



Environment-Congenial Biodiesel Production from Non-Edible Neem Oil

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Abstract

In developing countries like India, where edible oils are in short supply, the contribution of non-edible oils like neem as a source for biodiesel production will be of great importance in the coming days. Biodiesel was produced from non-edible neem oil having a free fatty acid content of 19% in a two-step process, as free fatty acid of more than 1% in the feedstock adversely affects the single step alkali catalyzed transesterification process by soap formation. The first step of acid catalyzed esterification reduced the free fatty acid content of neem oil to below 1%. The optimum combinations of parameters for pretreatment were found to be 0.60 volume by volume (v/v) methanol-to-oil ratio, 1% v/v H₂SO₄ acid catalyst and 1 hr reaction time. The next base catalyzed transesterification process converted the pretreated oil to neem biodiesel. The optimum combination of parameters for transesterification was found to be 0.24 v/v methanol-to-oil ratio, 1.08% weight by volume (w/v) catalyst concentration and 34 min reaction time. This two-step process gave an average yield of 90%. The fuel properties of neem biodiesel were found to be comparable to those of diesel, and conform to the latest American Standards for Testing of Materials Standards.

Keywords: Biodiesel, Esterification, Free fatty acid, Non-edible oil, Transesterification

1. Introduction

Global climate change due to fossil fuel emissions is a great concern of the present day. The accumulation of polluted gases like SO_x, CO and particulate matter in the atmosphere cause acid rain, global warming and health hazards. In its fourth assessment report, the Intergovernmental Panel on Climate Change (IPCC) confirmed that climate change was accelerating, and if current trends continue, energy-related emissions of carbon dioxide (CO₂) and other greenhouse gases will rise inexorably, pushing up average global temperature by as much as 6°C in the long term [1]. With 243.3 million tons of carbon released from the consumption and combustion of fossil fuels, India ranked fifth in the world behind the USA, China, Russia, and Japan.

One way to reduce these trends is to develop and use clean, sustainable bioenergy sources. Renewable bioenergy sources provide several significant benefits, such as energy security, reduced emission of pollutants, greenhouse gases and increased employment in the agricultural sector. Of all the renewable and non-polluting alternative energy sources, biodiesel fuel, which consists of the simple alkyl esters of fatty acids, has received growing interest as an alternative to conventional diesel fuels.

Biodiesel is produced from vegetable oils and animal fats. In most developed countries, biodiesel is produced from soybean, sunflower, rapeseed, etc., which in the Indian context are essentially edible. In India, edible oils are in short supply and are too expensive; hence non-edible oils, like jatropha, pongamia, neem, and mahua, have been found to be promising biodiesel feedstocks [2]. In a number of studies, appreciable research efforts have been put into producing biodiesel from non-edible oils like jatropha, mahua, rubber, and pongamia, giving much focus to jatropha [3-6].

The neem tree is an evergreen tree native to the Indian subcontinent and South-East Asian countries. It grows in almost every state of India, in drier areas, and in all kinds of soil. Neem oil has low toxicity, and its smell is rather strong. It is burnt in lamps throughout India, and acts as good charcoal. The high calorific value of neem oil matches diesel [7]. It blends with diesel, substituting for nearly 35% of the later, and has been suggested for use without any major engine modification and without any worthwhile drop in engine efficiency.

A mature neem tree may produce 30–50 kg of fruit each year. Neem seeds yield 40–60% oil [8]. Presently, billions of neem seeds are wasted in India, because of the lack of a proper collec-

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Received September 08, 2012 Accepted October 01, 2012

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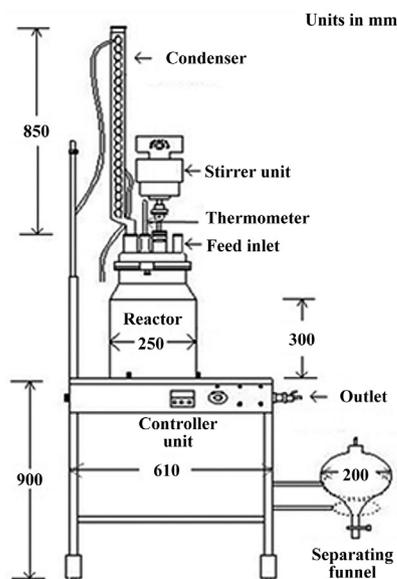


Fig. 1. Schematics of the biodiesel processor.

tion method. If the seeds fallen on the ground are collected, and oil is extracted by village level traditional expellers, a few million tons will be made available for lighting lamps in rural areas. Considering a conservative level of oil content of only 30%, the annual neem oil production in India could be to the tune of 30,000 tons [9].

Hence the present research work was undertaken to utilize neem oil for production of biodiesel, from the perspective of process optimization and fuel characterization.

2. Materials and Methods

The neem oil used in this present study was obtained from Sai Biocare, Bhubaneswar, India. All the chemicals used were of analytical reagent grades. Potassium hydroxide (KOH) was used in pellet form. The unrefined but filtered crude neem oil is dark brown in color. The acid value of crude neem oil was determined by acid base titration technique [10]. This oil had an initial acid value of 36 mg KOH/g, corresponding to a free fatty acid (FFA) level of 18%, which is far above the 1% limit for satisfactory transesterification reaction using an alkaline catalyst. Therefore, FFAs were first converted to esters in a pretreatment process using an acid catalyst, H_2SO_4 , with a volume by volume (v/v) ratio of 1%, to reduce the acid value of neem oil below 2 mg KOH/g. After pretreatment, transesterification of triacylglycerol present in the pretreated neem oil was carried out, using methanol as a reagent, and KOH as an alkaline catalyst.

2.1. Biodiesel Processor

The experiments were conducted in a laboratory scale setup developed in Bidhan Chandra Agricultural University, West Bengal, India. The basic purpose behind developing this setup was to have control over various process parameters, especially the reaction temperature and time for their optimization. Different criteria considered during designing the processor included the

demand for a lesser quantity of methanol, lesser reaction time, recovery of the extra methanol, proper sizing of the reactor tank, flexibility for further modifications, and research in terms of supplemental technologies, accessories and devices.

The processor consisted of a reaction flask, and digital rpm controlled mechanical stirrer and separating flask. The reactor consisted of three necks, for the stirrer, for the condenser, and for a digital temperature controller, as well as an inlet for the reactants. A 500 W heating element was fitted towards the bottom end of the reactor, along with a temperature sensor, relay and indicator arrangement, for controlling the reaction temperature within the desired range. With the relay and heater, the temperature inside the reactor was kept at 60°C. The reactor was designed to handle a 10 L batch of oil at a time. Both acid esterification and transesterification were carried out in the reactor. The reactor was fixed to a mobile frame of 900 × 610 × 500 mm.

The batch reactor had a valve at the bottom for collection of the final product. A separating funnel was used to separate the methanol-water mixture after pretreatment, and glycerol after transesterification. A schematic view of the developed biodiesel processor is presented in Fig. 1.

2.2. Biodiesel Production

2.2.1. Pretreatment

In this step, crude neem oil was poured into the reactor, and heated. The solution of concentrated H_2SO_4 acid (1% v/v) in methanol was heated to 60°C, and then added into the reactor. Different methanol to oil ratios by volume were used, namely of 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, and 0.80 v/v, to investigate their influence on the acid value of crude neem oil. After 1 hr of reaction, the mixture was allowed to settle for 2 hr. The methanol-water fraction at the top layer was removed. The acid value of the bottom layer was measured. The final product having an acid value less than 2 mg KOH/g was used for the main transesterification reaction.

2.2.2. Transesterification

A known quantity of acid pretreated neem oil was poured into the reactor, and heated at 60°C. KOH was dissolved in methanol by vigorous stirring, and then added to the pretreated neem oil. The KOH amount was decided based on the amount needed to neutralize the unreacted H_2SO_4 in the pretreated oil, plus the amount needed for the catalyst (1 wt. %), with respect to pretreated oil. The reaction was carried out for 1 hr at 60°C.

Biodiesel produced by this process contains soap, catalyst and glycerol. If biodiesel is used directly in the engine without removing these particles, deposition will occur in engine components, and the engine parts will be affected. Hence, the biodiesel was washed with an equal quantity of hot distilled water for three to four times, using a small aqua pump forming air bubbles. The moisture from the biodiesel was removed by heating it on a hot plate at 100–110°C.

3. Results and Discussion

3.1. Acid Pretreatment

The effects of methanol amount on acid values and FFA of the mixtures after a 1 hr reaction are shown in Fig. 2. The figure indicates that the acid value or FFA concentration was influenced

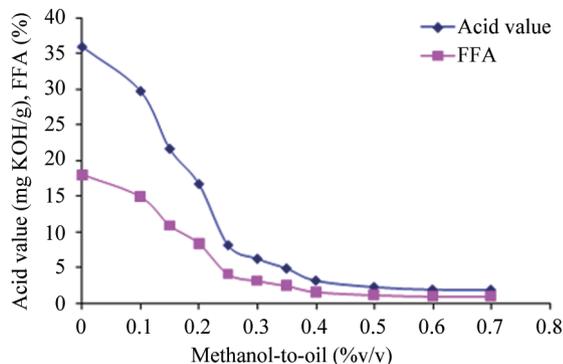


Fig. 2. Influence of methanol quantity on acid value and free fatty acid (FFA).

by the quantity of methanol. The FFA concentration reduced to 4% at a 0.25 v/v methanol-to-oil ratio, and then decreased gradually to less than 1% at a 0.60 v/v methanol-to-oil ratio. Increasing the methanol amount beyond that has no significant influence on the reduction of acid value. This is due to the fact that water produced during the esterification process retards the rate of reaction. However, the esterification process can be improved by continuous removal of water from the reaction mixture.

A very high amount of methanol (60% v/v) was required to lower the acid value of crude neem oil to below 2 mg KOH/g in 1 hr reaction time, in the presence of 1% v/v acid catalyst. This condition was selected as the optimum for the reduction of the acid value of crude neem oil. Similar findings were reported by Ghadge and Raheman [4], and Berchmans and Hirata [11], where 0.65 v/v and 0.60 weight by weight (w/w) ratio of methanol-to-oil were required for esterification of FFAs of mahua oil and jatropha oil, respectively. Canakci and van Gerpen [12] reported that

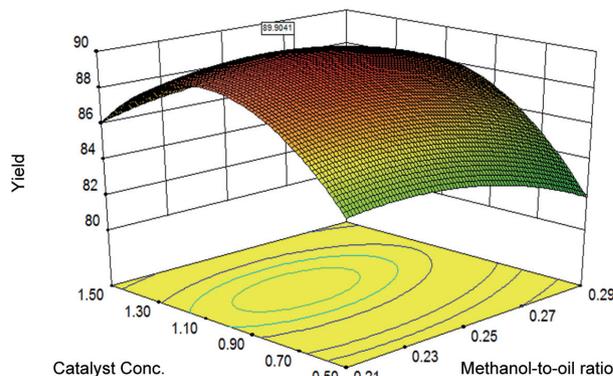


Fig. 3. Effect of methanol concentration on ester yield.

esterification of brown and yellow grease having 12–33% FFA required a methanol to oil molar ratio as high as 20:1.

3.2. Transesterification

In the present study, transesterification of neem oil was carried out with KOH as a catalyst at a concentration of 0.50–1.5% w/v of oil at 60°C, with a MeOH/oil ratio varying from 0.20 to 0.40 v/v in a reaction time of 20–40 min, to get the maximum amount of ester. A five-level-three factor central composite rotatable design (CCRD) requiring 20 experiments was employed for optimization of the transesterification process. The experimental, as well as predicted, values of ester yield obtained as a response at the design points are given in Table 1. Methanol-to-pretreated oil ratio (M'), catalyst concentration (C') and reaction time (T') were the independent variables selected to be optimized for the transesterification of pretreated neem oil. Figs. 3–5 show the

Table 1. Biodiesel yield (%) obtained with various treatment combinations

Design points	Point type	Level of variables			Ester yield (%)	
		Methanol-to-oil ratio (v/v)	KOH concentration (% w/v)	Reaction time (min)	Experimental	Predicted
1	Axial	0.18	1.00	30.00	88.00	89.51
2	Factorial	0.21	1.50	23.00	87.00	86.83
3	Center	0.25	1.00	30.00	90.00	89.51
4	Center	0.25	1.00	30.00	90.00	89.64
5	Factorial	0.29	0.50	37.00	82.00	81.41
6	Center	0.25	1.00	30.00	90.00	90.18
7	Center	0.25	1.00	30.00	88.00	87.84
8	Factorial	0.21	1.50	37.00	85.00	85.57
9	Factorial	0.21	0.50	23.00	83.00	83.24
10	Center	0.25	1.00	30.00	89.00	89.51
11	Axial	0.25	1.00	41.77	90.00	90.18
12	Factorial	0.29	1.50	23.00	85.00	85.76
13	Factorial	0.21	0.50	37.00	85.00	84.63
14	Axial	0.25	1.84	30.00	82.00	82.37
15	Axial	0.25	0.16	30.00	75.00	75.31
16	Factorial	0.29	1.50	37.00	86.00	86.03
17	Axial	0.32	1.00	30.00	85.00	84.88
18	Axial	0.25	1.00	18.23	88.00	88.08
19	Center	0.25	1.00	30.00	90.00	89.48
20	Factorial	0.29	0.50	23.00	80.00	79.44

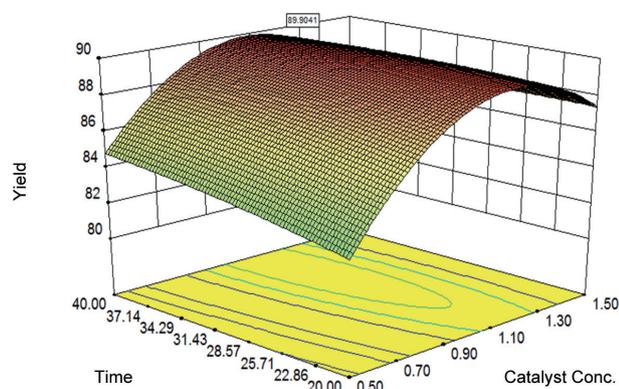


Fig. 4. Effect of catalyst concentration on ester yield at optimum methanol-to-oil ratio.

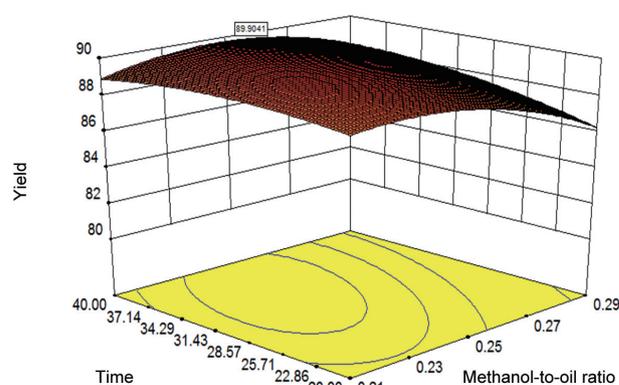


Fig. 5. Effect of reaction time on ester yield.

contour plots depicting the effect of methanol concentration, catalyst concentration and reaction time on ester yield. The optimum values of the variables were found to be a 0.24 v/v methanol-to-oil ratio, 1.08% weight by volume (w/v) ratio catalyst concentration, and 34 min reaction time. With these optimum combinations, the maximum amount of 90% ester was obtained. The predicted model for ester yield, obtained from Table 1, was found to be:

$$Y = 38.439 + 254.363 * M' + 32.705 * C' + 0.191 * T' + 31.250 * M' * C' + 1.339 * M' * T' - 0.179 * C' * T' - 695.684 * M'^2 - 15.766C'^2 - 4.678E - 003 * T'^2 \quad (1)$$

where, Y = Ester yield, %

M' = Methanol-to-oil ratio, v/v

T' = Reaction time, min

C' = KOH concentration, % w/v

Biodiesel was prepared in the laboratory scale processor using optimum conditions for both esterification and transesterification. The amounts of methanol-water mixture and ester obtained using different quantities of oil are presented in Table 2.

3.3. Effect of Methanol and Catalyst on Ester Yield

At low methanol concentrations, ester yield was less, even at a higher catalyst concentration. As the methanol-to-oil ratio increased, the ester yield also increased, with increase in catalyst concentration. This could be due to the fact that methanol

concentration is the most significant factor with positive effect. However, at higher catalyst concentrations, the response was less affected by increasing the methanol amount. This can be explained on the basis of the reactant (oil) concentration in the reaction mixture. By increasing the alcohol to oil ratio, the amount of alcohol was increased, therefore the oil and catalyst concentrations were diminished, which reduced the rate of reaction.

Results published by Boocock et al. [13] showed a similar trend, in which the methyl ester percentage decreased, as the alcohol-to-oil molar ratio increased. Berchmans and Hirata [11] also reported that the yield of jatropha biodiesel decreased with increase in methanol amount and catalyst concentration. At a higher methanol-to-oil ratio and catalyst concentration, there seemed to be less effect of increased reaction time on ester yield (Figs. 4 and 5). This could be due to the low positive coefficients of methanol-time interaction term, and negative coefficients of catalyst-time interaction.

Several investigators found that the reaction starts very fast, and almost 80% of the conversion takes place in the first 5 min. Kumar Tiwari et al. [3] obtained 99% biodiesel yield from crude jatropha oil in only 24 min reaction time, using 0.16 v/v methanol-to-oil at a 60°C temperature. Ramdhas et al. [5] obtained 90% biodiesel yield from rubber seed oil, using a 6:1 molar ratio of methanol-to-oil, 0.5% w/w NaOH, 50°C reaction temperature and 30 min reaction time. Veljkovic et al. [14] obtained 91% biodiesel yield from tobacco seed oil in 30 min reaction time, using a 6:1 molar ratio of alcohol-to-oil, and 1% w/w catalyst concentration.

It was observed that a high amount of methanol (total 0.84

Table 2. Biodiesel yield using optimized values of methanol and catalysts

Crude neem oil (mL)	Methanol (mL)	Neem biodiesel (pure, mL)	Glycerol (mL)	Methanol-water mix (mL)	Biodiesel recovery (%)
1,000	840	900	230	620	90.0
1,000	840	887	250	600	88.7
2,000	1,680	1,789	475	1,270	89.5
2,000	1,680	1,804	452	1,283	90.2
3,000	2,520	2,710	700	1,870	90.3
3,000	2,520	2,685	725	1,779	89.5

v/v methanol-to-oil ratio) was required for biodiesel production from crude neem oil by the two-step process. Several researchers [4, 11, 12] produced biodiesel from high FFA feedstocks, like mahua oil, crude jatropha oil and brown grease. They all required a higher amount of methanol to produce biodiesel by the two-step process.

The higher methanol consumption can be reduced by recovering part of it by fractional distillation of the methanol-water mixture, separated at the top after pretreatment of the oil. Continuous removal of water from the reaction mixture during pretreatment also reduces the amount of methanol consumption. It can also be seen from Table 1 that about 200 mL of glycerol was obtained per liter of crude neem oil as a byproduct, which could be dried and purified, to recover part of the production costs.

3.4. Properties of Neem Biodiesel

The fuel properties of crude neem oil, neem biodiesel along with diesel are presented in Table 3. It can be seen that the neem biodiesel has comparable fuel properties with those of diesel, and is within the limits prescribed in the latest American Standards.

The densities of neem oil and neem biodiesel were observed to be about 10.7% and 5.5% higher than that of high speed diesel. After transesterification, the density of neem oil was reduced by about 4.7%. The higher densities of neem oil and neem biodiesel, as compared to diesel, may be attributed to the higher molecular weights of triglyceride molecules present in them. After transesterification, biodiesel showed a substantial reduction (90%) in viscosity. The kinematic viscosity of neem biodiesel was higher than that of high speed diesel. But at 5% addition of biodiesel to the diesel fuel (B5), the higher viscosity of biodiesel has not been reported to make any appreciable difference in diesel engine performance [15].

The flash points of neem oil and biodiesel were found to be quite high, as compared to the flash point of high speed diesel. This might be due to the presence of components of longer chain in their molecules. Thus, the overall flammability hazard of both neem oil and neem biodiesel is much less than that of conventional diesel. Generally, a material with about 90°C or higher flash point is considered as non-hazardous, from a storage and fire-hazard point of view. The pour point of neem biodiesel was found to be quite high, as compared to diesel. From this result, it is clear that neem biodiesel (NBD) would be suitable as a die-

sel fuel substitute in tropical countries like India, except for a few high altitude areas, especially in winter months. The gross calorific values of neem oil and biodiesel were found to be 15% and 10% less than that of diesel. These data serve to indicate that approximately 10% more B100 biodiesel would be required, in comparison with the regular diesel fuel, to perform an equal amount of work. The lower calorific values of neem oil and neem biodiesel, in comparison to diesel, may be due to the difference in chemical composition of these oils from that of diesel. The acid value of esters derived from crude neem oil having high acid value was reduced substantially by using the two-step method, and was within the limit of the American Standards for Testing of Materials (ASTM) Standard (0.8 mg KOH/g), as shown in Table 3.

Fuels having less ash content are preferred for better engine operation and maintenance. Neem biodiesel was found to have the same ash content as that of diesel, and within the limit prescribed by ASTM standards. The iodine value of neem biodiesel was found to be quite higher than that of diesel. This implies that engines utilizing neem biodiesel are more susceptible to gum formation, than those utilizing conventional diesel fuel.

4. Conclusions

Biodiesel production from crude neem oil was carried out from the perspective of process optimization and fuel characterization. Neem oil contains about 18% FFA; hence, a two-step acid-pretreatment for the reduction of FFA content of oil to around 1%, followed by an alkaline transesterification process, was used to produce the esters. Increasing the methanol-to-oil ratio for the pretreatment step was found to have a decreasing effect on acid value, up to the optimum level. These parameters for transesterification were found to have an increasing effect on biodiesel yield up to the optimum level, and showed a second order polynomial relationship. The maximum ester yield with the optimum combination of parameters was about 90%. The properties of neem biodiesel were within the limits, and comparable with high speed diesel. The density of neem biodiesel was 5.5% higher, and the calorific value was 10% less, than those of high speed diesel. The viscosity of neem biodiesel was slightly higher than that of diesel. The flash point of neem biodiesel was higher than diesel, which confirms safe and non-hazardous storage. All of the properties of neem biodiesel met the ASTM Standards.

Table 3. Evaluation of neem biodiesel as per ASTM 6751

Sl. no.	Property	Testing procedure	Biodiesel standard (ASTM 6751-02)	Neem oil	Neem biodiesel	High speed diesel
1	Density (kg/m ³), 25°C	ASTM D4052	870–900	910	870	822
2	Viscosity (mm ² /sec), 40°C	ASTM D445	1.9–6.0	55.33	5.38	2.56
3	Flash point (°C)	ASTM D93	Min. 130	210	175	70
4	Pour point (°C)	ASTM D97	-15–10	11	10	-15
5	Calorific value (MJ/kg)	ASTM D240	-	36.04	38.40	42.5
6	Ash content	ASTM D97	-	0.98	0.01	0.01
7	Iodine value	ASTM D97	-	66.25	53.29	4.42
8	Pour point	ASTM D97	-	11.0	9.0	-15.0

ASTM: American Standards for Testing of Materials.

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