condition of the process was 6:1 methanol to oil mole ratio, 6.3g of NaOH catalyst at 60^{o}C reaction temperature in 60 minutes reaction time. The yield of biodiesel was not given but the fuel properties of the oil and the biodiesel produced was compared with that of petroleum diesel. With the exception of density and carbon residue all the biodiesel properties are higher than that of diesel as seen in Table 12.

Table 12. Properties of jatropha oil and biodiesel compared to that of diesel

Property	Jatropha oil	Biodiesel	Diesel
Density at 15^{o}C (Kg/cm^3)	925	850	878
Viscosity at 34 ^{o}C (cst)	48.4	4.76	2.7
Flash point ^{o}C	189	162	68
Carbon residue wt%	0.3	0.03	0.19
Pour point ^{o}C	- 6	- 6	- 20
Cetane number	24	53.8	48

It was concluded that the viscosity of jatropha oil reduced drastically with transesterification and biodiesel characteristics such as density, viscosity, flash point, carbon residue, pour point and cetane number are comparable to diesel.

Ong *et al.* (2013) studied the production and comparative fuel properties of non-edible oils of *Jatropha curcas*, sterculia foetida and ceiba pentandra with acid values of 12.79 mgKOH/g, 5.11 mgKOH/g and 11.99 mgKOH/g respectively. Two step transesterification process using H_2SO_4 and NaOH as acid / base catalysts were employed. The pre-treatment step was carried out using 10:1 methanol to oil molar ratio, 1% (v/v) H_2SO_4, 1200 rpm stirring speed at 60^{o}C for 180 minutes. The optimum transesterification condition of the second step are 10:1 methanol to oil molar ratio, 1200 rpm stirring speed, 1% (w/w) NaOH to oil, at 50^{o}C for 120 minutes reaction time. An optimum yield of 98.75%, 97.50% and 97.72% of biodiesel was recorded from *Jatropha curcas*, Sterculia foetidra and Ceiba pentandra respectively. Table 9 showed that Ong *et al.* (2013) and Jain and Sharma (2010b, c) used the same acid/base catalyst first step reaction time, temperature and amount of catalyst. But, Ong *et al.* (2013) obtained yield with shorter second step reaction time compared to Jain and Sharma (2010b,c). This may be due to the use of oil with less FFA, high stirring speed and high methanol to oil molar ratio by Ong *et al* (2013). The fuel properties of the biodiesel produce were shown in Table 13.

Table 13. Properties of JCME, SFME and CPME compared with ASTM specifications

Property	JCME	SFME	CPME	ASTM (D6751)
Kinetic viscosity at 40^{o}C (mm^2/s)	3.91	4.92	4.15	1.9 – 6.0
Density at 15^{o}C (Kg/m^3)	838.8	872	856.9	880
Flash point ^{o}C	161.5	160.5	163.5	100 – 170 min
Pour point ^{o}C	2.0	- 3.0	1.7	- 15 to - 16
Cloud point ^{o}C	3.0	1.2	2.5	- 3 to -12
Calorific value MJ/Kg	40.427	40.179	40.490	-
Cetane number	58.2	56.5	57.2	47 min
Water content wt%	0.035	0.031	0.045	0.05 max

JCME = *Jatropha curcas* methyl ester SFME = Sterculia foetida methyl ester
CPME = Ceiba pentandra methyl ester

Silitonga *et al*. (2013) carried out a global comparative review of biodiesel production from *Jatropha curcas* using different homogeneous acid (HCl and H_2SO_4) and alkaline (NaOH, KOH, CH_3ONa and CH_3OK) catalyst. The acid-catalyst esterification was carried out with 9:1 methanol to oil molar ratio, 1% (v/v) of acid catalyst to oil at 60°C for 180 minutes under 1000 rpm stirring speed in a reactor. The second step alkaline catalyst transesterification process, 9:1 methanol to oil molar ratio, with 1% w/w of alkaline catalyst at 50°C for 120 minutes and stirring speed of 1000 rpm. The properties of the biodiesel produced such as viscosity, density, flash point, cloud point, pour point, calorific value, acid value, iodine value, carbon residue and sulphate ash were determined and tabulated in Table 14.

Table 14. Properties of *Jatropha curcas* methyl esters produce via different catalysts

Properties	JCME (HCl – NaOH)	JCME (HCl – KOH)	JCME (H_2SO_4 – NaOH)	JCME (H_2SO_4 – KOH)	JCME (H_2SO_4 – CH_3ONa)	JCME (H_2SO_4 – CH_3OK)
Density Kg/m^3	862.9	876.6	861.8	862.7	862.6	863.4
Viscosity mm^2/s	4.84	4.62	4.36	4.76	4.79	4.77
Flash point °C	178.5	174.5	172.5	170.5	184.5	174.5
Cloud point °C	6.0	6.0	6.0	6.0	3.0	3.0
Pour point °C	-5.0	-5.0	-3.0	-1.5	-3.0	-3.0
Calorific value MJ/Kg	39.59	39.19	39.78	39.70	39.62	39.70
Acid value mgKOH/g	0.29	0.32	0.33	0.28	0.29	0.30
Iodine value g I_2/100g	109.5	109.4	101.6	105.5	102.7	102.6
Carbon residue w%	0.056	0.055	0.055	0.055	0.059	0.059
Sulphate ash w%	0.004	0.005	0.006	0.008	0.007	0.005
Water content mg/Kg	306	315	352	316	457	445
Methanol w%	0.04	0.04	0.04	0.04	0.04	0.04

*Two step transesterification process is a good alternative and efficient way to transesterify crude jatropha oil that have high free fatty acid (FFA) content. Utilization of acid and alkaline catalyst in the first and second stage would help to overcome the problem of slow reaction rate with acid catalyst and eliminate the soap formation by using alkaline catalyst.

*The use of a homogeneous catalyst such as H_2SO_4 would also create a waste water problem and purification method is needed to separate the catalyst from the product. The use of heterogeneous catalyst in each step of the process would help to overcome this problem. From Table 9 it can be seen that the use of ultrasonic irradiation employed by Xin *et al*. (2010) and Worampun *et al*. (2012) instead of using conventional stirrer was able to improve the mass transfer among the reactants and drastically reduce the reaction time and increase the yield of biodiesel. Also Berchmans and Hirata (2008) Xin *et al*. (2010) used the same amount of catalyst H_2SO_4/NaOH as catalyst, but reported biodiesel yield of 90% and 96.4% in 120 minutes and 60minutes respectively. The difference in yield and reaction time may be related to the high free fatty acid oil used by Berchmans and Hirata (2008) compared to that used by Xin *et al*. (2010)and also ultrasonic power employed by Xin *et al*. (2010).

Enzymatic transesterification

Enzymatic transesterification using lipase outstands the other methods of biodiesel production, advantages of lipase in biodiesel production includes high efficiency, complete conversion of free fatty acids (FFA) to alkyl esters, more selective, less energy consumption, mild reaction condition, low temperature and reduces the formation of side products and waste. But the main obstacle in using lipase for commercial biodiesel production is the high cost and deactivation of the lipase by methanol and glycerol. Methanol is insoluble in the oil, it inhibits the immobilised lipase and there by decrease the catalytic activity of the transesterification reaction while the hydrophobic by product glycerol is also insoluble in the oil and is easily adsorbed onto the surface of the immobilized lipase leading to negative effect on the lipase activity and operational stability. Researchers have used different methods trying to overcome these challenges through immobilization techniques such as cross linking, adsorption, entrapment and encapsulation. In immobilization of the lipase, it is crucial to identify a matrix which can satisfy the following parameters, such as low cost, non toxic, easy separation of products, safe disposal of waste, environmental friendly and degradability (Rahmah and Pogaku, 2013). Generally as can be seen from Table 5 enzymatic transesterification despite its advantages takes longer reaction time and lower yield compared to other transesterification processes as shown in Table 2, 3 and 4.

Shah *et al*. (2004) screened three different lipase (*Chromobacterium viscosum*, *Candida rugosa* and porcine pancreas) used for transesterification of jatropha oil in solvent (ethanol) free system to produce biodiesel. It was reported that only lipase from *Chromobacterium viscosum* was found to give appreciable yield. Immobilization of the lipase (*Chromobacterium viscosum*) on calite-545 enhanced the biodiesel yield to 71% from 62% yield obtained without immobilization of the lipase with a process time of 480 minutes at 40°C. It was also found that addition of water to the free (1% w/v) and immobilized (0.5% w/v) lipase preparations enhances the yield to 73% and 92% respectively. They observed that immobilization of lipase and optimization of transesterification conditions resulted in adequate yield of biodiesel in the enzyme base process; and thus concluded that *Chromobacterium viscosum* lipase can be used for ethanolysis of oil.

In another study Shah and Gupta (2007) investigated the production of biodiesel from jatropha oil in a solvent free system using various commercial lipase (*candida rugosa* (AYS), *p. cepacia* (PS), *pseudomonas fluorescens* (AK), *mucor javanicus* (M), *p. cepacia lipase* immobilized on celite (PS-D) and *p. cepacia lipase* immobilized on ceramic (PS-C)) preparations, immobilization, varying water content in the reaction media, enzyme used and temperature of reactions using different ethanol grades. The transesterification was carried out using 4:1 molar ratio of ethanol to jatropha oil (mol/mol) in a screw-capped vial, with 0.05g lipase and incubated at 40°C with a constant shaking at 200 rpm. The *pseudomonas cepacia lipase* immobilized on celite (PS-D) has the highest catalytic effect of 80% yield w/w, followed by *pseudomonas cepacia lipase* immobilized on celite (PS-L) in the lab having a yield of 78%. Comparing the reusability of PS-D and PS-L showed that PS-L was more superior and could be used four times without loss of any activity. It was also found that crude (commercial grade) ethanol which contains 5% water prove superior over the analytical grade ethanol, because there is no need of addition of water, it is also less cost since purification is not needed after preparation. It was then concluded that the best yield of 98% w/w was achieved using *pseudomonas cepacia lipase* immobilized on celite (PS-D) at 50°C in the presence of 4 – 5% (w/w) water in 8 hrs. The bio catalyst could be used four times without loss of any activity. In similar study carried out by Devanesan *et al.* (2007) on transesterification of jatropha oil using *pseudomonas fluorescens* lipase a maximum yield of 71% was reported at optimum condition of 40°C, PH of 7.0, 4:1 methanol to oil molar ratio, 3g of the lipase beads and reaction time of 2880 minutes. Shah *et al.* (2007) in their work screen out pseudomonas fluorescens because of low activity using ethanol, 0.05g of the lipase within 1440 minutes reaction. The difference in yield may be due to the different conditions employed in the transesterification.

Tamalampudi *et al.* (2008) carried out comparative study of immobilized whole cell of *Rhizopus oryzae* and commercial lipase Novozym-435 for the production of biodiesel from jatropha oil. The alcoholysis was carried out in 50 ml screw-capped vessel at 30°C with reciprocal shaking at 150 rpm, and a mixture consisting of 5 g jatropha oil, 3:1 alcohol to oil molar ratio using 0.2g lipase catalyst. Different alcohols as a hydroxyl donor were tested, and methanolysis of the jatropha oils progresses faster than other alcoholysis regardless of lipase used. This was due to low molecular weight and high polarity of methanol, which makes it easy to diffuse and access the lipase enzyme localized in the cell membrane of *Rhizopus oryzae* resulting in high reaction rate. They reported a maximum of 80wt% methyl esters content in the reaction mixture after 3600 minutes using ROL, whereas 76 wt% after 5400 minutes using Novozyn-435. Both lipases can be used for repeated batches and both exhibits more than 90% of their initial activities after five cycles. Also the presence of waster in the jatropha oil has significant effect on the rate of methanolysis and ROL exhibits highest activity in the presence of 5% (v/v) added water. It was concluded that whole cell ROL immobilized onto BSP can be used as a low cost biocatalyst for production of biodiesel from crude jatropha oil. Kawakami *et al.* (2011) carried out enzymatic methanolysis of crude jatropha oil containing 18% free fatty acid using *Burkholderia cepacia* lipase immobilized on n-butyl-substituted silica monolith. A biodiesel yield of 90% was reported in 720 minutes batch reactor using a stiochiometric mixture of methanol to oil molar ratio of 3:1, with 0.6% (w/w) water content, at a temperature of 40°C, 250 mg crude immobilized lipase and 1400 min^{-1} shaking. They found out that *Burkholderia cepacia* lipase immobilized in hydrophilic silicates was sufficiently tolerant to methanol and glycerol adsorption, but on the support disturbed the reaction to some extent. The continuous production of biodiesel was performed at steady state using a lipase immobilized silica monolith bioreactor loaded with 1.67g of lipase, and a yield of 95% was reported at a flow rate of 0.01 ml/min and was successfully operated for almost 50 days with 80% retention of the initial yield.

Rahmath and Pogaku (2013) also studied the biodiesel production from crude *Jatropha curcas* L. oil using immobilized *Burkholderia cepacia lipase* (biocatalyst). The biocatalyst was prepared by cross linking lipase of *Burkholderia cepacia* with glutaraldehyde followed by entrapment in hybrid matrix of equal proportions of alginate and α carrageenan. The results showed that the optimal condition for processing 10g crude jatropha oil were 30°C reaction temperature, 10:1 molar ratio of ethanol to oil, 1g water, 5.25g immobilized lipase, 6g RCF (mixing intensity) and 1440 minutes reaction time. At this optimal conditions 100% yield of fatty acid ethyl esters were reported and the catalyst was stable and retained 73% relative transesterification activity after six cycles reuse. Ethanol was chosen instead of methanol because of its less toxicity and can be generated from biomass. Comparing with the work of Kawakari *et al.* (2011) who use the same lipase but immobilized on n-butyl-substituted silica monolith, although the biodiesel yield was lower, the reaction time and methanol to oil molar ratio used was half (½) and 3 times respectively less than what was used by Rahmath and Pogaku (2013). The lower yield may also be due to the high FFA content of oil used by Kawakari *et al.* (2011).

Kumari *et al.* (2009) studied transesterification of jatropha oil in t-butanol solvent using immobilized lipase *Enterobacter aerogenes*. The use of t-butanol was to reduce the negative effects caused by methanol and glycerol on the lipase, since both of them are soluble in t-butanol and t-butanol is not a substrate because the lipase does not act on tertiary alcohols. They reported a maximum yield of 94% with oil to methanol ratio of 0.8:1 at 55°C after 2880 minutes of reaction time. It was noted that there is negligible loss of lipase activity even after repeated used for seven cycles. The properties of the oil such as viscosity, flash point and pour point were improved but are still outside the standard specifications as shown in Table 15.

Table 15. Properties of jatropha oil and biodiesel compared with standard specifications

Property	Jatropha oil	Jatropha biodiesel	ASTM 6751-02	EN14214
Viscosity (mm^2/s)	24.5	8.2	1.9 – 6.0	3.5 – 5.0
Flash point °C	210	82	> 130	> 120
Pour point °C	10	5	- 15 – 10	-
Calorific value (MJ/Kg)	36.2	36.5	33 – 40	-

Feng *et al.* (2011) used one step for the production of biodiesel from jatropha oil with high acid value using ionic liquids (ILs) with metal chlorides (MCl_n). It was reported that 1-butyl-3-metylimidazolium tosylate ((BMIm)(CH_3SO_3)) had the highest catalytic activity with 93% esterification rate for oleic acid at

140°C, but only 12% biodiesel yield at 120°C. When $FeCl_3$ was added to ((BMIm)(CH_3SO_3)), a maximum of biodiesel yield of 99.7% was achieved at 140°C in 300 minutes. The ionic liquid was also tested with other metallic chlorides such as $AlCl_3$, $ZnCl_2$, $CuCl_2$, $CoCl_2$ and $MnCl_2$ which gave biodiesel yield of 94%, 87%, 83%, 46% and 27% respectively. It was concluded that metal ions in ionic liquids can provide Lewis acidic site to promote reactions, and the Lewis acids provide by trivalent metallic ions are stronger than the bivalent ones. The ionic liquids used are commercialized and less expensive, but their cost is still relatively higher than other solvents or catalyst. Kumar *et al.* (2011) investigated the methanolysis of jatropha oil for biodiesel synthesis using immobilized lipase (*chromobacterium viscosum*) from *Enterobacter aerogenes* assisted by ultrasonication. The optimal reaction conditions for the biodiesel production was 4: 1 methanol to oil molar ratio, 5 wt% catalyst to oil, ultrasonic wave amplitude 50% (100 W/m^3), ultrasonic irradiation pulse 0.7 s cycle each second, reaction time 30 min, and a maximum yield of ≥ 84.5% of biodiesel was obtained. Ultrasonication reduced the reaction time comparing with the conventional batch process seen in the literatures. The properties of the biodiesel produced are within the ASTM specifications as seen in Table 16.

Table 16. Properties of jatropha oil and biodiesel compared with ASTM specifications

Property	Jatropha oil	Jatropha biodiesel	ASTM
Viscosity (mm^2/s) at 40°C	34.33	3.88	1.9 – 6.0
Density at 15°C (Kg/ml)	0.918	0.8633	0.575 – 9.00
Flash point °C	186	135	> 100
Pour point °C	-	-12	- 15 to +10
Cetane number	3	54	> 47
Carbon residue wt%	-	0.05	< 0.02
Water content (ppm)	-	230	< 500

From Table 17 the following fundamental observations can be made from enzymatic transesterification process: (i) Generally the process have the disadvange of longer reaction time. (ii) Immobilized lipase tends to have high activity compared to the non immobilized lipase; therefore higher yields were reported by most researchers using immobilized lipase. (iii) The addition of water to the process also favours the immobilized lipase transesterification and gives raise to higher yield. (iv) The use of ultrasonic irradiation employed by Kumar *et al.* (2011) with *Chromobacterium viscosum* immobilized on silica was able to overcome the mass transfer limitations which leads to longer reaction time associated with lipase tranesterification (Sim *et al*., 2009), the reaction was completed in 30 minutes with a yield of ≥ 85%. This is the shortest time recorded so far by all the literatures sited. Although Rathmath and Pogaku (2013) reported 100% yield using immobilized *burkholderia cepacia* using 6g RCF (mixing intensity) but the reaction time was 1440 minutes which was quite high. It can be seen from Table 17 that *pseudomonas cepacia* immobilized on cetite with addition of 5% water gives better yield of biodiesel as reported by Shah *et al.* (2007) and Shah and Gupta (2007) using ethanol and methanol as reactant respectively. Although the initial FFA of the oil used by Shah *et al.* (2007) was not given, all the reaction conditions are the same with the exception of higher reaction temperature used by Shah and Gupta (2007). This suggests that the transesterification of jatropha oil with *pseudomonas cepacia* immobilized on cetite with addition of 5% water and ethanol is more economical than using methanol. Tamalampudi *et al.* (2008) and Su and Wei (2008) both used *Candida Antarctica* lipase B (Novozym 435) at moderate reaction temperatures of 30 and 45°C respectively as shown in Table 17. They reported different yield of 75% and 98% respectively, this may be due to the use of co-solvent mixture of t-pentanol: iso-octane by Su and Wei (2008) which were able to eliminate the negative effect caused by both excessive methanol and by product glycerol from deactivating the lipase; thus giving a higher yield in about 3.75 times shorter reaction time compared to what was reported by Tamalampudi *et al.* (2008).

In situ biodiesel production from jatropha oilseed

The conventional method for producing biodiesel from oil seeds involves the extraction of oil followed by its refining process such as bleaching, degumming, dewaxing, deacidification and dehydration prior to esterification and transesterification. The oil is extracted from the oil seed either by solvent extraction or by mechanical expeller. The mechanical expeller is capable of extracting about 70% of oil present in the oil seed. The use of organic solvents i.e. n-hexane is efficient to extract the oil from the oilseed, which adds extra cost for organic solvent and the processing. Recently academic researchers have been focussing on investigating cost effective biodiesel production methods either via raw material or processing technology in order to become more competitive with the fossil fuel. In situ reactive extraction for biodiesel synthesis is a new approach to eliminate the processing steps involved in the conventional process for economic production of biodiesel. The process involve reactive extraction of oil from the seed and subsequent esterification/transesterification to fatty acid alkyl esters simultaneously in a relatively shorter operation time (Lim *et al*., 2010) more especially when supercritical alcoholysis conditions is employed as shown in Table 6. Shuit *et al.* (2010) reported the in situ oil extraction, esterification and transesterification for the synthesis of biodiesel from jatropha seeds. An optimum biodiesel yield of 98.1% was achieved under the reaction condition of temperature 60°C, methanol to seed ratio 10.5 ml/g, catalyst concentration 21.8% H_2SO_4 and a reaction time of 600 minutes. The most significant parameter that affects the methyl esters yield is catalyst concentration, followed by reaction temperature, reaction time and methanol to seed ratio. In a similar study Jaliliannosti *et al.* (2013) produced biodiesel from *Jatropha curcas* L. seed by two step in situ processes assisted with micro wave irradiation. In the first step, a mixture of ethanol/ seed ratio of 10.5% (v/w) volume to weight of jatropha seed, 20 g of jatropha seeds and sulphuric acid loading (7.5 wt%), 3000 rpm stirring speed and heated in microwave oven at 110 w average power for 35 min. The free fatty acid was reduced from 14% to less than 1%. The in situ transesterification in step two required some amount of base catalyst to neutralized the sulphuric acid, convert unreacted free fatty acid and catalyzed the transesterification of triglycerides. The highest biodiesel yield of 90.01% and FFA conversion of 97.29% were achieved in a short processing time of 48 minutes, at optimum condition of < 0.5mm seed size, 12.21 min irradiation time, 8.15 ml KOH catalyst loading and 351.32 rpm agitation speed by 110 w microwave power.

Table 17. Summary of enzymatic transesterification of jatropha oil

Authors	Initial FFA %	Final FFA %	Lipase	Time (min)	Reaction temp. (°C)	Stirring speed(rpm)	Alcohol/oil molar ratio	X (%)	Remarks
Shah *et al*. (2004)	_	_	*Chromobacterium viscosum*	480	40	200	4:1(Ethanol)	62	No water
			Chromobacterium viscosum on celite	480	40	200	4:1(Ethanol)	71	No water
			Chromobacterium viscosum	480	40	200	4:1 (Ethanol)	73	1% v/v water
			Chromobacterium viscosum on celite	480	40	200	4:1 (Ethanol)	92	0.5% v/v water
Shah *et al*. (2007)	_	_	*Pseudomonas cepacia* on cetite	480	40	200	4:1(Ethanol)	80	No water
			Pseudomonas cepacia on cetite	480	40	200	4:1(Ethanol)	98	4 – 5% w/w water added
Devanesan *et al*. (2007)	8.625	-	*Pseudomonas fluorescens* (immobilized by entrapment into sodiumalginate)	2880	40	150 oscillation	4:1 (Methanol)	71	No water
Shah and Gupta (2007)	2.71	-	*Pseudomonas cepacia* on cetite	480	50	200	4:1(Methanol)	98	Addition of 5% w/w of water
			Free *Pseudomonas cepacia*	1440	40	200	4:1(Methanol)	65	No solvent
			Pseudomonas cepacia on cetite	1440	40	200	4:1(Methanol)	91	No solvent
Su and Wei (2008)	_	_	*Candida Antarctica* lipase B(Novozym 435)	1440	45	150	5:1 (Methanol)	98	A mixture of 25% t-pentanol : 75% iso-octane were used as solvents
			Thermomyces lanuginosus (Lipozyme TL IM)						
			Rhizomocour meihei (Lipozyme RMIM)	1440	45	150	5:1(Methanol)	77	
				1440	45	150	5:1 (Methanol)	78	
Tamalampudi *et al*. (2008)	_	_	*Rhizopus oryzae* on BSPs (Biomass support particles)	360	30	150	3:1(Methanol)	80	Addition of water increases the yield
			Lipase Novozym-435	5400	30	150	3:1(Methanol)	76	
Kumari *et al*. (2009)	_	_	*Enterobacter aurogenes* on activated silica	2880	55	200	4:1(Methanol)	68	t-butanol was used as solvent
Tamalampudi *et al*. (2009)			*Rhizopus oryzae* on polyurethane foam	360	30		3:1	80	No solvent
			Candida Antarctica lipase B (Novozym 435)						
				5400	30		3:1	75	No solvent
Kumar *et al*. (2011)	0.775	0.25	*Chromobacterium viscosum* on Silica	30	Utrasonic wave applitude (100 W/m^3)	_	4:1(Methanol)	≥ 84.5	Using ultrasonic radiation
Kawakami *et al*. (2011)	18	-	*Burkholderia cepacia* immobilized on n-butyl-substituted silica monolith	720	40	(1400 min^{-1} shaking)	3:1(Methanol)	90	0.6% (w/w) water content
Rahmath and Pogaku (2013)	_	_	*Burkholderia cepacia Immobilized* by entrapment in biopolymer (sodium alginate and k-carrageenan)	1440	30	yes	10:1(Ethanol)	100	5.25g lipase and 6g RCF (mixing intensity)

X = fatty acid esters yield

Table 18. Summary of in situ esterification and transesterfication of jatropha curcas seed

Author	Alcohol	Ratio (alcohol to seed)	Catalyst	Catalyst amount	Reaction temperature °C	Reaction Time (min)	X %	Comment
Suit *et al*. (2010)	Methanol	10.5 ml/g	H_2SO_4	21.8%	60	600	99.8	No addition of co-solvent methanol acts as extracting solvent
Hailegiorgis *et al*. (2013)	Methanol	5.92:1 (w/w)	NaOH	1.52 wt%	37.63	103	89.8	BTMAOH was used as PTC and n-hexane was added for fast clarification. The use of ethanol is better than methanol in terms of yield and reaction conditions.
Hailegiorgis *et al*. (2013)	Ethanol	6.5:1 (w/w)	NaOH	1.38 wt%	34.9	92	99.4	
Jaliliannosti *et al*. (2013)	Ethanol	10.5% (v/w)	H_2SO_4 / KOH	7.5 ml / 8.15 ml	Microwave irradiation 110W, and $300^z/351.34^y$ rpm	35^x / 12.21^y	90.1	n-hexane was added for fast clarification. FFA reduces from 14% to less than 1%
Lim *et al*. (2010)	Methanol	10.0ml/g (methanol to seed)	SM	No catalyst	300 at 240 MPa	45 - 80	103.5	n-hexane was added as co-solvent (2.5ml/g n-hexane to seed). High temperature, pressure and methanol to seed ratio which gives higher yield in short reaction time
Lim and Lee (2013a)	Methanol	5.0 ml/g (methanol to seed)	SM	No catalyst	300 at 9.5MPa	30	99.6	No addition of co-solvent or any agitation source.
Kartika *et al*. (2013)	Methanol	6:1 (v/w) ml/g	KOH	0.075 ml/L	60 (with stirring speed of 700rpm)	240	80	100 ml of n-hexane was added as co-solvent (1:1 seed to n-hexane ratio (w/v))
Kartika *et al*. (2013)	Methanol	6:1(v/w) ml/g	KOH	0.075 ml/L	60 (with stirring speed of 800rpm)	300	85	Increase stirring increases the yield of biodiesel and reaction time
Lim and Lee (2013b)	methanol	4.0 ml/g	SM	No catalyst	208 at 8.0 MPa	30	107	1.0 ml/g pentane as co-solvent, n-hexane was used to facilitate separation of products
Lim and Lee (2013b)	methanol	4.0 ml/g	SM	No catalyst	208 at 8.0 MPa	30	102.3	50 bar of CO_2 as co-solvent, n-hexane was used to facilitate separation of products

z= first step reaction **y**= second step reaction **BTMAOH**= Benzyltrimethylammonium hydroxide **PTC**= Phase transfer catalyst **SM**= Supercritical methynation
x = fatty acid esters yield

Table 19. Summary of properties of biodiesel produce by various researchers and ASTM standard

Property	Umer *et al.* (2010)	Xin *et al.* (2010)	L u *et al.* (2009)	Anthony *et al.* (2011)	Kazi *et al.* (2010)	Joshua (2013)	Org *et al.* (2013)	Venkateswara and Srinivasa (2013)	Kumar *et al.* (2011)	Vyas *et al.* (2009)	Kumari *et al.* (2009)	Deng *et al.* (2011)	Tiwari *et al.* (2007)	Sahoo and Das (2009)	ASTM Standards
Density (Kg/m^3)	880±14.2	882	881	840	620	900	838.8	878	863.3	862	_	886	880	873	575 - 900
Viscosity mm^2/s	4.8±0.17	3.96	5.13	4.82	5.34	4.93	3.91	4.76	3.88	4.5	8.2	3.89	4.80	4.23	1.9 – 6.0
Flash point °C	188±3.0	133	164	128	255	137	161.5	162	135	110	82	186	135	148	100 – 170 minimum
Pour point °C	6.0±0.2	-2	2	- 2	-	-	2	-6	-12	6	5	-5	2	4.2	-15 to +10
Cloud point °C	10±0.2	_	2	8	_	37	3	_	-5	8	_	-	_	10.2	-3 to +12
Calorific value MJ/Kg	-	_	_	42.80	41	_	40.43	_	_	_	36.5	41.72	39.23	42.673	33 - 40
Cetane number	-	57	_	_	_	52	58.2	53.8	54	57	_	58	_	_	>47
Ash content wt%	0.016±0.001	_	_	_	_	ND	_	_	_	_	_	0.024	0.012	_	0.1 max
Acid value mg KOH/g	0.40±0.03	0.32	0.29	_	_	_	_	_	0.18	_	_	0.154	0.40	_	0.5 max

Lim et al. (2010) studied the novel biodiesel production technology using supercritical reaction extraction from *Jatropha curcas* L. oil seeds. Methanol was used to act both as an extraction agent and transesterification reagent while n-hexane was added to increase the oil solubility in the reaction mixture as well as separating the FAME from glycerol in the later process. An optimum conditions of 300°C reaction temperature, 240 MPa operating pressure, 10.0 ml/g methanol to solid (seed) ratio and 2.5 ml/g of n-hexane to seed ratio. The optimum oil extraction efficiency and fatty acid methyl esters yield reached up to 105.3% and 103.5% respectively; which exceeded the theoretical yield calculated based on n-hexane soxhlet extraction of jatropha oil seed. The reaction time was not studied but reported that the maximum yield was achieved between 45 to 80 minutes of reaction. In a recent study Lim and Lee (2013a) carried out in situ extraction and transesterification using supercritical reactive extraction with methanol in a high pressure batch reactor to produce fatty acid methyl esters (FAMEs) from *Jatropha curcas* L. seeds without use of catalyst. Materials and process parameters including space loading, solvent to seed ratio, co-solvent (n-hexane) to seed ratio, reaction temperature, reaction time and mixing intensity were varied one at a time and optimized based on two response i.e. extraction efficiency and FAME yield. Under the optimum condition of 54.0 ml/g space loading, 5.0 ml/g methanol to seed ratio, at 300°C reaction temperature, pressure 9.3 MPa, 30 min reaction time and without using n-hexane as co-solvent or any agitation source an extraction efficiency of 104.17% w/w and FAME yield of 99.67% was reported. The effects of space loading, methanol to seed ratio, temperature and reaction time gave significant influence towards the yield. In another recent work Lim and Lee (2013b) study the influence of co-solvent in supercritical extraction and transesterification of *Jatropha curcas* L. seed. The process was carried out in a high pressure batch reactor using methanol with different co-solvents (pentane, heptanes, toluene, tetrahydrofuran, nitrogen and carbon dioxide) with varying amounts(1.0 – 5.0 ml/g for liquids and 10 – 50 bar for gas) added to the process and the extraction efficiency and fatty acid methyl ester (FAME) yield were determined. It was found that pentane and CO_2 provided higher extraction efficiency and yield (102.6% and 107%; 100.4% and 102.3%) at concentration of 1.0 ml/g and 50 bar respectively. They also reported that the addition of pentane and CO_2 lowers the critical conditions of the reactant mixtures and could be achieved near optimum products yield at lower temperature (280°C), pressure (8.0 MPa) and lower methanol to seed ratio (4.0 ml/g). It was concluded that addition of appropriate co-solvents could increase the extraction rate (solid – liquid) and enhance methanol – oil interphase miscibility during the reaction phase. This result is an improvement over the previous work Lim and Lee (2013a) because of lower conditions of reaction as can be seen in Table 18.

In the summary of in situ process in Table 18, it can be seen that the transesterification with supercritical methynation and the use of microwave with high stirring speed drastically reduce the reaction time and give high yield of biodiesel. However the operation temperature and pressure of supercritical methynation is very high which will increase cost of production at commercial level. Although Lim and Lee (2013a) improve the supercritical methynation process with, lower methanol to seed ratio, less operation pressure and shorter reaction temperature compared the study carried out by Lim et al. (2010) as shown in Table 18. The use of H_2SO_4 catalyst by Shuit et al. (2010) also gives higher yield of 99.8% at mild temperature of 60°C, but it takes longer reaction time and use of large amount of catalyst. The use of ethanol and NaOH as catalyst by Heilegiorgis et al. (2013) gives higher yield at moderate conditions compared with the use of methanol.

The summary of the properties of jatropha biodiesel produce by some researchers and the ASTM standard are shown in Table 19. The kinematic viscosity which is a basic design specification for the fuel injectors used in diesel engines is an important property of biodiesel since it affects the operation of fuel injection equipment, particularly at low temperatures when the increase in viscosity affects the fluidity of the fuel (kywe and Oo 2009). High viscosity leads to poor atomization of the fuel spray, causing incomplete fuel combustion in diesel engines which leads to carbon deposits and eventually less accurate operation of the fuel injectors. With the exception of Kumari et al. (2009) who reported higher biodiesel viscosity above the ASTM specification all the other researchers reported biodiesel viscosity within the specification. The flash point is the temperature at which the biodiesel ignite when exposed to a flame or a spark. It also determines how the biodiesel may be shipped, stored and handled; usually fluids with flash point lower than 60°C are suggested to be handled as dangerous goods (Sylvain and Kouame 2011). The flash point of the biodiesels in Table 19 are above the minimum value specified by ASTM with the exception of the biodiesel produced by Kumari et al. (2009) which has lower value which could be an indication of the presence of more volatile materials in the biodiesel. The pour point and cloud point of the all the biodiesel as seen in Table 19 are within the ASTM specification with the exception of the value 37°C reported by Joshua (2013) which is three times above the maximum specification. The cetane number is one of the most significant properties that specify the ignition quality of compression ignition diesel engine. Jatropha biodiesel generally has high cetane number as can be seen in Table 19 which gives the fuel shorter ignition delay period than low cetane number fuel. The reduction in green house gases in using biodiesel as a fuel is generally attributed to the higher cetane number and oxygen content of biodiesel fuel (Taher et al. 2011). The high cetane number of jatropha biodiesel may be due to high concentration of saturated chains which allow them to be packed together very tightly and store chemical energy very densely (Sylvain and Kouame 2011). It can be seen from Table 19 that the biodiesel produced by Org et al. (2013) has the highest cetane number followed by the by Deng et al. (2011), which may be as a result of high concentrations of the saturated fatty acids (palmitic and stearic acids) in the oil used in Table 1. The calorific values of all the biodiesel reported by the researchers in Table 19 are slightly above the ASTM standard with the exception of Kumar et al. (2009) and Tiwari et al. (2007) whose values fall within the range. This implies that the biodiesel produce by Kumar et al. (2009) and Tiwari et al. (2007) has higher oxygen content which helps in complete combustion of fuel in diesel engines. The higher the oxygen content of biodiesel the lower the calorific value (Sahoo and Das 2009). The acid value (AV) of biodiesel is primarily an indicator of FFA, higher values are known to have been associated with fuel system deposit causing reduce life of fuel pumps and filters (Lu *et al*. 2009). All the acid values reported by the researchers in Table 19 are within the standard by ASTM.

Conclusion

From the above review the following conclusion could be made:

- Supercritical transesterifcation without the use of catalyst gives higher yield of biodiesel in a shorter reaction time, but at higher temperature, pressure and reactants molar ratio. The use of subcritical hydrolysis or addition of micro-NaOH catalyst employed with supercritical transesterification reduces drastically the reactants molar ratio and to some extent the temperature and pressure.
- The use of homogeneous catalyst for transesterification gives higher yield of biodiesel in shorter reaction time using jatropha oil of low FFA content compared to heterogeneous catalyst, but the use of heterogeneous catalyst assisted with microwave irradiation reduces the time of reaction drastically even with jatropha oil of high FFA content. Also the use of high stirring speed reduces the reaction time to some extent.
- Generally jatropha oil is known to have high FFA content and two step transesterifcation using acid/alkaline catalyst gives high yield of biodiesel. The process takes longer reaction time but when assisted with ultrasonic irradiation or high speed of stirring reduces the reaction time and improves the yield of biodiesel.
- The review of enzymatic transesterification showed that lipase immobilized and addition of 4 – 5% water or mixture of co – solvents such as t-pentanol: iso-octane gives higher yield of biodiesel. The longer reaction time associated with enzymatic transesterification reduces drastically with the use of ultrasonic irradiation and also increase yield of biodiesel.
- In situ esterification/transesterification of jatropha seed to biodiesel is affected by the reaction temperature and pressure, reaction time, amount and type of catalyst used, addition of co – solvent and type of alcohol used.
- The fuel properties of jatropha biodiesel reported by the researchers falls within the ASTM standard specifications with the exception of calorific values of biodiesel produce by Anthony *et al.* (2011), Kazi *et al.* (2010), Org *et al.* (2013), Deng *et al.* (2011) and Sahoo and Das (2009), and viscosity and flash point of the biodiesel produce by Kumari *et al*. (2009).
- All the transesterification processes adopted by many of the researchers gives higher biodiesel yield at various reaction conditions. There is a need to ascertain the economy of the processes before concluding on which process to be adopted for commercial production of biodiesel from jatropha.

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