Process Optimization for Biodiesel Production from Highly Acidic Hibiscus Cannabinus (Deccan Hemp) Oil

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Abstract. In this study, Hibiscus Cannabinus (deccan hemp) oil was used to convert its methyl ester. Methyl ester synthesis process involves of two-steps: esterification of sulfuric acid (Step-1) and alkaline transesterification (Step-2). Deccan hemp oil was found to have an initial acid value of 12.48 mg KOH/g. The acid value of deccan hemp oil was decreased to below 2 mg KOH/g in Step-1 taking consideration to get higher ester yield after alkaline transesterification process. The alkaline transesterification process parameters such as methyl alcohol to deccan hemp oil molar ratio, sulfuric acid catalyst amount, reaction temperature and reaction time were optimised and analysed in detail. This process gives ester yield of about 95.48%. The important properties of the synthesised methyl ester were determined and compared with IS 51607 and ASTM D6751 biodiesel standards.

1. Introduction

Compression ignition (CI) engines play the major role in the field of industry, transportation and agriculture due to their higher durability and thermal efficiency [1]. The government has focused on the use of renewable energy resources over the past 40 years due to the depletion of fossil fuels [2]. The use of naturally availability recourses such as crop or waste as an effective product, cost effective, local availability and sustainable source of energy has increased, this brings good opportunities to the farmers and government also benefits to the environment [3]. Naturally available renewable energy resources are more attractive because of their low cost and produce lower emission in combustion process [4]. For CI engines, vegetable oil may be utilised as an alternative fuel because it has a high cetane and a high calorific value, which are very similar to those of diesel engines [5].

Break thermal efficiency of the vegetable oil is lesser than the diesel this causes the high HC emission CO emission and smoke. This could be due to the low volatility and high viscosity of vegetable oil, resulting in difficulty in atomizing the fuel and poor combustion in the diesel engine. Generally, several methods are used for reduction of viscosity in vegetable oil, such as mixing with fossil fuel, thermal cracking, transesterification, emulsification and paralysis [6]. Among these methods’ transesterification is one of the most important processes for combining oil esters from vegetable oil and separating glycerides with the addition of alcohol. This removal process decreases the viscosity of the oil and value comparable to diesel fuel. Therefore, it improves combustion [7].

Biodiesel may be utilised as an alternative fuel for CI engines with or without a change in engine hardware [8]. Nisar et al. [9] used brassicaceae family plants for the biodiesel production by alkaline
 transesterification process. They concluded that brassicaceae family are best feed stocks for the biodiesel production. Many researchers synthesize the biodiesel from various vegetable oil such as pomace oil [10], soybean oil [11], safflower seed oil [12] and karanja oil [13]. The benefits of using biodiesel instead of diesel such as reduction of exhaust emission, decreased toxicity, high flash point and lower vapour pressure, improved biodegradability and lubricity [14].

Chai et al. [15] concluded that 2-Step transesterification (acid esterification followed by transesterification) is required for high free fatty acids (FFA) oils to obtain maximum ester yield. Makareviiene et al [16] preferred 2-Step transesterification for production of the spesiapopulnea L, oil. The molar ratio of methyl alcohol to vegetable oil, catalyst concentration, reaction temperature, and reaction time are the most important factors that affect the conversion efficiency of the process. Manjunath H et al. [17] studied the details of transesterification procedures for synthesis of methyl ester from mahua, simaruba and waste cocking oil using sodium methoxide as alkaline catalyst. They concluded that sodium methoxide catalyst exhibit greatest efficiency than other catalyst tested. India is the richest in forest resources and also has a large variety of trees producing a significant amount of oilseeds [18]. Some non-edible vegetable oils like mahua, jatropha, neem, simaruba, karanja, and castor are important sources for biodiesel production. Khan et al. [19] concluded from their investigation that biodiesel play the major role in the agriculture sectors, which also makes environment-friendly. Ravichandra et al. [20] carried out the experiment on biodiesel production using deccan hemp with the use KOH as alkaline catalyst. They concluded that deccan hemp oil (DHO) was a new source of energy for the production of biodiesel.

DHO is obtained from dry seed of its deccan hemp plant (DHP). Hibiscus Cannabinus is the botanical name for DHP. The plant is ploughed for the reason of replace jute as a fibre crop. deccan hemp plant is an important tropical plant, well-grown in a humid environment with a temperature range of 20-35°C. The yield of the seed depends on fertility of the soil. The dry seeds of the plant are undergoing milling and pressed, as an effect, 13% clear, odourless yellow fatty oil is obtained. This plant is known in southern countries like India, Indonesia, Thailand, Sri Lanka and Bangladesh [21]. The rate of production of deccan hemp in the world is 1,300,000 MT/year. The above climatic conditions are well suited to the Indian continents; hence a large quantity of plats is grown in India. According to ICAR reports, the Indian production rate of the DHP is 13.4 MT /year [22]. India will have lot of deccan hemp seed suppliers and few sell DHO directly. In local it’s called as Goukurain in Indian market.

There are two approaches are in use in order to mitigate the energy-related problems to certain extent. They are: (i) identify or develop new alternate energy source for the existing consumption devices; (ii) modify the hardware of the energy consumption devices to increase its combustion efficiency.

From the literature review, a lot of work has been done on biofuels such as mahua, palm oil, karanja, neem, and jatropha, but limited research has been conducted on DHO. Therefore, it is essential to further investigate the same oil. The objectives of the present research are to identify DHO as a new energy feedstock and produce its methyl ester meeting with specifications of biodiesel standards. According the researchers’ knowledge, no work has been conducted on the synthesis of biofuels from deccan hemp oil utilising sodium methoxide (NaOCH₃) as alkaline catalyst. The major benefit of using NaOCH₃ over potassium hydroxide (KOH) or sodium hydroxide (NaOH) is that the catalyst solution is virtually water free. This prevents unwanted side reactions, such as saponification process. The current investigation employs NaOCH₃ as an alkaline catalyst in the transesterification reaction process to produce biodiesel from DHO.

In the present investigation, methyl ester synthesis process involves 2-Steps: sulfuric acid esterification (Step-1) and alkaline transesterification (Step-2). In Step-1, the acid value (AV) of DHO was decreased to below 2 mg KOH/g in order to achieve a higher ester yield after the
transesterification process. The transesterification process parameters were optimised and analysed. The reaction process was optimized on single parameter while keeping the remaining parameters constant. The yield percentage was calculated by dividing the weight of the produced methyl ester by the weight of the oil.

2. Materials and Methods

2.1. Materials

DHO is extracted from the dried seeds of the DHP collected from indigenous growers. Sodium methoxide (99% pure), sulphuric acid (99% pure), methanol (AR Grade) and iso-propyl alcohol were purchased from Vasa Scientific Co., Bangalore, Karnataka.

2.2. Methyl ester (Biodiesel) synthesis process

2.2.1. Acid esterification

The DHO was first converted to its ester in the acid esterification process with the use of sulphuric acid as a catalyst. The experiment was carried out at 60°C using laboratory-scale apparatus, below the boiling temperature of methyl alcohol. Each reaction was permitted to proceed for 30 minutes. Experimental setup (Figure 1) consists of hot plate with magnetic stirrer, reaction flask, thermometer, and reflux condenser. The DHO was poured into the flat bottom reaction flask and heated up to 60°C. After that, the calculated amount of catalyst and alcohol mixture was added to the oil-containing reaction flask and the reaction speed was kept constant at 850 rpm throughout all experiments. The obtained reaction product was poured into a separating funnel (Figure 2) at the end of the reaction to remove excess methyl alcohol, impurities, and sulphuric acid. Reaction progress was controlled by measuring the AV of the DHO oil. The product with AV below 2 mg KOH/g using the least amount of catalyst and methanol in the acid esterification process was used for Step-2.

![Figure 1. Photographic view of reactor](image1)

![Figure 2. Photographic view of impurities separation from DHO](image2)

2.2.2. Transesterification

The pretreated deccan hemp oil (Product from Step -1) was transesterified with the use of NaOCH₃ as alkaline catalyst. The affecting factors like methyl alcohol to oil molar ratio (4.0:1-7.0:1), concentration of catalyst (0.3-0.5 wt %), reaction time (45-75 minute), reaction temperature (50-65°C)
was analysed. The laboratory apparatus and transesterification reaction process were the same as for the acid esterification experimentations except for the catalyst.

After completion of the transesterification reaction, glycerine layer was separated at the bottom side of the separating funnel (Figure 3). Top side separated methyl ester was undergoing water washing process using hot water. After that, washed methyl ester was heated up to 110˚C to get rid of water and excess alcohol. The procedure was repeated 3 times at the end of the optimization process to see the repeatability. The obtained biodiesel was tested and compared to biodiesel standards (BS) and diesel.

Figure 3. Photographic view of glycerol separation from DHO

2.3. Properties of methyl ester of Deccan hemp oil

FFA composition of DHO was determined by Agilent 6890N gas chromatograph (GC). The fuel properties such as acid value (mg KOH/g), density (kg/m³), calorific value (MJ/kg), flash point (˚C), and viscosity (cSt) of the oil and diesel fuel have been evaluated under the following Indian and European standards. IS1448-16 (Density) 1990, IS1448-25 (Viscosity) 1976, IS1448-20 (Flash point) 1998, IS1448-10 (Cloud point) 1970, IS1448-10 (Pour point) 1970, IS1448-8 (Carbon Residue) 2012, IS1448: 6 (Heat of combustion of liquid hydrocarbon fuels) 1984, EN ISO 2160 (Copper strip test) and EN14104 (acid number), respectively.

3. Results and Discussions

3.1. Oil properties of Deccan hemp oil (DHO)

The FFA composition of DHO is presented in Table 1. The total saturated and unsaturated fatty acid composition of DHO was 25.04% and 75.16% respectively. Table 2 shows the important fuel properties of produced DHME. The viscosity (51cSt) and density (921 kg/m³) of DHO are higher than ASTM standards prescribed for biodiesel. Therefore, it is difficult use in diesel engines; hence transesterification is needed to reduce viscosity and density of DHO to use in diesel engines. The acid value of DHO was determined according to the procedure mentioned in literature. The acid value of DHO was found to 12.48 mg KOH/g. Hence, single stage transesterification is not possible since higher free fatty acid content in DHO reacts with base catalyst leads to a saponification [23]. Thus, esterification followed by transesterification is much suitable process.
Table 1. FFA composition and specific properties of the DHO

| Properties                  | Deccan hemp oil |
|-----------------------------|-----------------|
| **Fatty acid composition ( wt% )** |                 |
| Butyric acid C 4:0          | 0.14            |
| Palmitic acid C 16:0         | 19.31           |
| Stearic acid C 18:0          | 4.68            |
| Arachidic acid C 20:0        | 0.91            |
| Palmitoleic acid C 16:1      | 0.38            |
| Oleic acid C 18:1            | 38.65           |
| Linoleic acid C 18:2         | 32.37           |
| Alpha-linoleic acid C 18:3   | 0.43            |
| Eicosenoic acid C 20:1       | 1.5             |
| Eicosatrienoic acid C 20:3   | 1.54            |
| Eicosapentanoic acid C 20:5  | 0.29            |
| **Fuel properties**          |                 |
| Density at 30˚C ( kg/m³)     | 921             |
| Viscosity at 40˚C (cSt)      | 51              |
| Flash point (˚C)             | 253             |
| Fire point (˚C)              | 268             |
| AV (mg KOH/g)                | 12.48           |
| Calorific value (MJ/kg)      | 37.96           |

3.2. Factors affecting the AV of Deccan hemp oil

3.2.1. Effect of methyl alcohol to oil molar ratio
In the acid esterification process, the molar ratio of methyl alcohol to oil was estimated to a range of 6.5:1-9.5:1. Figure 4 shows the effect of methyl alcohol on the AV of DHO. In each experiments, the reaction was carried out with 0.75 (v/wt %) sulphuric acid catalyst. After the reaction, the AV of the DHO was decreased to 1.98 mg KOH/g at 9.5:1 of molar ratio, which is within the ASTM limit. Further increase the molar ratio, which increases the cost of production. Based on the results of present investigation, the molar ratio of 9.5:1 was maintained constant for all remaining experiments [24].

3.2.2. Effect of concentration of catalyst
The acid esterification process was investigated for different concentrations of sulphuric acid. The concentrations of sulphuric acid ranged from 0.5 -1%. Figure 5 shows the effect of concentration of catalyst on the AV. The maximum AV reduction of DHO oil was found to be 0.75% of sulphuric acid. The catalyst amount was increased to 1% acid value was go to higher. It may be due to the influence of production of water during free fatty acid esterification, which prevents further reactions [25].
3.3. Major affecting factors on yield of the Deccan hemp oil methyl ester (DHME)

3.3.1. Effect of methyl alcohol to oil molar ratio

Figure 6 shows the methyl alcohol to oil molar ratio effect on the ester yield. In the present study, methyl alcohol to oil molar ratio was varied in the ranging of 4.0:1-7.0:1. The catalyst amount was fixed as 0.4%. Each reaction was left at 60°C for 60 min. The molar ratio was increased from 4:1-5:1 showed encouraging effects on ester yield. The maximum yield was reached at the methyl alcohol to oil molar ratio of 5.0:1. No significant improvement in the ester yield was seen by further increases in the molar ratio (beyond 5.0:1) [17].

3.3.2. Effect of catalyst amount

The effect of the amount of catalyst on the yield of the ester is shown in Figure 7. The alkaline catalyst was used between 0.3-0.5 (wt %) in each case, and the reaction was permitted to proceed for 60 minutes at 60°C. From the figure it was found that minimum percentage of yield was obtained at smaller amount of catalyst due to an incomplete reaction. Yield was increased while addition of catalyst amount. The optimum yield was found to be at 0.4%. A further increase in catalyst (above 0.4%) results in a lesser yield; this could be due to the formation of an emulsion, which increases the viscosity [26].
3.3.3. Effect of reaction temperature

Figure 8 shows the effect of reaction temperature on the ester yield. In the present work, temperature range was selected from 50-65°C. The maximum percentage of yield was reached at 60°C. Further increasing in the reaction temperature (beyond 60°C), no significant improvement was observed. The decrease in ester yield may be due to gel formation at higher temperature (above 60°C) [24].

3.3.4. Effect of reaction time

In this investigation, the reaction time was calculated using the optimal values found in the preceding sections. Figure 9 shows the effect of reaction time on the yield. The experimentations were performed for different time periods ranging from 45 to 70 min. The yield was observed to be lower for a shorter duration and increased with an increase in time duration of up to 60 min. Very little significant improvement in ester yield was obtained when the reaction time exceeded 60 min [25].

![Figure 8. Effect of reaction temperature on yield](image1)

![Figure 9. Effect of reaction time on yield](image2)

3.4. Fuel properties of DHME

Table 2 shows the important fuel properties for produced methyl ester together with the limits of BS. The density of the prepared DHME is around 864.8 kg/m³. It is well suited for the Indian and American biodiesel standards and a little higher than that of petroleum diesel fuel. These biodiesel properties directly affect the performance characteristics of the CI engine [23]. The viscosity is the one of important property of the fuel it flows through the injectors and fuel pump to atomize the fuel in the engine cylinder. The viscosity of the produced methyl ester was found to be 1.85 times that of diesel fuel. This value is within the limits of biodiesel standards. Flash point of produced methyl ester was found to be 158°C, which is higher than diesel. Therefore, it is safer to store than the petroleum diesel.

However, the high flash point liquid fuel can avoid spontaneous combustion and fire problems at high temperature in transportation. The cloud and pour points of the DHME were found to be 160°C and 40°C, respectively. These values are higher than that of diesel due to presence of wax. By blending produced methyl ester with alcohols and diesel fuels, the problems of could flow property can be minimized. It has been found that the carbon residue in DHME is negligible. It is considered to be an extra benefit of methyl ester. This property tests a fuel's tendency to form deposits of carbon in the CI engine. The copper strip test (CST) shows the existence of acid in the fuel. To determine the relative degree of corrosivity, the test was performed on generated methyl ester and it was compared with Indian and American standards.

In present research work, the copper strip obtained for the methyl ester produced showed classification code 1. This result shows that the methyl ester does not cause corrosion to other materials. The AV of
DHME was found to be 0.48 mg KOH/g. This value is acceptable range when compared to biodiesel standards. The calorific value of DHME was found to be 39.42 MJ/Kg. This value is lesser when compared with petroleum diesel. However, the fuel property is not specified in the BS.

Table 2. Important fuel properties of produced DHME compared with BS and diesel.

| Properties                        | DHME   | Diesel | IS15607:2005 | ASTM D6751 |
|-----------------------------------|--------|--------|--------------|------------|
| Density at 30°C (kg/m³)           | 864.8  | 822    | 860-900      | 1.9-6.0    |
| Kinematic viscosity at 40°C (mm²/s) | 4.348 | 2.36   | 2.5-6.0      |            |
| Flash point (°C)                  | 158    | 66     | 120 min      | 130 min    |
| Cloud point (°C)                  | 16     | 6      |              |            |
| Pour point (°C)                   | 4      | .9     |              |            |
| Carbon residue (% mass)           | Nil    | .a     |              | 0.05       |
| Copper strip corrosion at 50°C Class 1 | .a     | Class 1 | No.3 max    |
| AV (mg KOH/g)                     | 0.48   | 0.34   | 0.5 max      | 0.8 max    |
| Calorific value (MJ/Kg)           | 39.42  | 42.10  |              |            |

a: Not determined
b: Not specified

3.5 Kinetic study
In the present study, kinetic study of transesterification of DHO methanolysis includes reaction between triglycerides and methanol over sodium methoxide as catalyst.

\[
\text{UCO} + 3M \xrightarrow{\text{K}_1} 3\text{UCOME} + \text{GL} \quad (1)
\]

\[
\frac{d[\text{UCO}]}{dt} = k[\text{UCO}] \quad (2)
\]

\[
\frac{d[\text{UCO}]}{[\text{UCO}]} = -kd\text{t} \quad (3)
\]

The kinetics of transesterification reaction of DHO was carried at optimum conditions of 0.4% NaOCH₃, 5.0:1 methyl alcohol to DHO molar ratio at 60°C after 60 minutes of reaction. The time interval at different temperature shows the exponential increase in conversion of triglycerides to methyl ester and confirms the pseudo-first order kinetics. By plotting the graph between −ln[1 − x] v/s t the rate constant was determined as shown in Figure 10(a). The activation energy (Ea) was determined by plotting graph between ln k v/s 1/T as shown in Figure 10(b) and was found to be 29.77 kJ/mol.
4. Conclusions

The following conclusions are obtained from the biodiesel synthesis investigation.

- Synthesis of DHME process involves two-steps: esterification of sulfuric acid (Step-1) and alkaline transesterification (Step-2).
- The AV of DHO was lessened to 1.98 mg KOH/g in the sulfuric acid esterification process.
- Methyl alcohol to deccan hemp oil molar ratio of 9.5:1, 0.75% sulfuric acid, and 30 minutes reaction time for 60°C was optimum to reduce the AV of DHO. The pretreated oil (from Step-1) was transesterified with the use of NaOCH₃ as alkaline catalyst. The maximum ester yield (95.48%) was obtained at 0.4% NaOCH₃, 5.0:1 methyl alcohol to deccan hemp oil molar ratio at 60°C after 60 minutes of reaction. The fuel properties of DHME are comparable to those of IS 51607 and ASTM D6751 biodiesel specifications.

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