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Biodiesel Production from *Pongamia pinnata* Oil using Synthesized Iron Nanocatalyst

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Abstract: Biodiesel is a clean-burning renewable substitute fuel for conventional petroleum diesel, which is made from vegetable oils or animal fats by a monoalcoholic transesterification process. Biodiesel production using nanocatalyst is one of the approaches in the search of alternative fuel. In this present investigation, the synthesized iron nanoparticles were used as a nanocatalyst for the production of biodiesel using *Pongamia pinnata* oil with methanol. The transesterification reaction for the conversion of triglycerides into fatty acid methyl esters was carried out at a molar ratio of 3:1 methanol to oil, reaction time of 2 h, stirring speed of 400 rpm at 65°C. The amount of iron nanoparticles used for this study was 1% (wt/wt). The physico-chemical properties of the *Pongamia pinnata* fatty acid methyl esters including specific gravity, kinematic viscosity, flash point, cloud point, water content, carbon residue, refractive index, copper corrosion and calorific value were 0.873, 4.6 mm^2/s at 40°C, 178 °C, 5°C, 0.012 vol. %, 0.033 mass %, 1.445, 1b and 3788 cal/gm respectively. The obtained values of physico-chemical properties are in accordance with the specifications of biodiesel as per ASTM D6751 standard. These findings conclude that the synthesized iron nanoparticles acted as a catalyst to produce biodiesel and the obtained biodiesel was considered as suitable alternatives to the conventional diesel.
Keywords: Biodiesel; Transesterification; *Pongamia pinnata*; Iron nanocatalyst.

1. Introduction

Biodiesel plays a vital role as an alternative fuel due to the depletion of fossil fuel resources. The pure vegetable oils can not be used as fuels for diesel engines due to its high viscosity[1]. To overcome this problem, the vegetable oils are converted into biodiesel by performing transesterification reaction. Technically, biodiesel is the fatty acid alkyl ester made by the transesterification of plants seed oil or animals fat, with short chain alcohols such as methanol or ethanol. The unique properties of biodiesel are biodegradability, low toxicity, low sulphur content, high flammability and high cetane number[2].

Vegetable oils are becoming a promising source for the production of diesel fuel, because they are renewable in nature and environmental friendly as well. Edible vegetable oils (sun flower, canola, palm, soybean, corn) and non-edible vegetable oils (Jatropha curcas, tallow and neem oil) are used for biodiesel production and found to be good as a diesel substitute[3]. Among the sources of non-edible oils, *Pongamia* *pinnata* is found almost all part of India mainly in the Western Ghats of India and it grows on any types of soil ranging from clayey to sandy. *Pongamia pinnata* is a native to many countries including India, Malaysia, Indonesia, Taiwan, Bangladesh, Sri Lanka and Myanmar. The *Pongamia pinnata* kernel contains about 30 - 40% of oil and hence, it is considered as a potential source for the biodiesel production[4].

Catalyst plays a major role in the production of biodiesel, which improves the reaction rate of tranesterifications process and produces high yield of biodiesel. Homogeneous base catalysts such as potassium hydroxide, sodium hydroxide, sodium methoxide, potassium methoxide and homogeneous acid catalysts such as strong mineral acids, p-toluene sulphonic acids are most frequently used in the industrial process to produce biodiesel[5,6]. However, the transesterification process by homogeneous catalyst generates saponification and hence, it requires additional downstream process to remove the homogeneous catalysts, thus reflecting the high cost of production. But, the heterogeneous catalysts such as zeolites and ion-exchange resins possess many advantages, since they are non-corrosive, easy separation and require no washing of the ester. The disadvantage of biodiesel produced by heterogeneous catalyst gives low yield of product and disposal problems[7,8]. Therefore, the focus on the development of new approaches is greatly increasing to achieve the efficient process for biodiesel production.

Recently, nanomaterial has gained special attention as a catalyst for biodiesel production, owing to its large specific surface area, high catalytic activity, high resistance to saponification and good rigidity[9]. In nanocatalyzed transesterification process, KF treated nano Al_2O_3 catalyst used to produce biodiesel from canola vegetable oil with the conversion of 97.7%[10]. Qiu et al., (2011) reported that the transesterification using soyabean oil and methanol was catalyzed by zirconia nanoparticles loaded with potassium bitartrate for the production of biodiesel[11]. Biodiesel yield of 95.2% obtained using nanocatalyst derived from hydrotalcites with Mg/Al for the jatropha oil[12]. The study for the production of biodiesel using nanoparticles as catalysts is very limited. To the best of our knowledge, there is no report available on biodiesel production from *Pongamia pinnata* oil with methanol using iron nanoparticles as a catalyst.

The objective of this work was to investigate the synthesized iron nanoparticle as catalyst for the transesterification of *Pongamia pinnata* oil with methanol and physico-chemical properties of the obtained biodiesel were compared with the biodiesel standards ASTM D6751. Also, the compatibility of physico-chemical properties of resulting fatty acid methyl ester was evaluated with the existing conventional diesel fuel.

2. Materials and Methods

2.1 Materials

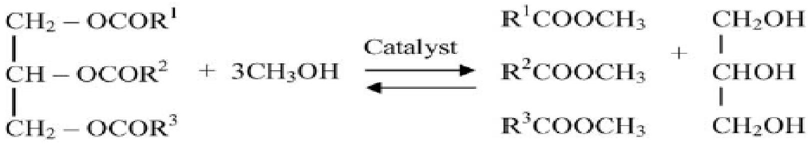
Pongamia pinnata oil was purchased from local suppliers in Tiruchirappalli, Tamilnadu, India. The methanol was procured from Merck Specialties Private Ltd, India.

2.2 Preparation of Catalyst

Iron nanoparticles were synthesized by chemical reduction method from ferric chloride solution using sodium borohydride solution as reducing agent. The conditions for the synthesis of iron nanoparticles and their characteristics were reported in our earlier work[13]. The size of the synthesized iron nanoparticles was in the range of 40 - 70 nm.

2.3 Reaction procedure

The experiments were conducted in a 500 ml three-necked round bottom flask equipped with heating, condensing and stirring facility. 3:1 molar ratio of methanol and *Pongamia pinnata* oil was taken in a round bottom flask. The temperature of the reaction mixture was maintained at 65^oC. To prevent the methanol loss during a reaction, a water-cooled condenser was used. The reaction was started by charging the catalyst about 1% (wt/wt) of synthesized iron nanoparticles and it was carried out for a period of 2 h at 400 rpm. After the completion of the reaction, the mixture was cooled to the room temperature and transferred to a separating funnel. The biodiesel was allowed to separate from the mixture. Then, the crude biodiesel was separated and the excess methanol was removed using rotary vacuum evaporator. The transesterification reaction for biodiesel production is generally described as below.



In the present investigation, iron nanoparticles were used as a catalyst for the production of biodiesel. The quality of obtained biodiesel was expressed in terms of the physico-chemical properties including specific gravity, viscosity, flash point, cloud point, water content, carbon residue, refractive index, copper corrosion and calorific value. These properties of the biodiesel were determined as per the methods of American Standards for Testing and Materials (ASTM).

3. Results and Discussion

3.1. Physico-chemical properties of *Pongamia pinnata* oil and biodiesel

The quality of *Pongamia pinnata* oil was expressed in terms of the physico-chemical properties including acid value, iodine value, saponification value and moisture content. These properties of the oil were determined as per ASTM standards (Table 1). The fuel properties of *Pongamia pinnata* oil methyl ester and the experimental procedures adopted for the analysis are given in Table 2. The experimental results were compared with biodiesel standard ASTM D6751 and the values were found within the specification range. Also, the obtained results were compared with the biodiesel produced using conventional acid/base catalyst (Table 3). It was noted that the results of produced biodiesel was superior in quality in terms of specific gravity, kinematic viscosity, flash point, cloud point and carbon residue when compared to the literature values.

Table 1: Physical and chemical properties of *Pongamia pinnata* oil

Sl.No	Physico-chemical properties	Units	ASTM Test method	Properties of *Pongamia pinnata* oil
1	Color	-	Visual	Light Reddish Brown
2	Specific gravity at 40°C	-	D 4052	0.932
3	Kinematic viscosity at 40°C	mm^2/s	D 445	30.0
4	Acid value	mg KOH/gm	D 92	5.6
5	Sponification value	mg KOH/gm	D 94	182.0
6	Flash point	°C	D 93	240.0
7	Cloud point	°C	D 97	8.0
8	Carbon residue	% mass	D 524	0.068

Table 2: Fuel properties of produced biodiesel from *Pongamia pinnata* oil using iron nanoparticles and ASTM specification.

Physico-chemical properties	ASTM Test Method	Biodiesel specification as per ASTM D6751	Properties of produced biodiesel
Specific gravity at 40°C	D 4052	0.81-0.90	0.873
Kinematic viscosity at 40°C (mm^2/s)	D 445	1.9-6.0	4.6
Flash point (°C)	D 93	≥ 130	178
Cloud point (°C)	D 97	-3 to 12	5
Water content (% vol)	D 2709	≤ 0.05	0.012
Carbon residue (% mass)	D 524	≤ 0.05	0.033
Refractive index	-	-	1.445
Copper strip Corrosion	D 130	No.3 max.	1b
Calorific value (cal/gm)	P 6	-	3788

Table 3: Fuel properties of *Pongamia pinnata* biodiesel using different Conventional catalysts and synthesized iron nanocatalyst

Type of catalyst	Specific gravity at 40°C	Kinamatic viscosity at 40°C (mm^2/s)	Flash point (°C)	Cloud point (°C)	Carbon residue (% wt)	Water content (% vol)	Calorific value (cal/gm)	Ref.
Sulphate Zirconia +KOH	-	4.33	170	-	0.005	0.005	-	[17]
CaO + Eggshell	-	5.4	158	5	0.02	0.005	41.5 kJ/gm	[18]
NaOH	0.942	34.66×10^{-6} Ns/m^2	-	-	-	0.16	40.216 kJ/gm	[20]
Acid + Base	0.88–0.89	5.52–5.79	-	-	-	-	37.8–39.69	[21]
Alhoxide	0.860	4.78	144	6	0.005	0.02	3700	[16]
H_2SO_4 + NaOH	0.883	4.37	163	14.6	-	-	4213	[15]
NaOH	0.865	5.75	110	-	-	-	36,540 kJ/gm	[14]
NaOH	0.917	5.51	110	2.0	0.64	-	-	[22]
Iron Nanoparticles	0.873	4.6	178	5	0.033	0.012	3788	Present study

3.1.1. Specific gravity

The specific gravity of *Pongamia pinnata* oil was found to be 0.923 (Table 1). After transesterification process, the specific gravity was reduced to 0.873. The obtained value agrees with the specification of biodiesel standard ASTM D6751 (Table 2). A similar result was observed by Mahanta et al., (2011)[14] who found that the specific gravity was 0.865 (Table 3). However, the specific gravity of conventional diesel varies from 0.825 and 0.835. The specific gravity of obtained biodiesel was observed to be slightly higher than that of the conventional diesel. This result indicates that the slightly greater mass of obtained biodiesel may be delivered into the diesel engine.

3.1.2. Kinematic viscosity

Viscosity is the most important property of biodiesel because it affects the fluidity of the fuel. The kinematic viscosity of the *Pongamia pinnata* oil was about 30 mm^2/s at 40^oC (Table 1), whereas the viscosity of produced biodiesel was about 4.6 mm^2/s. The obtained results are within the limits as per standard (Table 2). The similar kinematic viscosity values of 4.37 and 4.78 mm^2/s were observed by Sahoo et al., (2009)[15] and Bobade et al., (2012)[16], respectively (Table 3). Besides, the kinematic viscosity of the conventional diesel ranges between 2 and 4.5 mm^2/s at 40^oC. Thus it can be concluded that the viscosity of produced biodiesel is similar to both the conventional diesel and biodiesel standard ASTM D6751. Hence, the produced biodiesel can be used for the existing diesel engine without any design modification.

3.1.3. Flash point

The flash point is the temperature at which fuel vapor given off momentary flash when an external flame is introduced under specified test conditions. It is an important parameter for safe storage and handling of fuel. The flash point of the produced biodiesel was about 178°C (Table 2), whereas the flash point of *Pongamia pinnata* oil was about 240°C (Table 1). This value is much higher than that of the minimum value (130^oC) as indicated in the ASTM standard. The similar flash point values of 163^oC and 170^oC were obtained by Sahoo et al., (2009)[15] and Thiruvengadaravi et al., (2012)[17], respectively (Table 3). The flash point specification for conventional diesel fuel is about 35^oC minimum. The result indicated that the produced biodiesel was considered to be safer than the conventional diesel for storage and handling purposes.

3.1.4. Cloud point

The cloud point means that the temperature at which a sample of the fuel starts to become cloudy when the fuel is cooled in prescribed conditions. The cloud point of vegetable oil and biodiesel produced in the present study was about 8 ^{o}C and 5^{o} C, respectively (Tables 1 and 2). The observed value of biodiesel matches with the specifications of ASTM. A similar result was observed by Bobade et al., (2012)[16] and Sharma et al., (2010)[18] (Table 3). The cloud point of conventional diesel fuel is between -10 to -15 ^{o}C. The result of the study suggests that the obtained biodiesel may not be used as fuel at low temperatures when compared to the conventional diesel. At very low temperature, the fuel tends to become a gel that cannot be pumped.

3.1.5. Carbon residue

Carbon residue of the fuel is indicative of carbon depositing tendencies of the fuel in diesel engine. The carbon residue of vegetable oil and biodiesel produced in the present study was about 0.066 and 0.033 wt%, respectively (Tables 1 and 2). The obtained result agrees well with the specification of biodiesel standard ASTM D6751. The carbon residues specification for conventional diesel is 0.01 wt%. The result acquired from carbon residue test showed that the impurity of biodiesel obtained in this study was less when compared to the vegetable oil. The carbon residue value of obtained biodiesel was slightly higher than that of the conventional diesel, because the biodiesel may contain inorganic impurities and biopolymers[19].

3.2.6. Water content

Water content in fuels imposes engine corrosion problems or reacts with glycerides to produce soaps and glycerol. In the present study, water content of produced biodiesel was about 0.012 vol.% (Table 2). A similar result was observed by Sahoo et al., (2009)[15] and Thiruvengadaravi et al., (2012)[17] who found that the water content of 0.005 vol.% (Table 3). The result showed that the produced biodiesel may resist the corrosion formation in diesel engine.

3.2.7. Copper strip corrosion

The copper corrosion test was carried out at 100^{o}C for a period of 3 h. The value of copper corrosion test for the produced biodiesel was found to be 1b. The results revealed that the biodiesel was observed to be superior quality, when compared to the conventional diesel and hence, it may lead to good resistance for copper corrosion. The calorific value and refractive index of the produced biodiesel were 3788 cal/gm and 1.445, respectively. The similar result was observed by Bobade et al., (2012)[16] for calorific value and Evera et al., (2009)[20] for refractive index.

4. Conclusion

. The production of biodiesel from *Pongamia pinnata* oil with methanol was successfully conducted using iron nanoparticles as catalyst. The properties of resulting biodiesel of *Pongamia pinnata* oil agrees well with the specifications of biodiesel standards ASTM D6751. The use of iron nanoparticles as catalyst showed more advantageous than the conventional acid/base catalyst for the production of biodiesel, because of its large specific surface area, high catalytic activity and high resistance to the saponification. Hence, the produced biodiesel can be considered as an alternative to the conventional diesel.

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