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Article

Preparation and Characterization of Biodiesel from Karanja Oil by Using Silica Gel Reactor

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Abstract: The oil extraction and biodiesel preparation from Karanja oil have different available methods namely acid catalyzed trans-esterification, acid catalyzed two-step and three-step method etc. The available methods are studied for biodiesel preparation from Karanja oil. The biodiesel conversion by esterification reaction may contain some moisture which may causes to slowdown the reaction rate and affects on the quality of biodiesel by making emulsion. The adsorption technique by using powder form of silica gal has been used in the reactor to improve the reaction rate. The data has been collected at the time of silica gel dosing and the amount of silica gel dosed for every reaction to optimize it. The optimum dosing condition were recorded by selecting the best dosing properties of biodiesel like specific gravity, free fatty acid (FFA) and viscosity etc. The properties of biodiesel namely specific gravity, viscosity, lower calorific value, cetane number, FFA, flash point, pour point, cloud point, iodine value and saponification value etc. have been carried out at optimum reaction condition. The fuel properties has been tested to meet the ASTM standards and compared with the conventional diesel fuel and standard biodiesel.

Keywords: Karanja oil; Biodiesel; Silica gel; Esterification reaction; Free fatty acid.

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1. Introduction

The world energy demand is increasing gradually which also leads to increase environmental pollution. Due to these reasons energy engineers are searching new, noble, and renewable energy resources to meet the increasing energy demand. Renewable energy is the cost effective and pollution free energy source which is largely undeveloped worldwide. It can take an important role to meet the energy demand and save the environment. Biodiesel from vegetable oil is one of the most efficient forms of renewable energy which can be alternative to the fossil fuel [1]. Vegetable oils (edible and non-edible) are widely available from various sources and the glycerides present in the oils can be considered as a viable alternative for diesel fuel. Biodiesels are renewable, biodegradable and has lower emissions compared to petroleum diesel. More specifically, biodiesel cuts down on the amount of carbon dioxide, hydrocarbons, and particulate matter released into the environment [2]. Biodiesel consists of the fatty acid esters formed by the transesterification with an alcohol of vegetable oils or animal fats. Different vegetable oil species are canola [3], palm [4], jatropha [5], palm kernel [6], sunflower [7], and coconut [8] which has been studied previously as precursors for biodiesel production. There are lot of methods are available in literatures to convert vegetable oil into biodiesel. But for commercial biodiesel production, chemical alkaline or acidic processes have been used [9]. Methyl ester of karanja oil has been investigated as an alternative renewable fuel by Srivastava and Verma [10]. They are quick reactions with high conversions but consume much energy and methanol, have difficulty of glycerol recovery, and also generate a large amount of waste water [11-14]. Esterification of carboxylic acids, especially direct esterification between carboxylic acids and alcohols has wide academic as well as industrial applications [15].

Esterification from carboxylic acids is an equilibrium dependent reaction. In order for equilibrium reactions to proceed, the removal of water can be achieved in several ways. Firstly, by the physical removal of water using molecular sieves, however the dehydration efficiency of molecular sieves is relatively low. Alternatively, chemical removal using homogeneous dehydrating agents (coupling reagents) such as 1, 3-dicyclohexylcarbodiimide (DCC) have been employed from many years ago [16]. Silica gel's high surface area (around 800 m^2/g) allows it to absorb water readily, making it useful as a desiccant (drying agent). Once saturated with water the silica gel can be regenerated by heating it to 120 °C (250 °F) for two hours. Some types of silica gel will "pop" when exposed to enough water. This is caused by breakage of the silica spheres when contacting the water [17]. In esterification reaction due to methanolysis little amount of water formed and another little amount of water may remain with the converted free fatty acid (FFA). De-touching the unwanted water or moisture by silica gel from the conversion better biodiesel can be prepared. By using three steps method followed by saponification, acidification and esterification biodiesel prepared from karanja oil with and without silica gel. Different fuel properties has been carried out and compared to each other for both processes. The most economical way for biodiesel conversion by using silica gel has been investigated in this work.

2. Materials and Methods

2.1. Chemicals

The chemicals used for biodiesel conversion are namely, silica gel 60 (0.040-0.063 mm), sodium hydroxide (97%), hydrochloric acid (37%), sulfuric acid (98%), phenolphthalein (reagent grade *pH* 8.2-9.8), diethyl ether (96-98%), methanol (99.8%), ethanol (99%), glacial acetic acid, chloroform, potassium iodide and iodine. Oil extracted from Karanja seed by both soxhlet extraction method and mechanical extraction.

2.2. Three step method

The raw/virgin vegetable oil is heated at 40°C with magnetic stirring in a three necked conical flask containing cooling system to control the reflux and inside temperature. For this method the oil is saponified, acidified and esterified sequentially [18]. With the stoichiometric amount oil and sodium hydroxide the reaction is continued for 1:30 hour. This sodium hydroxide is dissolved in water before mixing with oil for saponification. The reaction is run with vigorous stirring and at 100°C. Then the reaction was stopped and the saponification product was cooled to 60°C. Soap made and then it was acidified by stoichiometric amount of hydrochloric acid with vigorous stirring at 70°C until the soap was dissolved fully. Then it converted to 100% FFA and transferred to the separatory funnel and given hot water wash to remove mineral acid. FFA (upper layer) was separated and dried by vacuum distillation. Finally its FFA content was measured by titrimetric method. Esterification is done by two systems. One is without silica gel and other is with silica gel. The molar ratio of FFA to methanol catalyst concentration kept same for both systems. Reaction temperature kept 65°C with vigorous stirring. Then the product is cooled to room temperature, transferred to separatory funnel, hot water washed and the upper layer (biodiesel) is separated after half hour. The biodiesel is then distillated under vacuum to remove moisture at 100°C and then biodiesel properties were measured. The saponification reactions by sodium hydroxide can be summarized as follows [19]: The experimental setup, feedstock and finish product is presented in Figure 1.

$$\begin{array}{lcccl} CH_2-OOC-R_1 & & R_1COONa & & CH_2OH \\ & & | & & | \\ CH-OOC-R_2 + NaOH & \Leftrightarrow & R_2COONa & + & CH-OH \\ | & & | & & | \\ CH_2-OOC-R_3 & & R_3-COONa & & CH_2OH \\ \text{(TG)} & & \text{(Soap)} & & \text{(Glycerine)} \end{array}$$

$$\begin{array}{lcl} R-COOH + NaOH & \Leftrightarrow & R-COONa + H_2O \\ \text{(FFA)} & & \text{(Soap)} \end{array}$$

Where, R, R_1, R_2 and R_3 denote any hydrocarbon chain.

In acidification step following reaction was occur for sodium soap:

$$R-COONa + HCl \Leftrightarrow R\text{-}COOH + NaCl$$

In esterification, the above product is kept in a 250 ml three necked flask and metho-sulfunic acid solution was added to that.

$$\underset{(FFA)}{R-COOH} + \underset{(Alcohol)}{CH_3OH} \Leftrightarrow \underset{(FAME)}{R\text{-}COOCH_3} + H_2O$$

(a) (b) (c) (d)

Figure 1: (a) Karanja seed kernel **(b)** Silica gel **(c)** Experimental setup for the biodiesel production using three-step catalyzed method using silica gel and **(d)** Produced biodiesel.

2.3. Three step method with silica gel

It's almost similar with the three step method described before. Here just at the starting of the esterification 5 gm dried silica gel (silica gel: oil=1:5) is added to the esterification mixture and the esterification run for only 20 minutes. The reaction runs with 60◦C with 550 rpm stirring under reflux condensation. Then the product is cooled to room temperature, transferred to separatory funnel, hot water washed and the upper layer (bio-diesel) is separated after half hour. The bio-diesel is then distillated under vacuum to remove moisture at 100◦ C. It's cooled to room temperature and properties of this bio-diesel are measured by maintaining different ASTM standards.

2.4. Effect of silica gel in esterification reaction

Different amount of dry silica gel was given in the reaction mixture at different time intervals. The performance of silica gel was measured in esterification reaction. Performance was measured by measuring the FFA content remaining in biodiesel. In esterification reaction water is produced and this water reduces the reaction rate. Silica gel absorbs water and promotes the reaction rate. Different dosing systems are employed in esterification reaction at different time interval given below in Table 1.

Table 1. Preparation of biodiesel with different dosing of silica gel in esterification.

Observation	First Step	Second Step	Third Step	Fourth Step
Dose 1	Initially (0 g SG)	After 20 min (3g SG)	After 20 min (2g SG) and continued to140 min.	
Dose 2	After 20 min (5g SG) and continued to160 min.			
Dose 3	After 10 min (2g SG)	Then after 10 min (2g SG)	Then after 10 min (1g SG) and continued to 150 min.	
Dose 4	After 5 min (2g SG)	Then after 5 min (2g SG)	Then after 5 min (1g SG) and continued to 165 min.	
Dose 5	Initially (1g SG)	Then after 5 min (2g SG)	After 5 min (2g SG) and continued to 170 min.	
Dose 6	Without silica gel the reaction continued to180 min.			
Dose 7	Initially (5g SG) and continued to 180 min.			
Dose 8	Initially (5g SG)	After 20 min (2g SG)	Then after 20 min (2g SG)	Then after 20 min (1g SG) and continued to120 min.
Dose 9	Initially (10g SG) and continued to 180 min.			
Dose 10	Initially (5g SG)	After 15 min (5g SG) and continued to 165 min.		

Note: SG refers to silica gel.

The properties of biodiesel like FFA [20-21], viscosity [22-23], saponification value [24], specific gravity [25] are measured mainly to compare with different methods.

3. Result and Discussion

3.1 Three step method without silica gel

Biodiesel was prepared from karanja oil by three step method without silica gel. The properties of the produced biodiesel were measured and given in Table 2.

Table 2. Properties of biodiesel produced by three step method without silica gel.

Property	Measured value
Color	Radish-black
Viscosity (mm^2/s)	4.57
Saponification value (mg KOH/gm oil)	138
FFA (wt %)	4.91
Specific gravity	0.89

After the reaction viscosity of oil reduced from 64 mm^2/s to 4.57 mm^2/s and FFA reduced from 12.14% to 4.91 %. The reduction of FFA in esterification reaction with respect to time is shown in figure 2.

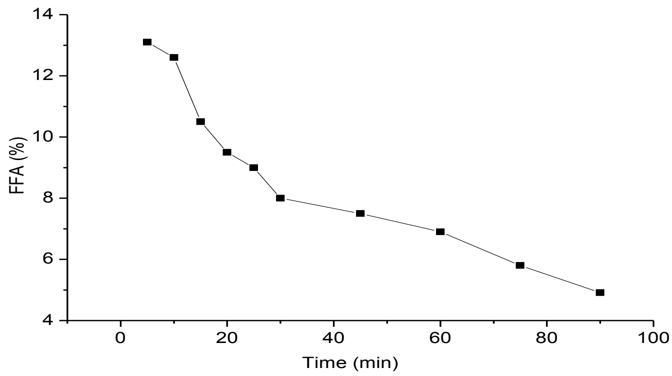

Figure 2. FFA reduction in Esterification reaction without silica gel [catalyst (H_2SO_4) concentration 5 wt% of FFA, Methanol/FFA= 9:1 molar ratio, vigorous stirring and reaction time 90 min at 60 ^{0}C.]

3.2 Three step method with silica gel

Biodiesel prepared from karanja oil by three step method with silica gel mentioned above. The properties of the produced biodiesel were measured and given in Table 3.

Table 3. Properties of biodiesel produced by three step method using silica gel.

Property	Measured value
Color	Radish-black
Viscosity (mm^2/s)	3.75
Saponification value (mg KOH/gm oil)	140
FFA (wt %)	2.20
Specific gravity	0.87

After the reaction viscosity of oil reduced from 64 mm^2/s to 3.75 mm^2/s and FFA reduced from 12.14% to 2.20 %. The viscosity of the product is better than biodiesel standard and the FFA content is match with the biodiesel standard. So this biodiesel can be used as an alternate of petro-diesel as it's other properties are also matched with biodiesel standard. The reduction of FFA in esterification reaction with respect to time is shown in figure 3.

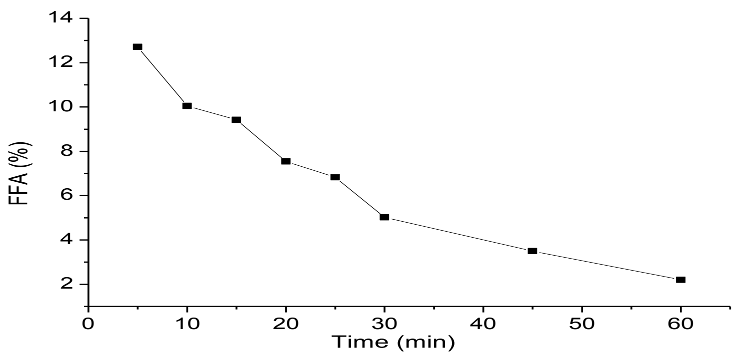

Figure 3. FFA reduction in Esterification reaction with silica gel [catalyst (H_2SO_4) concentration 5 wt% of FFA, Methanol/FFA= 9:1 molar ratio, vigorous stirring and reaction time 60 min at 60 ^{0}C. Here saponification run for 1:30 hour, esterification for one hour only but the properties are better than the above three step method (without silica gel). So it's the good effect of silica gel.

According to the above discussion it's apparent that using silica gel in esterification reaction for biodiesel preparation gives better product than esterification without silica gel.

3.3 Effect of amount of silica gel in esterification

In esterification reaction, the effect of silica gel was observed and the results are represented in Table 4. The reaction was carried out at molar ratio of FFA to methanol 1:6, catalyst (H_2SO_4) concentration 5 wt% of FFA at a temperature of 60 ^{0}C under reflux with vigorous stirring.

Table 4: Properties of biodiesel produced after one hour esterification reaction with and without silica gel.

Amount of silica gel initially fed in esterification	FFA (%) of Bio-diesel	Viscosity (mm^2/s) of Bio-diesel
No silica gel	4.91	4.53
5 gm	3.32	4.01
10 gm	3.22	4.01

From the above results using 5 gm silica gel for 25 ml oil as 1:5 w/v is remarked as optimum.

Now silica gel was introduced at different time interval in esterification reaction. The effect of silica gel was observed and the results are represented in Table 5. The reaction are carried out at molar ratio of FFA to methanol 1:6, catalyst(H_2SO_4) concentration 5 wt% of FFA at a temperature of 60 ^{0}C under reflux with vigorous stirring.

Table 5. Properties of biodiesel produced after one hour esterification reaction with and without silica gel at different time interval

Silica gel fed with the variation of time interval	FFA (%) Of Bio-diesel	Viscosity (mm^2/s) Of Bio-diesel
Dose 1	5.82	4.80
Dose 2	7.52	4.91
Dose 3	7.41	5.13
Dose 4	7.59	4.77
Dose 5	5.47	4.41
Dose 6	6.73	4.42
Dose 7	3.28	4.82
Dose 8	3.99	4.11
Dose 9	2.63	4.02
Dose 10	3.36	4.16

From the above result silica gel dosing was more effective when it was given in the reaction at initially.

4. Conclusions

Biodiesel prepared by three-step method (without silica gel) has 4.91% FFA content, 4.57 mm^2/s viscosity. Biodiesel prepared by three-step (with silica gel) has 2.16% FFA, 3.75 mm^2/s viscosity. Optimum silica gel, oil ratio is 1: 5 (wt/vol). In esterification reaction using silica gel initially is the best. The biodiesel preparation using silica gel results better properties within shorter time. Finally it can be concluded that the karanja biodiesel prepared by the three-step method with silica gel is better and suitable to use. Further study is needed in these fields for engine performance and emission study by using this biodiesel and their blends.

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