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# Approaches in the utilization of *Jatrophacurcas* oil as feedstock for biodiesel synthesis: A review

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ABSTRACT

Apprehension about environmental degradation and the diminishing reserve of fossil fuel are the major drives toward search for alternative energy source. The most prominent biofuel employed in recent times in transportation of vehicles and propelling of machinery are biodiesel and bioethanol. The utilization of these liquid fuels has witness unprecedented growth in the last two decades due in part to the growing concern of depletion of fossil fuels and on account of environmental impact of the combustion of fossil fuel. Biodiesel is an alternative fuel similar in properties and performance to conventional or fossil fuel. It is a mixture of fatty acid alkyl esters produced from renewable raw materials such as animal fat which is a solid biomass at room temperature or vegetable oil which is a liquid state material. It is produced via transesterification of triglycerides with monohydric alcohol usually in the presence of a chemical or biological catalyst. Biodiesel of vegetable oils origin such as *Jatrophacurcas* oil, possess similar qualities to diesel fuel. *Jatrophacurcas* oil is non-edible oil which can avoid food-fuel competitiveness. *Jatrophacurcas* is considered as feedstock due to its non-food property, easy propagation, resistant to drought and high yield generation. *Jatrophacurcas* alkyl ester (*Jatropha* biodiesel) has properties close to diesel fuel and its utilization reduces $CO_2$ emission to the atmosphere. *Jatrophacurcas* oil use in diesel engine faces many problems owing to the viscosity which is caused by its large molecular weight. As a result, reduction of its viscosity is of prime importance and this is achieved through several approaches devised over time. This paper reviews production routes for biodiesel production utilizing *Jatrophacurcas* as feedstock. High conversion is reported in array of routes for *Jatropha* biodiesel synthesis.



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## INTRODUCTION

The urge for energy and environmental sustainability, government policies and incitement for alternative fuel consumption and improved world production capacity has necessitated the need for biodiesel fuel production from renewable sources [1]. For instance, 11.1 billion gallons of renewable fuels were to be mixed into energy supply as included in renewable fuels standard (RFS) of the United States Independence and Security Act of 2007, by the end of 2009 10.5 billion of this volume was proposed to be corn-based ethanol for use in gasoline. The remaining 600 million gallons of renewable fuels was expected to be from biomass based diesel fuel of which biodiesel is a prominent part [1]. Kotrba [2] reported that as at 2012 a billion gallons of biomass-based diesel was required under the RFS.

Besides, the high cost of raw materials-vegetable oils and animal fat- used for the production have called for inventory into economically viable alternative non-food feedstock for research consideration. There exist some characteristics features which include propagative adaptability of the plant (rainfall, soil condition, latitude etc.), regional presence, high oil content, suitable fatty acid composition, compatibility with existing farm infrastructure, low agricultural inputs (water, fertilizer etc.), uniform seed maturationrates, potential markets for agriculturally undesirable lands that makes the vegetable oil suitable for biodiesel production and oil that meet most of the aforementioned features will be a very good candidate as alternative energy source [1].

Basically, oilseed feedstocks in many country of the world are subject to available vegetable oil of which the country is the highest producing nation. For instance, in Malaysia and Brazil, biodiesel synthesis in these countries source for feed stocks from palm oil and soybean respectively. Other oilseeds that are predominantly

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used in biodiesel production include canola, corn, sunflower, cotton seed, coconut oil etc. depending on their relative abundance.

The utilization of alternative feed stock in regions where these oilseeds are not available or as part of effort to abate dependence on fossil fuel importation has made vegetable oil such as non-edible *jatropha curcas* oil being considered feedstock for biodiesel production[3,4,5].

*Jatropha curcas* oil is a potential feed stock for biodiesel production. Apart from palm oil and algae no other biodiesel feed stock is capable of producing high yield of biodiesel as *Jatrophacurcas*[6]. And as such the food-energy feud of palm oil and the complexity involve in algae-oil generation among other constraints has intensify the improved interest in *jatropha curcas* for consideration in biodiesel production.

In Malaysia, ultimate energy usage has increased drastically at an annual growth rate of 7.2% to 44.9 Mtoe over the last two decades [7]. Besides, report shows that Malaysian crude oil reserves stood at 3.39 billion barrels in 2001. Natural gas estimated reserve also reduced to 82.5 trillion standard cubic feet (tscf) for the same period[8].

Following this trend in production, the Malaysia oil and gas reserve are 16years and 32 years, respectively. This implies that if no other alternative sources are sought for, Malaysia will be a net importer of petroleum by the 2100s[9]. The pressing concern that Malaysia needs to tackle is energy supply security as limited domestic energy resources coupled with increasing energy demand will decrease the economy, export capability and raise the dependence on imported energy sources.

A vital approach to reduce fossil fuel dependence is to invest in exploitation of the nation's abundant renewable energy sources such as solar,mining, hydro and biomass [10]. Following this proposition, biodiesel stands prominent due to its low or noemission of greenhouse gases and itsfeedstock that is generated from renewable resources.

*Jatropha curcas:*

**Fig. 1:** *Jatropha curcas* plant

**Fig. 2:** *Jatrophacurcas* seed

*Jatropha curcas* L. is a small tree or large perennial shrub which belongs to the genus euphorbiaceae. It is valuable as oilseed crop[7,11]. It is a tropical plant [12]that can be propagated in low to high rainfall ranging from 250 to 3000mm[13] either in the farm as a commercial crop or on the fence of fields and farmland[14]. *Jatropha* is known to require little irrigation and it is well adapted to arid and semi-arid condition, hence it is considered drought resistance [7]. *Jatropha curcas* is a non-edible vegetable oil due to the presence of phorbol

esters which accounts for its toxicity. The concentration of phorbol esters in jatropha oil ranges from 3.10 to 3.77 mg/g [12].

Openshaw[15]reported that the basic use of *jatropha curcas* was in area of erosion control, land reclamation, utilization as live fence to exclude animal intrusion and as raw material for soap production. The plant has ability to spread far beyond its original distribution as a result of easy propagation, rapid growth, and easyestablishment [16]. These features place *jatropha curcas*a better choice over other non-edible oilseeds.

**Table 1:**Physico-chemical properties of *jatrophacurcas* oil.[11,17].

| Properties | Composition |
|---|---|
| Density | 0.93292 |
| Kinematic Viscosity | 52.76 |
| Cetane Number | 38.00 |
| Flash Point ($^0$C) | 210.00 |
| Calorific Value (MJ/Kg) | 38.20 |
| Saponification Value | 198.00 |
| Iodine Value | 94.00 |
| Peroxide Value | 1.93±0.012 |
| Viscosity at Room Temperature (cp) | 42.88 |
| Physical State at Room Temperature | Liquid |

In countries where edible oilis very scarce, *jatropha curcas* becomes the feedstock for biodiesel synthesis. For instance in India at present, 40 million tonnes of diesel is consumed annually and as such India grows about 7.4 million hectares of *jatropha* making her the largest producer of the plant[11]. *Jatropha* plant is a perennial crop of long productive period of about 50 years on average producing high yield annually[7]. The seed of *jatropha* is about 0.8kg/m$^2$per year[18] while the oil content being in the range of 30%-50 %[19].

Recently *jatropha curcas* has attracted research interest specifically in consideration for it potentials as oil crop feedstock for biodiesel production[12,16,20].

*Jatropha curcas*oil is a-branched triglycerides. It alkyl esters properties are similar to fossil diesel and it is capable of reducing $CO_2$ emission to the surrounding when utilized in diesel engine. Although the direct use of the oil is known to cause some problems subject to its viscosity and chemical structure [21]. Thus, reduction of its viscosity is of prime importance and these have been achieved through chemical and enzymatic approaches using various types of catalyst [22].

These approaches include preheating of theoil, micro-emulsion with solvent, dilution with diesel fuel, thermal cracking and Pyrolysis, transesterification[19,23,] and recently hydroesterification in a two-step enzyme-chemical procedure [24,25]. The prospect of*jatropha curcas* usage as feed stock in biodiesel synthesis is still at the level of ongoing research in Malaysia [7].

**Table 2:** Fatty Acid Composition of Jatrophacurcas oil [17]

| Fatty Acid | Composition |
|---|---|
| Palmitic Acid (16:0) | 14.2 |
| Stearic Acid (18:0) | 7.0 |
| Oleic acid (18.1) | 44.7 |
| Linoleic Acid (18:2) | 32.8 |
| Palmitoliec Acid(16:1) | 0.7 |
| Linolenic Acid (18:3) | 0.2 |
| Arachidic(20:0) | 0.2 |
| Margaric Acid (17:0) | 0.1 |
| Myristic Acid (14:0) | 0.1 |

*Production procedures of jatrophabiodiesel:*

Biodiesel synthesis via transesterification of *jatropha* oil was investigated by[22] in a two-step acid/alkaline-catalyzed transesterification. The optimum reaction condition observed for the reaction was found to be 483K, 25kPa, 1.0% w/w catalyst loading and trimethypropylene molar ratio of 4:1 producing a yield conversion of 95%in the process.

Berchmansand Hirata[26]produced biodiesel from high free fatty acid *jatropha curcas* oil. The high free fatty acid of the crude *Jatrophacurcas* oil was reduced to less than 1% by the two-step pretreatment process adopted. The first step was the pretreatment process to reduce the FFA level of the feed stock to less than 1% with an acid value of 2mgKOH/goil. The second stage of the process utilized alkali to catalyzed the transesterification process with production yield of 90%. Biodiesel synthesis was achieved by [27] from *jatrophacurcas* oil using a heterogeneous solid super base catalyst (calcium oxide).

Rathore and Giridhar[28]investigated biodiesel production from edible and non-edible vegetable oils. Among the non-edible oils investigated was *jatropha curcas* oil in super critical Methanol and Ethanol without the use of any catalyst from 200$^0$C to 400$^0$C at 200bar pressure. Jatropha methyl esters production via transesterification reaction utilizing heterogeneous solid base-catalyst ($KNO_3/Al_2O_3$) was studied by [29]. An optimum yield of 84% was recorded at 70$^0$C using methanol to oil molar ratio of 12:1 at 360min reaction time

and 6% catalyst ($KNO_3/Al_2O_3$) in the medium. It was observed that the solid catalyst was strong to catalyst the transesterification reaction of *jatropha* oil and it could be recycled at least for three cycles.

Harry and Shizuko [30]studied biodiesel production from *jatropha curcas* L seed oil. In their research, a two-step catalytic transesterification procedure was investigated. The first step was acid esterification which is primarily a pretreatment process. The second step was alkali-based catalyzed transesterification to produce the alkyl esters. Although the process was observed to be time consuming, a high biodiesel conversion was achieved.Liao and Chung[31] applied response surface methodology to continuous microwave process in order to observe the effect of three selected parameters: methanol to oil molar ratio, amount of catalyst and flowrate.

A continuous microwave irradiation reactor was developed to convert *jatropha curcas* oil to alkyl ester by NaOH. It was observed that microwave irradiation accelerates the chemical reaction and a high product conversion was achieved in no distant period. A two-step transesterification process utilizing low-cost high FFA *jatropha* oil was studied by Patil and Deng[32]. In this process, the first stage esterification was at $40^0$C uses 0.5% $H_2SO_4$ with methanol to oil molar ratio of 6:1. It was then followed by oil molar ratio of 9:1 with 2% KOH in the second alkali transesterification phase at $60^0$C. This mechanism of two-step esterification achieved a yield of 90-95% for the *jatropha* alkyl esters.

Kasim and Harvey [33]studied the reactive extraction of *jatropha curcas* for biodiesel production so as to bypass the extraction procedure which in part expose the workers to danger of toxicity of the oil. In this method chemically resistant 250ml Schott bottle was filled with methanol of required molar ratio. NaOH catalyst was then dissolved in it using magnetic stirring /hot plate. *Jatropha* seed of predetermined amount were put in the bottle after the mixture reached previously set temperature. The reaction was conducted in incubator shaker with controlled Temperature, agitation speed and reaction time. It was discovered that a production yield of about 64.0%-86.1% was recorded depending on the particle size. Only the two smallest particle sizes investigated in the study were capable of producing yield above 80%.

Raja *et al*[34] studied the base catalyzed transesterification reaction. The *jatropha curcas*oil used in this process was preheated at $70^0$C to evaporate moisture in the oil; methanol and NaOH were mixed and made to react with the oil at atmospheric pressure and $60^0$C for 60 minutes. It was affirmed subject to the findings that alkaline transesterification was a promising area of research for biodiesel production in large scale. Shah and Gupta[35] carried out biodiesel synthesis from jatropha oil with lipase catalyst in a solvent free system. It was discovered that the best yield (98%) was obtained with *pseudomonas cepacia* lipase immobilized on Celiteat $50^0$C in the presence of 4-5% water for 8hrs. it was observed that the grade of alcohol used does not have any influence on the yield.

Tiwari *et al*[36] conducted the optimum combination aimed at reducing the FFA of *jatrophacurcas* oil from 14% to less than 1%. 1.43% $H_2SO_4$ acid catalyst, 0.28 (v/v) Methanol to oil molar and 88min reaction time at temperature of $60^0$C was required. The product of the acid-pretreatment was transesterified with alkali catalyst and methanol (0.16v/v) as acyl acceptor to produce biodiesel in 24min. Average production yield above 99% was recorded which possess properties that satisfy biodiesel acceptance and standards.

The ultrasonic transesterification of *jatrophacurcas* was investigated by [37]. The steps involve acid esterification and alkaline transesterification reactions. In the first step, the acid value of *Jatrophacurcas* oil was observed to reduce from 10.45 to 1.2mg KOH/g after treatment with $H_2SO_4$ for 1 hr. with NaOH used for the second, a production yield and an acid value of 96.4% and 0.32mgKOH/g respectively was recorded after 30min of reaction time. It was deduced that the two step ultrasonic radiation procedure of biodiesel synthesis was effective and time saving.

Kay and Yasir[38]studied biodiesel production from low quality crude *jatropha* oil utilizing heterogeneous catalyst. In this research crude *jatropha curcas* oil was deteriorated at high temperature condition of $140^0$C and air flow at 10L/h using Rancimat. The heterogeneous catalyst used in this research was natural Zeolite. It was observed that biodiesel content increased gradually with increasing molar ratio of methanol to oil and a production yield above 96.5% was obtained. Also, it was discovered that biodiesel content increased with increasing mass ratio of modified Zeolite to *jatropha curcas* oil which was varied within the range of 3.0-10.0wt%. The maximum biodiesel content was obtained by adding 5% modified Zeolite catalyst which reached 97.8% at 6h reaction time.

Crude *jatropha curcas* oil was utilized as feed stock in a two-step catalyzed process using $SiO_2$.HF solid catalyst for FFA esterification step in biodiesel production by Corro *et al*.,[39]. Subsequent transesterification of the triglycerides in the *jatropha* oil was achieved with methanol catalyzed by NaOH. Analysis of the alkyl ester produced showed that the process resulted in very high quality biodiesel which satisfied it usage as fuel. Similarly a study conducted by [40] via transesterification process of *jatropha curcas* oil utilizing 1.3% KOH as catalyst and a methanol to oil molar ratio of 6:1 at $64^0$C. A production yield of the biodiesel obtained was higher than 98% in 20 min reaction time.

Kumera *et al*. [41]used a continuous coil flow reactor at temperature of $70^0$C with KOH as catalyst to obtain a purity and conversion of biodiesel of 99.04% with methanol to oil ratio of 5:1. Besides,[42] investigated the effect of calcinations temperature and calcinations duration of sulfated zirconia alumina(SZA)

catalyst as well as the interaction between both variable on the yield of fatty acid methyl esters produced from high free fatty acid *jatropha curcas* oil. Result obtained showed that these variables and their interaction considerably affect the FAME yield from 60.3wt% to 70.8wt%. Although, further increase of the variables cause the yield to decline as a result of conformational changes in the surface area of the catalyst.

Continuous-flow transesterification of crude *jatropha* oil with micro wave irradiation was studied by Tippayawong and sittisun[43]. This research employed sodium methoxide as catalyst and a microwave power of 800W was utilized. Variation in the catalyst concentration (0.25%-1.5%), irradiation time between 10-40s and oil to methanol molar ratio of 1:3-1:9 resulted in optimum yield of 96.5% biodiesel.

**Table 3:** Production Routes, Yield, Advantages and Disadvantages

| Production route | Product yield | Advantages | Disadvantages | References |
|---|---|---|---|---|
| Acid catalyzed reaction | 90% | No soap formation | High temp. Requirement<br>Longer reaction time | Kay and tasir[2012] |
| Alkaline catalyzed reaction | 90-95% | High yield<br>Low reaction time and temp. | Soap formation<br>Product contamination | [34] |
| Acid/alkaline catalyzed reaction | 90-95% | High yield<br>Low temp requirement | Long reaction time | [22, 26] |
| Heterogeneous solid base catalyst | 84% | Low temp.<br>Catalyst recycle | Long reaction time<br>Excess alcohol usage | [27,29] |
| Super critical alcohol condition | 80%, 60-70% | No catalyst is required | High energy requirement | [28] |
| Continuous microwave process | 96.5% | Reaction rate increase<br>High yield | High power requirement | [23,31] |
| Reactive extraction | 80% | No danger of toxicity | Difficult to commercialize | [33] |
| Lipase catalyzed process | 98% | Product purity<br>Low reaction temp. | Longer reaction time | [35] |
| Ultrasonic transesterification | 96.4% | Short reaction time<br>Effective in product yield | High power requirement | [37] |

*Emissions from JatrophaCurcas Alkyl Esters:*

Agarwar and Agarwar[44]studied the features of emissions produced from *Jatropha* oil blends in a direct injection compression ignition engine. The proportion of the *jatropha* biodiesel in the oil blend was observed to determine the amount of emissions when compared to pure biodiesel taken as standard. The effect of injection timing and high injection pressure was investigated by [45]. It was recorded that emission reduction of HC, CO and smoke was commensurate with *jatropha* methyl ester as fuel in diesel engine, thoughdifferent result was obtained for compression ignition engine.

Jindal *et al*.[46] investigated the emissions from pure *jatropha* oil, diesel fuel and *jatropha* biodiesel. The study revealed that when the injection pressure and compression ratio were increased, emission of HC, $NO_x$, smoke opacity and temperature of exhaust were reduced in *jatropha* oil in comparison with conventional diesel. However, *jatropha* biodiesel was observed to produce increased HC and CO, crude *jatropha* produced more smoke and PM.

Banapurmath *et al*[18] studied the emission characteristics of DI compression ignition engine utilizing *jatropha* biodiesel. The smoke opacity, HC and CO for the *jatropha*biodiesel was observed to be higher in relation to conventional diesel fuel, while $NO_x$ is lower in the *jatropha* biodiesel compared to diesel as a result of low cylinder peak pressure and lower heat proportion generated. Chauhan *et al*. [47] reported the effect of fuel inlet temperature on engine emission using dual fuel engine test rig with tube heat exchanger. High $NO_x$ emission was recorded for *Jatropha* oil. Although, pretreatment of the oil resulted in high emission of $CO_2$ while other emissions such as CO, HC, and smoke opacity were reduced.

Predeep and Sharma [48] recommended the use of hot exhaust gas recirculation (EGR) for control of $NO_x$ in diesel engine utilizing *jatropha* oil. Result shows that effective reduction of $NO_x$ was achieved. However 15% of EGR was optimized to reduce $NO_x$ emission without pronounced effect on the performance, smoke and other emission.

*Conclusion:*

Among the more than three hundred oil seed crops identified, the prospect of *jatrophacurcas* cannot be underestimated.Its advantages as a non-food oil has propel research in utilizing *jatrophacurcas* oil as feedstock in myriad of production processes for optimum yield at minimum resource utilization. Production of biodiesel is observed to be successful industrially via alkali-catalyzed transesterification process compared to acid-catalyzed which occur at higher reaction temperature and longer reaction time. However, heterogeneous acid-catalyzed reaction for biodiesel production promised to be more effective because the problem of product purification complexities is averted.

Besides, quest for eco-friendly route has revealed the catalytic efficiency of lipase enzyme in esterification and transesterification processes. Of all the emissions produced by combustion of biodiesel in comparison with diesel fuel, $NO_x$ is the only emission known to be more in biodiesel while HC, $CO_2$ and PM are reduced commensurately.

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