

The Ethanolysis of *Pongamia pinnata* Oil by a Two-stage Acid-base Catalyst Transesterification Process for Production of Biodiesel

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Abstract To standardize the production process of ethyl ester from *Pongamia* oil, which has high free fatty acids, a two-stage transesterification was developed. In first-stage acid transesterification, parameters like ethanol, quantity, and reaction time were optimized to reduce free fatty acids below 1% using H₂SO₄ catalyst. In second-stage alkaline transesterification, parameters like molar ratio, degree proof of ethanol, catalyst concentration, and reaction temperature were optimized to obtain the highest yield with lower viscosity from pretreated oil. The ester recovery was estimated with spectrophotometry and was found to be 91%. The fuel characteristic properties of *Pongamia* ethyl ester were inline with specified BIS standards.

Keywords ethyl esters, free fatty acids, fuel characteristic properties, *Pongamia* oil, transesterification

1. Introduction

Pongamia (Leguminosae, Pappilionaceae) is a medium-sized tree found almost throughout India up to an altitude of 1,200 m. The average yield from a tree is around 20–30 kg of seed, grown as biofuel plantation (CRIDA, 2006). The oil content of the kernel is 30–40% (Lakshmikanthan, 1978). *Pongamia* oil is one of the potential non edible oils in India with a yearly production of 200 million tons per annum, out of which 6% is being presently utilized as raw material for local consumption (Lakshmikanthan, 1978). Presently *Pongamia* oil is being used by farmers in many remote villages of southern India to run generators for irrigating their fields (Shrinivas, 2001). It has become popular due to its low cost and ready availability. Short-term experiments with the usage of raw *Pongamia* oil alone or blended with diesel in different proportions as fuel in CI engines revealed some associated problems (Bhatt et al., 2004), which could be overcome by the use of esterified *Pongamia* oil (Meher et al., 2006). Many of the past researchers worked on production and usage of methyl ester as CI engine fuel. However, the cost and availability of methanol is limiting its usage for biofuel production.

Vegetable oils are chemically triglyceride molecules, in which three fatty acid ester groups are bound to one glycerol molecule. The triglyceride molecules differ by the nature of the alkyl chain bound to glycerol. Transesterification is the process of reacting a triglyceride of vegetable oil with alcohol in the presence of a catalyst to produce

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fatty acid esters and glycerol. Many researchers reported that the neat vegetable oils or refined oils with free fatty acids content less than 1% (acid value less than 2%) be used in the transesterification process to obtain maximum ester formation (Freedman and Pryde, 1981). The parameters of the esterification process, like molar ratio, reaction time, reaction temperature, catalyst type and concentration, and settling time, have a profound effect on recovery of ester. The esterification process was rapid with an alkali-based catalyst rather than base catalyst. However, an acid base catalyst can be used for low grade fat or oils having high free fatty acids content as fatty acids deactivate the alkaline reaction (Freedman et al., 1984). Ester conversion is strongly affected by molar ratio of alcohol to oil, and a higher molar ratio is required in an acid-catalyzed process compared to an alkali-catalyzed process (Canakci and Van Gerpen, 1999). Esterification reaction starts at room temperature but maximum recovery of ester is observed at reaction temperatures closer to the boiling point of alcohol used in the reaction and again recovery decreased after boiling point due to the evaporation of alcohol in the reaction (Freedman et al., 1984). All of these parameters influenced the biodiesel production significantly. It is observed from the literature that limited findings were reported on ethanolosis of non-edible oil having high free fatty acid content. *Pongamia* oil that has high free fatty acids needs to be transesterified before using as an engine fuel. Hence, this article highlights the attempts made for development of ethyl ester production process for *Pongamia* oil. Ethanol was used in this experiment to replace methanol because it is cheaper and renewable in nature. The authors' experiments in the lab closely agreed with the reported literature that the presence of high free fatty acids (FFA; due to the presence of non saturated fatty acids) made the transesterification reaction difficult due to formation of soap with an alkaline catalyst. In the present set of experiments, the alternative route of using an acid-base catalyst was standardized for biodiesel production from *Pongamia* oil.

2. Materials and Methods

Commercially available *Pongamia* seeds were procured from a local market and the oil was extracted using a conventional oil expeller, which is normally used for edible oil extraction. The experiments for production of ethyl ester from *Pongamia* oil were carried out at Central Research Institute for Dry Land Agriculture, Hyderabad. The crude *Pongamia* oil obtained by the expeller was greenish yellow in color. The fatty acids profile of experimental *Pongamia* oil is given in Table 1. Its acid value (which is the indication for

Table 1
Fatty acid composition of *Pongamia* oil

Sl. no.	Fatty acids	Structure	Formula	Composition, %
1	Palmitic acid	16:0	C ₁₆ H ₃₂ O ₂	10.6
2	Stearic acid	18:0	C ₁₈ H ₃₆ O ₂	6.8
3	Oleic acid	18:1	C ₁₈ H ₃₄ O ₂	49.0
4	Linoleic acid	24:0	C ₂₄ H ₄₈ O ₂	19.3
5	Arachidic acid	20:1	C ₂₀ H ₄₀ O ₂	4.1
6	Behenic acid	22:0	C ₂₂ H ₄₄ O ₂	5.3
7	Lignoceric acid	18:2	C ₁₈ H ₃₂ O ₂	2.4

presence of free fatty acids) was determined by a standard titrimetry method described by Cox and Pearson (1962). The oil had an initial acid value of 16.02 mg KOH/g corresponding to a FFA value of 8%, which is far above the 1% limit for satisfactory transesterification reaction using alkaline catalyst. Therefore, FFAs were first converted to esters in the pretreatment process using an acid catalyst (H_2SO_4 , 1% v/v) to reduce the acid value of Pongamia oil below 2 mg KOH/g. Experiments were conducted in a laboratory-scale set up, which consisted of 250 cc glass flasks with air tight caps that retained vaporized ethanol if any were present in the reaction mixture. The flasks were kept in a water bath shaker maintained at 70°C temperature just below the boiling point of ethanol, and the mixture was stirred at the same rate for all runs by constant shaker speed.

2.1. Pretreatment Process

The pretreatment reaction was carried out with different ethanol-to-oil ratios (0.15, 0.20, 0.25, 0.30, 0.35, and 0.40 v/v) and reaction times (0.5, 1.0, 1.5, and 2.0 h) at 70°C reaction temperature were used to investigate their influence on the acid value of crude Pongamia oil. After the reaction, the mixture was allowed to settle for 1 h in a separating funnel and the ethanol–water fraction that separated at the top was removed. The progress of reaction was monitored by measuring acid value at frequent intervals. The acid value of the product that separated at the bottom of separating funnel was determined by using the standard titration method. The final product produced with the lowest quantity of ethanol and least reaction time with an acid value less than 2 mg KOH/g was used for the main transesterification reaction.

2.2. Alkaline Catalyst Transesterification Process

In order to standardize the process parameters, the effect of variables, such as three levels of molar ratios (3:1, 6:1, and 8:1), four levels of degree proof of ethanol (140, 150, 160, and 170°), six levels of catalyst (KOH) concentration (1.0, 1.25, 1.5, 1.75, 2.0, and 2.25%), and four levels of reaction temperature (30, 60, 70, and 80°C), were studied in the experiment. In the present study, aqueous ethanol of different degree proof was used in place of anhydrous ethanol to improve polarity for dissolving the specified amount of catalyst. Reaction with ethanol having 180, 190, and 200° (absolute ethanol) proof did not take place due to lower polarity, which made it difficult for the catalyst to be dissolved. The esterification was carried out at 3:1, 6:1, and 8:1 molar ratios in order to obtain maximum recovery of ester with the lowest possible kinematic viscosity by preliminary experiments. The reaction was carried out at selected molar ratio and degree proof of alcohol at different levels of catalyst concentration for different reaction temperatures in a shaking water bath and then allowed to settle for 24 h in order to separate the lighter ester layer at the top and heavy glycerol layer at the bottom.

2.3. Estimation of Ester Recovery in Transesterification Reaction

The conversion of Pongamia oil to ester was estimated by comparing the glycerol content in the vegetable oil and its ester at different reaction times with different variables of molar ratio, degree of proof of ethanol, catalyst concentration, and reaction temperature. The glycerol content was estimated using spectrophotometry as per the method of Renkonen as reported by Work and Work (1972). A Systronics (model 169, Systronics, Gujarat,

India) spectrophotometer was used to measure the absorbance of standard glycerol having selected micromole, blank, and glycerol present in the samples (Sangha et al., 2000).

2.4. Characteristic Fuel Properties

The fuel properties, namely density at 15°C; kinematic viscosity at 38°C; flash and fire point; cloud and pour point; ash content; carbon residue; acid value; and gross heat of combustion of Pongamia oil, Pongamia biodiesel, and conventional diesel, were determined as per the procedure given by the Bureau of Indian Standards, New Delhi.

3. Results and Discussion

3.1. Effect of Ethanol Quantity and Reaction Time on Acid Value during the Pretreatment Process

The changes in the acid value of the mixture on pretreatment are plotted in Figure 1, to show the nature of variation. From this figure, it was observed that the rate of reaction was greatly influenced by both the quantity of ethanol and reaction time. The reaction progressed rapidly during the first hour showing over 50% reduction in acid values at low ethanol and over 80% for high ethanol ratios. After 1 h, there was no significant reduction in the acid value. This may be due to the effect of water produced during the esterification of FFA, which prevented further reaction. Since the reaction time was not that effective after 1 h, the ethanol quantity was increased for further investigation. With the ethanol-to-oil ratio increased beyond 0.35, the acid value could be lowered in the desirable range of 2 mg KOH/g. The combination of 0.35 v/v ethanol-to-oil ratio and a 1-h reaction time reduced the acid value from 16.02 to 1.98 mg KOH/g and was selected as optimum for the pretreatment process.

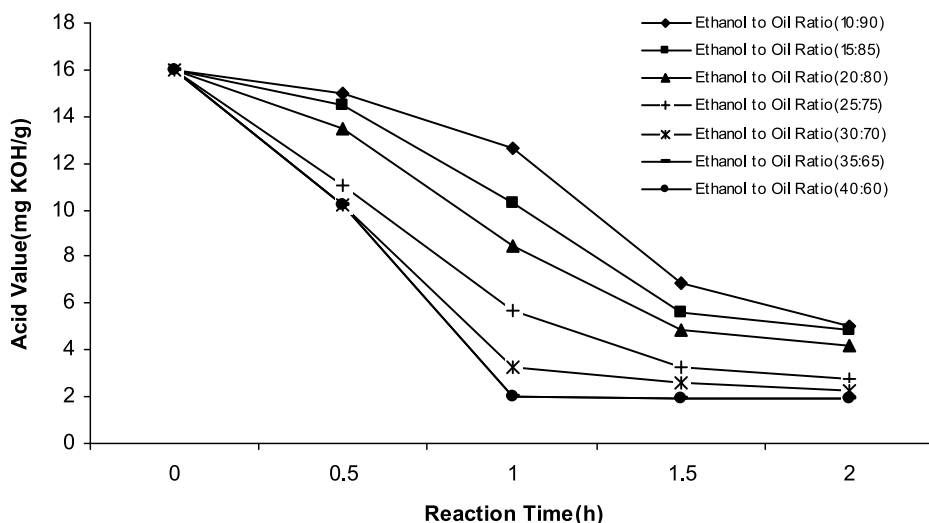


Figure 1. Effect of reaction time and ethanol to oil ratio on acid value of Pongamia oil during pretreatment process.

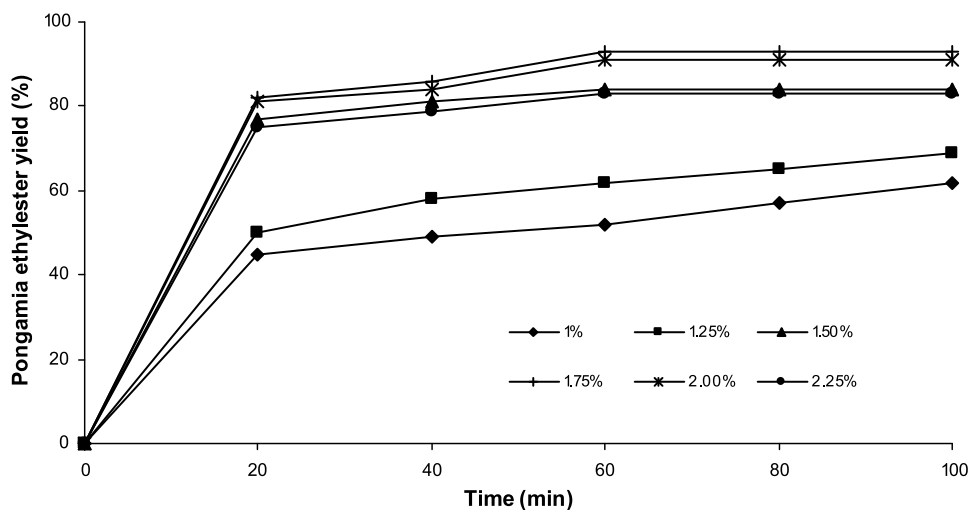


Figure 2. Effect of catalyst (KOH) concentration on Pongamia ethyl ester yield.

3.2. Effect of Catalyst Concentration on Pongamia Ethyl Ester Recovery and Kinematic Viscosity

The transesterification reaction of pretreated Pongamia oil was carried out with different catalyst (KOH) concentrations of 1 to 2.25 wt% of oil at 70°C with ethanol of 160° proof in the ratio of 6:1 with oil. The yield of ethyl ester with reaction time and its viscosity with reaction time at different catalyst (KOH) concentrations are plotted in Figures 2 and 3, respectively. The recovery of Pongamia ethyl ester observed at different process parameters for 60 min varied between 52 to 93% and kinematic viscosity varied between 22.43 to 7.12 cSt. The Pongamia ethyl ester having the lowest kinematic viscosity of 7.12

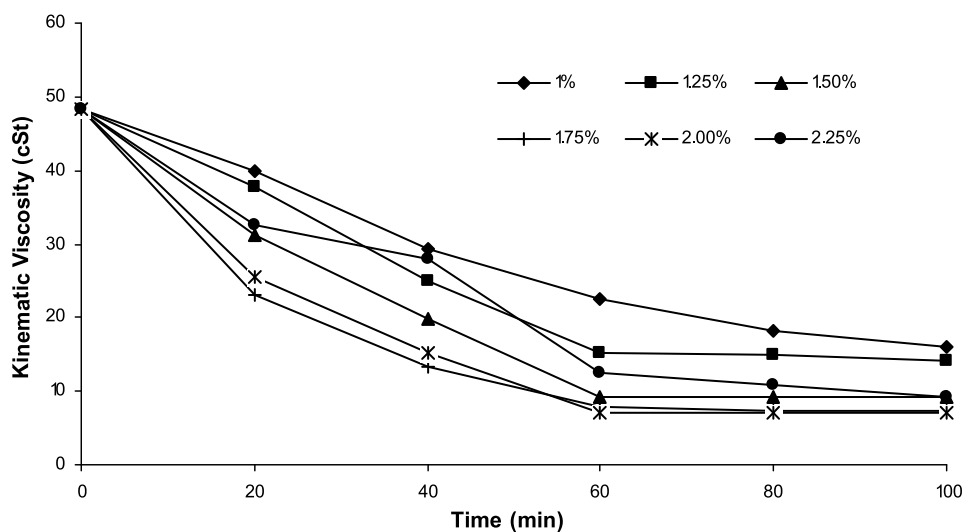


Figure 3. Effect of catalyst (KOH) concentration on kinematic viscosity of Pongamia ethyl ester.

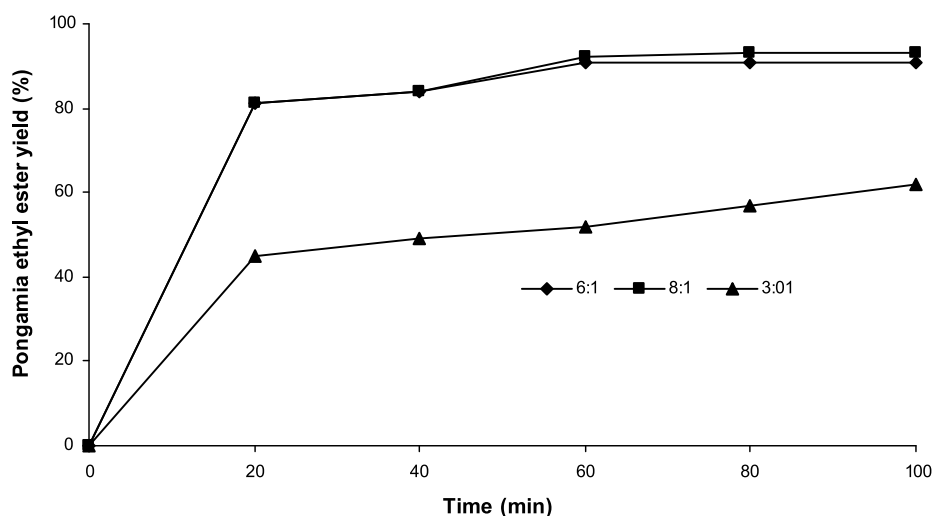


Figure 4. Effect of molar ratio on Pongamia ethyl ester yield.

cSt was obtained when the pretreated Pongamia oil was reacted with 160° proof ethanol in 6:1 molar ratio at 70°C reaction temperature for 60 min in the presence of 2% KOH; ester having a viscosity of 7.54 cSt was obtained with 1.75% KOH concentration keeping other parameters remaining constant. It was observed that an increase in KOH catalyst concentration beyond 2% showed a decrease in the ethyl ester recovery due to formation of soap, which led to the increase in viscosity of the ester. Although 1.75% KOH catalyst concentration gave a slightly higher recovery of 93% as compared to 91% for 2.0% KOH catalyst concentration, keeping the viscosity in view of 2.0% KOH catalyst concentration was optimal for the alkaline transesterification process.

3.3. Effect of Molar Ratio on Pongamia Ethyl Ester Recovery

The effect of molar ratio on Pongamia ethyl ester recovery was studied by comparing the recovery of Pongamia ethyl ester with reaction time at selected molar ratios of 3:1, 6:1, and 8:1 at 70°C with 160° proof of ethanol as shown in Figure 4. From the experiments, it was observed that the ester recovery was increased with an increase in molar ratio. The maximum ester yield was obtained with the molar ratio of 6:1. The ethyl ester recovery more or less remains the same with a further increase in molar ratio and it reduced with a decrease in molar ratio. Hence, the molar ratio of 6:1 was standardized for alkaline transesterification.

3.4. Effect of Degree Proof of Ethanol on Pongamia Ethyl Ester Recovery

The effect of degree proof of ethanol on Pongamia ethyl ester recovery was studied by comparing the recovery of Pongamia ethyl ester with the reaction time at selected ethanol having a degree proof of 140, 150, 160, and 170 in 6:1 molar ratio at 70°C with 2% catalyst concentration (see Figure 5). It was observed that the ethyl ester yield increased with an increase in degree proof of ethanol up to 160° and, thereby, decreased

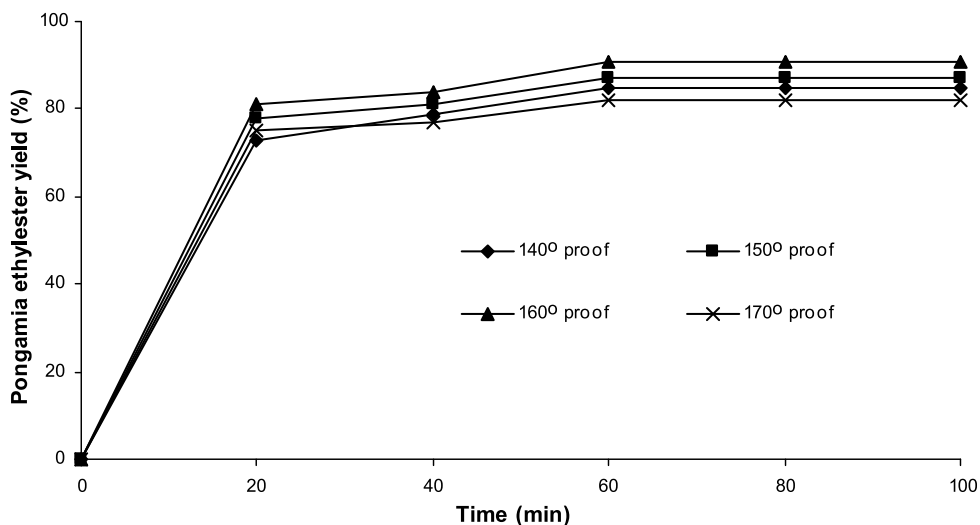


Figure 5. Effect of degree proof of ethanol on Pongamia ethyl ester yield.

with an increase in degree proof of ethanol due to incomplete dissolution of catalyst concentration. Hence, 160° proof of ethanol that gave a maximum yield with less viscosity was standardized for the alkaline transesterification process.

3.5. *Effect of Reaction Temperature on Pongamia Ethyl Ester Recovery*

The effect of reaction temperature on Pongamia ethyl ester recovery was studied at selected reaction temperatures of 30, 60, 70, and 80°C with 2% catalyst concentration and 160° proof of ethanol in 6:1 molar ratio by comparing ethyl ester yield with reaction time as shown in Figure 6. It was observed that the ester yield was increased with an increase in reaction temperature up to 70°C, which is near the boiling point of ethanol. The ester recovery after 70°C decreases due to increased saponification of glycerides by the alkaline catalyst before completion of the alcoholysis. Hence, 70°C temperature reaction was standardized for the alkaline transesterification process.

3.6. *Fuel Characteristic Properties of Pongamia Ethyl Ester*

The Pongamia ethyl ester produced using the two-stage acid-base catalyst process was used to evaluate fuel characteristics as per the standards, which are shown in Table 2. It is evident from the table that the viscosity of Pongamia biodiesel was found to be 7.12 cSt, which is well within the limits of IS 1448 (1974b) specification of biodiesel. Its gross heat of combustion was found to be lower than that of diesel because of more inbuilt oxygen content. The flash point of Pongamia ethyl ester was 162°C, which is higher than that of conventional diesel. Hence, storage of ethyl ester and ethyl ester-diesel blends was safe as compared to diesel alone. The carbon and ash content of ethyl ester was found to be lower than diesel, which decreased the emissions during combustion in the engine cylinder. The acid value of the biodiesel was found to be 0.64 mg KOH/g, which was within the limit of IS 1460 (1974b) specification of biodiesel.

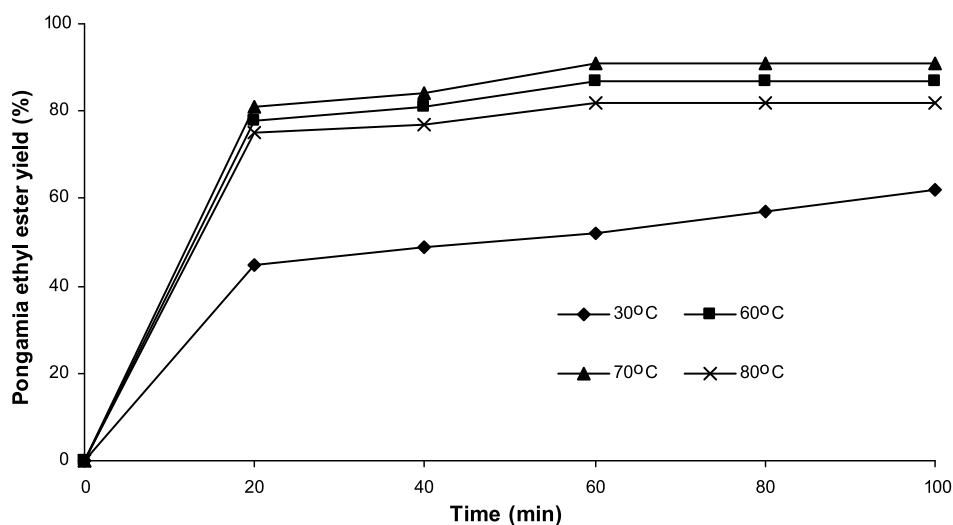


Figure 6. Effect of reaction temperature on Pongamia ethyl ester yield.

Table 2

Fuel characteristic properties of Pongamia biodiesel produced by two-stage acid-base catalyst process

Characteristic properties	Limits	Test standards	Biodiesel quality
Relative density at 15°C	0.87–0.90	IS: 1448 [P: 32]: 1992	0.891
Kinematic viscosity at 38°C, cSt	2.0–7.5	IS: 1448 [P: 25]: 1976	7.12
Flash point, °C	>100	IS: 1448 [P: 32]: 1992	162
Fire point, °C	—	IS: 1448 [P: 32]: 1992	169
Cloud point, °C	—	IS: 1448 [P: 10]: 1970	22
Pour point, °C	—	IS: 1448 [P: 10]: 1970	9
Ash content, %	0.02	ASTM D482	0.0097
Carbon residue, %	1.0	ASTM D189	0.816
Acid value, mm KOH/g	0.8	ASTM D974	0.64
Gross heat of combustion, MJ/kg	—	IS: 1448 [P: 6]: 1984	38.74

4. Conclusions

The experimental results revealed that the Pongamia oil reacting with 0.35 v/v ethanol-to-oil at 70°C temperature in the presence of 1% H₂SO₄ for a 1-h reaction time reduced the acid value from 16.02 to 1.98 mg KOH/g in the pretreatment process. The alkaline-catalyst transesterification of pretreated Pongamia oil reacting with 160° proof of ethanol in a 6:1 molar ratio in the presence of 2% KOH at 70°C reaction temperature for a 1-h reaction time gave the highest ethyl ester recovery of 91% with the lowest viscosity of 7.12 cSt. The fuel characteristics of Pongamia ethyl ester produced at optimum parameters were inline with standards specified by the Bureau of Indian Standards, New Delhi.

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