Process optimization for biodiesel production from Jatropha, Karanja and Polanga oils

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ABSTRACT

Petroleum sourced fuels is now widely known as non-renewable due to fossil fuel depletion and environmental degradation. Renewable, carbon neutral, transport fuels are necessary for environmental and economic sustainability. Biodiesel derived from oil crops is a potential renewable and carbon neutral alternative to petroleum fuels. Chemically, biodiesel is monoalkyl esters of long chain fatty acids derived from renewable feed stock like vegetable oils and animal fats. It is produced by transesterification in which, oil or fat is reacted with a monohydric alcohol in presence of a catalyst. The process of transesterification is affected by the mode of reaction condition, molar ratio of alcohol to oil, type of alcohol, type and amount of catalysts, reaction time and temperature and purity of reactants. In the present paper various methods of preparation of biodiesel from non-edible filtered Jatropha (*Jatropha curcas*), Karanja (*Pongamia pinnata*) and Polanga (*Calophyllum inophyllum*) oil have been described. Mono esters (biodiesel) produced and blended with diesel were evaluated. The technical tools and processes for monitoring the transesterification reactions like TLC, GC and HPLC have also been used.

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1. Introduction

In view of the escalating energy (fuel) crisis and environmental degradation, biodiesel is one of the sources for replacement of petro-diesel, thereby reducing country's dependence on importing crude petroleum from overseas country. Crude petroleum resources are finite and therefore search for alternative fuel is continuing all over the world. The rising prices of petroleum fuels, depletion of oil reserves and stiff regulations on exhaust emissions have necessitated the substitution of fossil fuels with less polluting and easily available renewable fuels for use in internal combustion engines. Development of biodiesel as an alternative and renewable source of energy for the mechanized agricultural and transportation sector has become critical in the national effort towards maximum self-reliance for the corner stone of our energy security strategy.

The concept of using biofuels in diesel engines was originated from the demonstration of first diesel engine by the inventor of diesel engine "*Rudolf Diesel*" at the World Exhibition at Paris in 1900 by using peanut oil as fuel. However, due to abundant supply of petro-diesel, R&D activities on vegetable oil were not seriously pursued. It received attention only recently when it was realized that petroleum fuels are dwindling fast and environment-friendly renewable substitutes must be identified [1]. In the recent years,

serious efforts have been made by several researchers to use different source of energy as fuel in existing diesel engines. The use of straight vegetable oils is restricted by some unfavorable physical properties, particularly their viscosity. Due to higher viscosity, the straight vegetable oil cause poor fuel atomization, incomplete combustion and carbon deposition on the injector and valve seats resulting serious engine fouling. It has been reported that when direct injection engines are run with neat vegetable oil as fuel, injectors gets choked up after few hours and lead to poor fuel atomization, less efficient combustion and dilution of lubricating oil by partially burnt vegetable oil. One possible method to overcome the problem of higher viscosity is blending of vegetable oil with diesel in proper proportion and the other is transesterification of oils to produce biodiesel.

A study has been conducted on eleven straight vegetable oils; namely castor, corn, cotton seed, crambe, linseed, peanut, canola, safflower, sesame, soybean and sunflower and determined their fuel properties [2]. It is reported that compared to commercial diesel fuel, all the vegetable oils were much more viscous, much more reactive to excess oxygen and had higher cloud and pour points. The viscosities of vegetable oils were found to be 10–20 times greater than diesel fuel. Increased carbon chain length and reduced number of double bonds were associated with increased oil viscosity, cetane rating and reduced gross heat content. It was found that except for castor oil, there was little difference between gross heat content of any of the vegetable oils. Heat contents were approximately 88% of that of diesel. Peterson [3] reviewed vegetable oils

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as possible substitute for diesel fuel. The most predominantly oil bearing crops considered as fuel substitute were sunflower, safflower, soybean, cotton, winter rape, canola and peanut. Further, the investigator discussed the transesterification, oil processing, storage, and filtration as well as engine test aspects. A comprehensive review was done on vegetable oils as fuels for internal combustion engines [4]. The observed major difference between diesel fuel and vegetable oil included, for the later, the significantly higher viscosities, moderately highly densities, lower heating values, rise in the stochiometric air–fuel ratio due to the presence of molecular oxygen and the possibility of thermal cracking at the temperatures encountered by the fuel spray in the naturally aspirated diesel engines. These characteristics often result in poor atomization, coking tendencies, carbon deposits and wear. These were generally experienced in most of the tests which adversely affect the durability of the engine. It has been reported that high viscosity and low volatility of vegetable oils are generally observed to be the major drawbacks for their utilization as fuel in diesel engines [5]. The high viscosity of vegetable oils cause problems in the injection process leading to an increase in smoke levels and the low volatility of the vegetable oils result in oil sticking of the injector or cylinder walls, causing the deposit formation which interferes with the combustion process.

Bari et al. [6] conducted short term performance tests using crude palm oil (CPO) as a fuel for a diesel engine and showed CPO to be a suitable substitute with diesel. However, prolonged use of CPO caused the engine performance to deteriorate. After 500 h of cumulative running with CPO, the maximum power was reduced by about 20% and the minimum brake specific fuel consumption was increased by about 26%. Examination of the different parts after the engine was dismantled revealed heavy carbon deposits in the combustion chamber, traces of wear on the piston rings as well as on the plunger and the delivery valve of the injection pump, slight scuffing of the cylinder liner and uneven spray from the nozzles. The main reason for engine performance deterioration was 'valve sticking' caused by carbon deposits on the valve seats and stems. This resulted in leakage during the compression and power strokes and a reduced effective compression ratio which subsequently affected the power & fuel economy.

Schlick et al. [7] evaluated the performance of a direct injection, 3-cylinder, 2600 series Ford tractor engine with 1:3 (v/v) blends of soybean oil and sunflower oil with diesel fuel for 200 h of engine operation. After the 200 h test it was concluded that as far as power output, thermal efficiency and lubricating oil data were concerned, the 1:3(v/v) blends of soybean oil and sunflower oil with diesel fuel performed satisfactory. However, after 200 h of operation combustion chamber parts and injector tips were coated with carbon deposits. The investigators suggested that either different operating conditions or modification of vegetable oils could help in improving the conditions of the engine. Gerhard [8] reported that transesterification of vegetable oil to its methyl ester reduces its molecular weight and viscosity and increases its cetane number.

Peterson et al. [9] reported that the transesterification process has been proven worldwide as an effective means of biodiesel production and viscosity reduction of vegetable oils. As described earlier it is the process of reacting triglyceride with an alcohol in the presence of a catalyst to produce glycerol and fatty acid esters. Temperatures, catalyst type, concentration ratio of alcohol to fuel and stirring speed rate have been observed to influence the transesterification process to a greater extent. Freedman et al [10] found that a 30:1 ratio of methanol to soybean oil with 1% sulphuric acid gave higher conversion after 44 h of heating at 60 °C. They emphasized that if vegetable oils have more than 1% free fatty acids, the acid catalyst becomes more effective than alkali catalyst.

Canakci and Gerpen [11] studied the effects of process variables on acid-catalyst transesterification of soybean oil. They reported that ester conversion reached 98.4% at the methanol to oil molar ratio of 30:1 with suphuric acid as catalyst at 60 °C. It was reported that the ester conversions were 8.3%, 57.2% and 87.8% at 25, 45 and 60 °C temperatures, respectively. The specific gravity of ester decreased with increasing reaction temperature. They studied the effect of catalyst amount by conducting reaction for 48 h at 60 °C with a 6:1 molar ratio of methanol to oil. They reported that ester formation increased from 72.7% to 95.0% as the catalyst was increased from 1% to 5%. The investigators also studied the comparative effect of methyl alcohol, ethyl alcohol, propyl alcohol and butyl alcohol on the yield of biodiesel production. Ester conversion increased from 87.8% to 95.5% when the reaction time was increased from 48 to 96 h. The conversion to ethyl ester was 95.8% compared with 92.9%, 92.1% and 87.8% for 2-propyl ester, 1-butyl ester and methyl ester, respectively. They added different amount of distilled water to the vegetable oil to study the effect of water on transesterification. It was reported that the addition of 5% water reduced the ester conversion by 5.6%.

Ramadhas et al. [12] developed a double stage process for producing biodiesel from high free fatty acid rubber seed oil in which crude rubber seed oil was treated with 0.5% sulphuric acid along with 200 ml methanol per litre of crude oil in the first step for reducing FFA to about 2% followed by alkaline catalyzed transesterification in the second stage. They found that excess addition of acid often darken the product. The maximum ester conversion was achieved at the reaction temperature of 45 ± 5 °C and the viscosity of biodiesel was nearer to diesel.

Ramadhas et al. [13] also found that no significant engine problems were reported in large-scale tests with urban bus fleets running on B20. Fuel economy was comparable with diesel fuel and the fuel consumption of biodiesel blend being only 2–5% higher than that of conventional diesel. They observed another advantage of biodiesel blends is the simplicity of fuel preparation, which only requires mixing of the components. Ester blends have been reported to be stable, for example, a blend of 20% peanut oil ester with 80% diesel did not separate at room temperature over a period of three months. One limitation to the use of biodiesel is its tendency to crystallize at low temperatures below 0 °C. Methyl and ethyl esters of vegetable oils tend to crystallize and separate from diesel at temperatures often experienced during operation in winter. Such crystals can plug fuel lines and filters, causing problems in fuel pumping and engine operation.

A brief study was conducted by Masjuki et al. [14] on the use of biodiesel from coconut oil (50/50 blend), "B50" in motor coaches. This study revealed that it is a viable and a practical alternative fuel for older in-service engines. Particulate matter was almost negligible with the use of this fuel. Operators reported that the test vehicles had no noticeable drivability downsides. On the other hand it was observed the vehicles had some improved power performance while operating under city traffic conditions.

A Cummins N14-410 diesel engine was operated by Ali et al. [15] on an 80:13:7 (v/v) blends of diesel fuel, methyl tallowate and ethanol. The power output, torque produced and brake specific fuel consumption of the engine were more or less constant throughout the test. Their studies on the use of hybrid fuels, formed by micro emulsifying aqueous ethanol in soybean oil, were evaluated by burning them in a diesel engine. The fuels performed nearly as well as diesel despite having lower cetane numbers and less energy content. However, the hybrid fuels are currently too expensive to compete with diesel fuel but could serve as an emergency fuel if petroleum supplies are interrupted.

The investigations relating to the higher percentage of substitution of diesel fuel with biodiesel derived from non-edible oils in compression ignition engines have been scantily reported in the literature. Hence there exists a definite need to carry out more investigations for suitable production process to derive biodiesel

from various non-edible oils which keep biodiesel–diesel blends stable and subsequently maintain the fuel quality such as cetane number, calorific value and viscosity for proper operation of diesel engines. Moreover the technology has not been well developed in India. Extensive studies have to be carried out for the production of biodiesel, efficient utilization and improved burning of biodiesel and biodiesel–diesel blends. Further, comparative assessment of the engine performance, emission and combustion characteristics of biodiesel from Jatropha, Karanja and Polanga seed oils are scantly reported in literature. Hence, in the present work it is proposed to assess the scope of development of biodiesel production process from Jatropha, Karanja and Polanga seed oils.

2. Experimental setup and procedure for biodiesel production

Biodiesel from Jatropha, Karanja and Polanga were produced in a laboratory scale set up (Fig. 1) which consists of heating mantle, reaction flask and mechanical stirrer. The working capacity of reaction flask is 1 l. It consists of three necks for stirrer, condenser and inlet of reactant as well as for placing the thermocouple to observe the reaction temperature. The flask has a stopcock at the bottom for collection of the final product. The procedure for preparation of methyl esters varies from oil to oil depending upon their chemical composition and free fatty acids (FFA) content. Process parameters such as the mode of reaction condition, molar ratio of alcohol to oil, type of alcohol, type and amount of catalysts, reaction time and temperature and purity of reactants were optimized.

2.1. Analysis of straight vegetable oils (Karanja, Jatropha & Polanga)

Vegetable oils are water insoluble, hydrophobic substances of plant and animal origin, which are primarily composed of the fatty esters of glycerol, so called triglycerides. The chemical structure of vegetable oils, in general, is shown in Fig. 2. R_1, R_2 and R_3 represent the hydrocarbon chain of fatty acids. The R_1, R_2 and R_3 may be the same, depending upon the particular oil, but ordinarily are different in chain length and number of double bonds. Free fatty acids play vital role during the biodiesel production process which lead to formation of soap and water. The types and percentage of fatty acids contained in vegetable oils, depends on the plant species and on the growth conditions of the tree. The yield of esterification process and quality of biodiesel decreases considerably if acid value is greater than 4 mg KOH/g, i.e. free fatty acid content is more than 2%. Therefore, it is essential to determine the FFA content of these oils selected for the study.
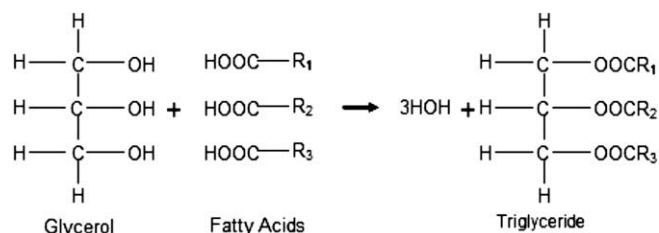

Fig. 2. Chemical structure of a typical triglyceride (vegetable oil).

Acid value of vegetable oil is defined as the number of milligrams of potassium hydroxide required to neutralize the free acid present in 1 gm of the oil sample. Acid value of these oils was determined by a standard titrimetry method. The percentage composition of FFA was also determined by gas chromatographic analysis and total percentage of FFA was calculated from the acid value i.e. half of the acid value.

2.2. Refining of Jatropha, Karanja and Polanga oil

After oil expelling the crude vegetable oils contain some of the impurities such as uncrushed seed cake and other particulates. Therefore, it was essential to refine the crude vegetable oils. The crude non-edible oils such as Jatropha, Karanja and Polanga oil were refined in the laboratory through simple filtration methods. These were filtered by using 4 micron filter paper under vacuum condition. These filtered oils were dried in a vacuum drier at a constant temperature of 60 °C for 4 h to remove the traces of moisture. The dried oils were stored in the air tight dry PVC cans. The oils were filled up to the brim of the can to avoid any chances of oxidation. These cans were stored in a room at ambient temperature. The composition of the physically filtered Jatropha, Karanja and Polanga oil were determined in the laboratory by following the standard methods and techniques.

2.3. Process optimization for biodiesel preparation from crude oils in lab scale

It is reported that high FFA content of crude vegetable oils lead to soap formation and lower yield of biodiesel. Therefore, the following methods adopted for process optimization to get maximum yield of Jatropha, Karanja and Polanga oil based biodiesel in a 1 l reactor (Fig. 1). The progress of the reaction was observed by measuring the acid value. In the course of the tests, it was observed that the appropriate quality of biodiesel could be produced from Jatropha, Karanja and Polanga oil in the following three stages so that the physico-chemical properties were close to those of petro-diesel. The completeness of transesterification for each experiment in all the stages was monitored with standard HPLC method.

2.3.1. Zero-catalyzed transesterification
The first stage removes the organic matters and other impurities present in the refined filtered Jatropha, Karanja and Polanga oil using reagent. The raw Polanga oil was extracted by mechanical expeller in which small traces of organic matter, water and other impurities were present. These materials were creating problems in yield and in the phase separation between the glycerin and esters. This necessitates the pretreatment of crude vegetable oils in the first stage. This is a type of zero-catalyzed transesterification in which mixture of crude oil, methanol, ortho-phosphoric acid and toluene was stirred at a constant speed and temperature for 0.5–4 h. One litre of oil was mixed with 350 ml of methyl alcohol, 5 ml of toluene and 5 ml of ortho-phosphoric acid as a reagent. Toluene helps in dissolving the organic matter with methanol and
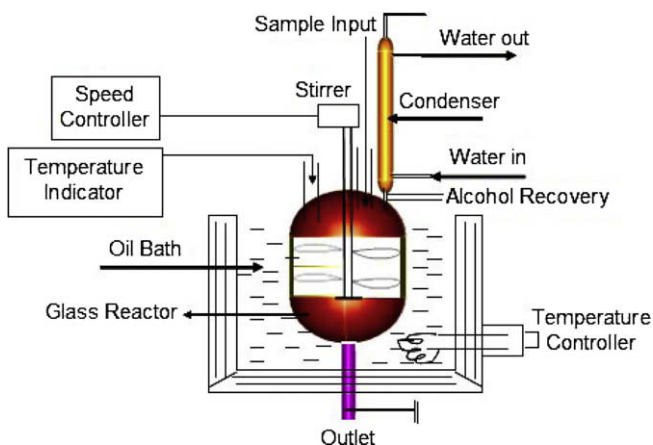

Fig. 1. Schematic layout of the experimental set up of biodiesel reactor.

separating it from the neat oil along with other impurities. Different methanol to oil ratio in percentage volume basis (6% to 40%) and reaction times (0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 h) were used to investigate for the optimization and their influence on the acid value of crude vegetable oils. The mixture was stirred in the air closed reaction flask for 2 h at 66 °C. The heating set up should be just above the boiling point of the alcohol i.e. 66 °C to accomplish the reaction. The speed of the stirrer was kept same for all test runs. The reactions were carried out with continuous stirring by mechanical stirrer at a stirring speed of 450 rpm. The product from the first stage was allowed to settle for one hour and complete phase separation was visualized. The upper layer which consisted of methanol – water fraction, organic matter, gum, toluene and other impurities was separated from the lower layer. The acid value of lower layer, which was raw material for the second stage, was further measured and discussed.

2.3.2. Acid-catalyzed transesterification

Anhydrous sulphuric acid (98.4%) was used as catalyst in the acid-catalyzed transesterification. The product of the first stage was mixed with various proportion of anhydrous sulphuric acid (98.4%) starting from 0.1% (v/v) along with methanol in volume basis and stirred at a temperature of 55 °C with reaction time of 0.5, 1.0, 1.5, 2.0, 2.5, 3, 3.5 and 4 h. The stirring speed was maintained 350 rpm for all the experiments.

2.3.3. Alkaline-catalyzed transesterification

The product of the intermediate stage (pure triglycerides) was transesterified to mono-esters of fatty acids (biodiesel) using alkali catalyst (KOH). The product of second step having FFA less than 2% was used as the raw material for the final stage. Similar trend, as acid-catalyzed transesterification, was adopted for third stage. After the reaction was completed the products were allowed to separate in two layers. The lower layers contained impurities and glycerol. The top ester layer was separated and purified by using warm water. After washing, the final product was heated up to 70 °C for 15 min under vacuum condition to remove water and stored for further use. This resulted in a clear light liquid with a viscosity close to petro-diesel.

2.4. Biodiesel characterization

The physico-chemical properties of the Jatropha, Karanja and Polanga oil based biodiesel (B100) and their various blends with diesel were evaluated as per the ASTM standards and the experimental procedure for evaluating physico-chemical properties were followed. The fuel properties data of Jatropha, Karanja and Polanga oil methyl esters and their different blends with diesel are summarized in a tabular form as shown in Table 1.

3. Results and discussion

3.1. Composition of Jatropha, Karanja and Polanga oil

The fatty acid composition and other physico-chemical properties of Jatropha, Karanja and Polanga oil is presented in Table 2. It is observed that free fatty acid (FFA) content of most of these oils is more than 2% except Jatropha oil. Therefore, development of any method to produce the appropriate quality of biodiesel from these oils is significant particularly to study the performance, emission and combustion characteristics of diesel engines.

Polanga oil contains 24.96% saturated acids (Palmitic and Stearic) and 72.65% unsaturated acids (Oleic, Linoleic and Linolenic). Saturation fatty acid alkyl esters increase the cloud point, cetane number and stability. Karanja oil consists of 94.09% pure triglyceride esters and rests were free fatty acids and lipid associates, particularly flavonoids, which is the measure of un-saponifiable matter. The free fatty acid content of unrefined jatropha oil was about 1.9%. The yield of esterification process decreases consider-

Table 2
Fatty acid composition and important properties of straight vegetable oils.

Sl. No.	Property of the oils	Polanga (*Calophyllum inophyllum*)	Karanja (*Pongamia pinnata*)	Jatropha (*Jatropha curcas*)
1	Fatty acid composition (%)			
	Palmitic acid $C_{16:0}$	12.01	11.65	16.0
	Stearic acid $C_{18:0}$	12.95	7.50	6.5
	Oleic acid $C_{18:1}$	34.09	51.59	43.5
	Linoleic acid $C_{18:2}$	38.26	16.46	34.4
	Linolenic acid $C_{18:3}$	0.3	2.65	0.80
2	Specific gravity	0.896	0.913	0.920
3	Viscosity (cSt) at 40 °C	71.98	27.84	18.2
4	Flash point (°C)	221	205	174
5	Calorific value (MJ/kg)	39.25	34.0	38.5
6	Acid value (mg KOH/gm)	44	5.06	3.8
7	Free fatty acid (%) – FFA	22	2.53	1.9

Table 1
Properties of biodiesel (JOME, KOME and POME) and their blends.

SN	Fuel blend	Density (kg/m³)	CV (kJ/kg)	Viscosity (cSt)	Flash point (°C)	Cloud point (°C)	Pour point (°C)
1	Diesel	850	44,000	2.87	76	6.5	3.1
2	JB20	852	43,759.5	3.02	88	6.9	3.3
3	JB40	854	43,519	3.41	97	7.1	3.4
4	JB50	857	43,323	3.59	113	7.3	3.4
5	JB60	860	43,038	3.64	119	7.6	3.6
6	JB80	866	42,912	3.98	131	8.3	3.9
7	JB100	873	42,673	4.23	148	10.2	4.2
8	KB20	851	43,690	3.04	96	8.9	3.1
9	KB40	854	43,150	3.51	99	10.9	3.6
10	KB50	856	43,307	3.62	106	11.2	4.2
11	KB60	859	42,937	3.81	123	11.6	4.3
12	KB80	871	42,318	4.01	149	12.3	4.9
13	KB100	883	42,133	4.37	163	14.6	5.1
14	PB20	852	43,109	2.98	86	7.8	2.9
15	PB40	854	42,873	3.30	91	8.5	2.8
16	PB50	857	42,542	3.42	93	8.7	2.9
17	PB60	860	42,351	3.61	96	10.6	3.2
18	PB80	862	41,963	3.72	111	10.8	3.6
19	PB100	869	41,397	3.99	140	13.2	4.3

ably if FFA value is greater than 2%. It has been found that the alkaline catalyzed transesterification process is not suitable to produce esters from unrefined oils having FFA greater than 2% due to presence of moisture leading to soap formation and lack of phase separation. Important physico-chemical properties and fatty acid composition of refined Jatropha, Karanja and Polanga seed oil is taken in to consideration for production of methyl esters by triple stage transesterification.

3.2. Triple stage transesterification

In good vegetable oils, the acid value should be minimum (<4 mg KOH/gm). Increase in acid value should be taken as an indicator of oxidation of the oil which may lead to gum and sludge formation besides corrosion. It is observed from the Table 1 that acid value of the refined Polanga and Karanja oils are more than 4 mg KOH/gm i.e. FFA is greater than 2%. This is due to the presence of gum and organic matter in the refined vegetable oils.

First stage transesterification for all these three oils result in lowering the acid value. It is observed that the raw material, which consists of mono-esters (biodiesel), di-esters, triglycerides and FFA, for second and third stage after zero-catalyzed transesterification having FFA below 2% except in case of Polanga oil. The optimize parameters such as reaction temperature, reaction duration, stirring speed, amount of catalyst and volume of methanol per litre of refined Jatropha, Karanja and Polanga oils for all the three stages are presented in Table 3.

In course of preliminary tests, it is observed that reduction of FFA below 2% is essential for Polanga oil as it has high FFA (14.5%). This necessitate extra step (acid-catalyzed transesterification) for Polanga oil in which the lower layer of zero-catalyzed transesterification is treated with anhydrous sulphuric acid as catalyst and methanol for 4 h. Extra FFA of Polanga oil has been converted to triglycerides during the second stage of transesterification. The final FFA content of the Polanga oil mixture, which consists of mono-esters (biodiesel), di-esters, triglycerides and FFA, is found to be 1.62%. Experimentally, it has been optimized that 0.65% by volume of the H_2SO_4 acid and an oil to methanol volumetric ratio of 7.5:1 give the maximum conversion efficiency of free fatty acids to triglycerides and thereby reducing the acid value of the product of second stage below 4 mg KOH/gm. The optimize duration of the reaction is 4 h.

It is also observed (Table 3) from the experiments conducted for base-catalyzed transesterification that an optimum oil to methanol volumetric ratio of 11.5:1 and the 0.9% by weight per volume of potassium hydroxide is found to give the maximum Polanga oil methyl ester (POME) yield for reaction duration of 4 h leading to 85% of ester yield. The formation of Jatropha oil methyl ester (JOME) and Karanja oil methyl ester (KOME) by base-catalyzed transesterification requires optimum oil to methanol volumetric ratio of 9.7:1 and 10:1 for every litre of triglyceride which is sufficient to give 93% and 91% yield of ester respectively. It might be anticipated that, in such an equilibrium system, the observed phase separation of the by-product, glycerol, would play a major role in achieving a conversion close to 100. However, transesterification is an equilibrium reaction in which an excess of the alcohol is required to drive the reaction close to completion.

3.2.1. Effect of methanol amount on biodiesel formation

The amount of alcohol added to vegetable oil is one of the important factors that affects conversion efficiency as well as production cost of biodiesel. The conversion efficiency is defined as the yield of the process represented in terms of percentage. The amount of methanol required for base-catalyzed transesterification is analyzed in terms of volumetric ratio. Stoichiometrically, the methanol/triglyceride molar ratio required is 3:1. But, in practice this is not sufficient to complete the reaction. Higher amount of alcohol is required to drive the reaction to completion at faster rate.

It is observed that lower amount of methanol requires longer reaction period. The conversion efficiency of base-catalyzed transesterification in relation with amount of alcohol obtained during present study is shown in Fig. 3a. The maximum conversion efficiency is achieved very close to the volumetric ratio of oil to methanol are 11:1, 11.5:1 and 12:1 for Jatropha, Karanja and Polanga oil, respectively. With further increase in volumetric ratio there is no improvement in the conversion efficiency. Also, it has been found that the reduction in viscosity increases with increase in volume of methanol in the mixture.

3.2.2. Effect of catalyst on methyl esters yield

The alkaline catalyst, potassium hydroxide concentration in the range 0.5–1.5% (weight of KOH/volume of oil) is used in the present experimental analysis. The effect of catalyst amount on conversion

Table 3
Optimized parameters for biodiesel production from 1 l refined Jatropha, Karanja and Polanga oils.

| Sl. No	Parameters	Jatropha oil			Karanja oil			Polanga oil		
		1st stage	2nd stage	3rd stage	1st stage	2nd stage	3rd stage	1st stage	2nd stage	3rd stage
1	Refined Vegetable oil (litre)	1	–	1.135	1	-	1.13	1	1.155	1.05
2	Methanol (ml/l of SVO)	350	–	110	350	-	115	350	75	120
3	Toluene (ml/l of SVO)	4	–	–	5	–	–	5	–	–
4	Ortho phosphoric acid (ml/l of SVO)	4	–	–	5	–	–	5	–	–
5	Sulphuric acid (ml/l of SVO)	–	–	–	–	–	–	–	6.5	–
6	Potassium hydroxide (gm/l of SVO)	–	–	8	–	–	11	–	–	9
7	Reaction temperature (°C)	66	–	66	66	–	66	66	55	66
8	Reaction duration (hours)	2	–	3	2	–	3.5	2	4	4
9	Stirring speed (RPM)	450	–	500	450	–	500	450	350	500
10	Settling time (hours)	1	–	13	1.5	–	15	2	2	13
Results										
11	By-product (ml)	215	–	315	220	–	335	195	180	320
	GUM + OM + EARTH + Methanol	213	–	–	218	–	–	179	–	–
	FFA (%)	1.6	–	–	1.9	–	–	14.5	1.62	–
	Methanol recovered	–	–	199	–	–	205	–	–	225
	Glycerol (ml)	–	–	58	–	–	53	–	–	62
12	Final yield (ml)	1135	–	930	1130	–	910	1155	1050	850
13	Final yield (%)	113.5	–	93	113	–	91	115.5	105	85
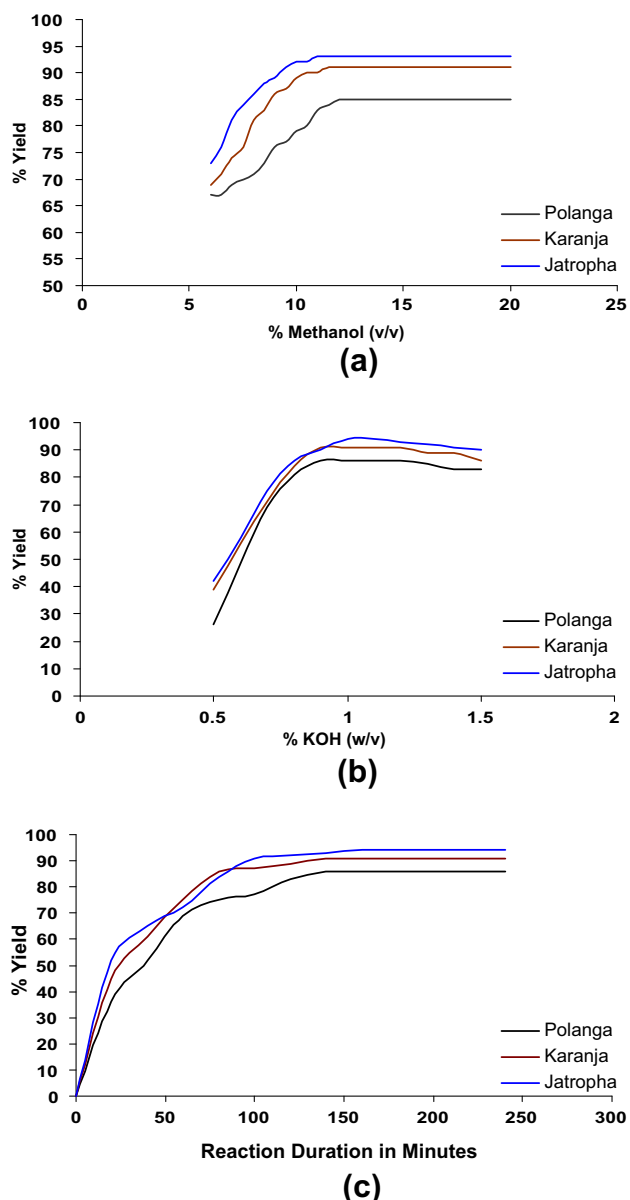
Fig. 3. (a) Effect of methanol quantity on yield during the third step. (b) Effect of catalyst on yield during the third step. (c) Effect of reaction duration on yield during the third step.

efficiency is shown in Fig. 3b. The maximum conversion efficiency during base-catalyzed transesterification is achieved at 1.1%, 1% and 0.9% of KOH for Jatropha, Karanja and Polanga oil respectively. In the course of the tests, it is observed that addition of excess amount of catalyst, give rise to the formation of an emulsion, which has increased the viscosity and led to the formation of gel. It is also observed that excess catalyst also reduces the total yield. Transesterification does not take place for insufficient amount of KOH addition.

3.2.3. Effect of reaction duration on methyl esters yield

In order to achieve an effective interaction between the catalyst and the oil during transesterification, it is essential that they must be stirred well at constant rate. It has been observed from Fig. 3c that the ester yield increases with increase in reaction duration. Results obtained from the present experiments with Jatropha, Karanja and Polanga seed oil reveal that about 120 min of reaction

is sufficient for the completion of the base-catalyzed transesterification.

3.3. Characterization of biodiesel from Jatropha, Karanja and Polanga oil

The fuel properties of JOME, KOME, POME and their blends in comparison with that of diesel are shown in Table 1. Most of the fuel properties of JOME, KOME, POME and their blends are comparable to those of diesel. The present results obtained show that, the transesterification process improved the fuel properties of the oil with respect to density (kg/m^3), calorific value (kJ/kg), viscosity (cSt), flash point (deg C), cloud point (deg C) and pour point (deg C). The comparison of these properties with diesel shows that the methyl esters of Jatropha, Karanja and Polanga oil have relatively closer fuel property values to that of diesel. Hence, no hardware modifications are required for handling these fuels (biodiesel and their blends) in the existing engine.

The calorific values of all the biodiesel and their blends are lower than that of diesel because of their oxygen content. The presence of oxygen in the biodiesel helps for complete combustion of fuel in the engine. The flash point of all the biodiesel and their blends is lowered by transesterification but it is still higher than that of diesel. Addition of a small quantity of biodiesel with diesel increases the flash point of diesel. Hence, it is safer to store biodiesel–diesel blends as compared to diesel alone.

4. Conclusion

The production of fuel quality biodiesel from low-cost, high FFA feed stocks is investigated in the present study. A three step 'acid–base' process; acid-pretreatment followed by main base-transesterification reaction; using methanol as reagent and H_2SO_4 and KOH as catalysts for acid and base reactions, respectively, was followed to produce biodiesel from Polanga oil. Single stage base-catalyzed transesterification was adopted for Jatropha and Karanja oil.

It has been conclusively observed that biodiesel production from feed stocks with high FFA is extremely difficult using alkaline catalyzed transesterification process. This is because the alkaline catalysts react with FFAs to form soap that prevents the separation of the glycerin and ester. A two step transesterification for Jatropha and Karanja; and a triple stage transesterification for Polanga oil are developed to convert the high FFA oils to its ester. The first step (zero-catalyzed transesterification) reduces the FFA content of the oil to less than 2% for Jatropha and Karanja oils. The second step (acid-catalyzed transesterification) reduces the FFA content of Polanga oil to less than 2%. The alkaline catalyzed transesterification process converts the products of the first step for Jatropha and Karanja and products of second step for Polanga oil to its mono-esters and glycerol. The effects of alcohol to oil volume, catalyst amount and reaction duration are analyzed in each step. Excess addition of sulphuric acid darkens the product.

It has been also found that the conversion efficiency is strongly affected by the amount of alcohol. The volumetric ratio of 11:1, 11.5:1 and 12:1 of alcohol favors the completion of alkaline catalyzed transesterification process within 2 h for the formation of JOME, KOME and POME, which is sufficient to give 93%, 91% and 85% yield of ester, respectively. The viscosity of biodiesel is nearer to that of diesel. The flash point of biodiesel is greater than that of diesel and calorific value is slightly lower than that of diesel. This triple stage transesterification method reduces the overall production cost of the biodiesel, as it uses low-cost unrefined non-edible oils. The addition of biodiesel to diesel fuel changes the physico-chemical properties of the blends. With the increase of biodiesel concentration in diesel–biodiesel blends density, kinematic viscos-

ity, cetane number, high heat value, flash and fire point of the blends increase.

The present analysis reveals that biodiesel from unrefined Jatropha, Karanja and Polanga seed oil is quite suitable as an alternative to diesel. However, further research and development on additional fuel property measures, long term run and wear analysis of biodiesel fueled engine is also necessary along with engine hardware modification.

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