TRANSESTERIFICATION OF CASTOR OIL USING NANO-SIZED IRON CATALYST FOR THE PRODUCTION OF BIODIESEL

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ABSTRACT

Biodiesel is a green and clean-burning alternate fuel for conventional fossil fuels. In the current study, the biodiesel was synthesized from castor oil using synthesized iron nanoparticles. The FTIR results confirmed the presence of methyl and ester group in the produced biodiesel. The specific gravity, kinematic viscosity, flash point, cloud point, water content, carbon residue, refractive index, copper corrosion and calorific value according to ASTM test methods for biodiesel were 0.914, 9.8mm^2/s at 40 ºC, 185ºC, 6ºC, 0.17 vol. %, 0.042wt %, 1.460, 1a and 9295cal/gm respectively. The physicochemical properties of produced biodiesel were compared with conventional diesel and ASTM D6751 standard of biodiesel specifications. The results of this study reveal that the produced biodiesel using synthesized iron nano-catalyst was considered as prospective alternate fuel to the conventional diesel fuel.

KEYWORDS: Castor oil; Biodiesel; Transesterification; Iron nanocatalyst.

1. INTRODUCTION

Biodiesel has increased attention in the field of renewable energy as alternate fuel to the crude oil based diesel due to the fuel price, energy requirement, crisis of petroleum availability and stringent environmental regulation (Zillillah et al., 2012). It has many advantages in its fold such as biodegradability, lower toxicity, superior lubricity, renewability, engine adaptability and environmental friendly (Fattah ,2014).Also, biodiesel has ability to reduce the emissions of carbon monoxide, particulate matter, carcinogenic aromatics and sulfur to the environment (Minsookim et al.,2013). Biodiesel can be produced from edible and non-edible vegetable oil, algae, animal fats, grease and even from waste cooking oil (Atabani et al., 2011).

Currently, non-edible vegetable oil has become an attractive feed stock for biodiesel production, since it is lower in price compared to edible oil and easily available. The prime feedstock for the production of biodiesel in India can be non-edible oils which obtained from plant species such as Ratanjot (*Jatrophacurcus*), Karanja (*Pongamiapinnata*), Neem (indica) and Castor (*Ricinuscommunis*). India is the world's largest producer and exporter of castor oil. India annually exports around 2.0-2.4 lakh tons of commercial castor oil. 42% to 48% of castor oil can be extracted from the Indian variety of castor plant seed. Castor plants can grow well under hot and humid tropical conditions without any fertilizer. These plants are cultivated about 7, 00,000 hectares in India. The average yield of seed per hectare is about 1250 kg (Shrirame et al., 2011).Hence, the castor oil was considered as a potential source for the production of biodiesel in India.

In the process of biodiesel production, catalyst plays a significant role to increase the yield and reduce the cost of product. Sodium hydroxide, potassium hydroxide, sodium methoxide and potassium methoxide as homogeneous base catalysts and hydrochloric acid, sulphuric acid and p-toluene sulphonic acids as homogeneous acid catalysts have been widely used in commercial process (Zullaikah et al., 2005). Mostly, the homogeneous catalysts are employed for transesterification process at large scale level (Meneghetti et al., 2006).They cannot be reusable, and the process generates inferior quality of glycerol and huge amount of wastewater which causes environment pollution. On the other hand, heterogeneous catalysts such as zeolites and ion-exchange resins results in simplified purification processes, reusability of catalyst, non-corrosive and an economically attractive. However, heterogeneous catalyst also have limitations like low catalytic activity while reuse, vigorous mixing of reactor, low yield of product, disposal problems and high cost (Suppes et al., 2004). Therefore, the focus on the development of new catalysts is greatly increasing for the efficient biodiesel production process.

Nowadays, nanomaterials are playing significant role as a catalyst for the production of biodiesel, since it has higher catalytic activity, large specific surface area, high resistance to saponification reaction and good rigidity (Hu, 2011). Qiu et al., (2011) conducted nanocatalysed transesterification of sunflower oil using ZrO_2 loaded with $C_4H_4O_6HK$ catalyst and the conversion was about 98.03%.Yan et al., (2010) reported that 93.7% biodiesel yield was obtained from food grade soya bean oil with modified ZnO nanoparticles. The production of biodiesel studies using metal/metal oxide nanoparticles as catalyst is very limited. To the best of our knowledge, there is no report available on biodiesel production from castor oil using iron nanoparticles as a catalyst.

The objective of this work was to investigate the synthesized iron nanoparticle as catalyst for the Transesterification of castor oil with methanol and evaluate the physico-chemical properties of produced biodiesel in concurrence with the biodiesel standards ASTM D6751. Also, the physico-chemical properties of biodiesel were compared with the existing conventional diesel fuel.

2. MATERIALS AND METHODS

2.1 Materials: Castor oil was purchased from local suppliers in Tiruchirappalli, Tamilnadu, India. The methanol was procured from Merck Specialties Private Ltd, India. Iron nanoparticles were synthesized in our lab and used as catalyst for this study.

2.2 Preparation of iron nanoparticles: Chemical reduction method was used for the synthesis of iron nanoparticles from its precursor ferric chloride solution and sodium borohydride solution as a reducing agent. The synthesized iron nanoparticles were characterized for their composition, size and shape using XRD, SEM, EDAX and TEM. The preparation method and obtained results for iron nanoparticles were reported in our earlier work (Rengasamy et al., 2014).

2.3 Biodiesel synthesis: The experiments were conducted in a 500 ml three-necked round bottom flask equipped with heating mantle, reflux condenser, digital thermometer and mechanical stirrer. One mole of methanol and nine moles of castor oil were taken in a round bottomed flask. The temperature of the reactant was maintained at 65ºC with an accuracy of ±1°C. The temperature of the reaction was monitored by digital thermometer. To prevent the methanol loss during a reaction, a water-cooled condenser was used to condense the vapours and reflux it back into the reactor. The reaction was started by charging the catalyst about 1 wt % of synthesized iron nanoparticles (relative to castor oil weight) and the reaction was carried out for a period of 2 hrs at 400 rpm. After the completion of the reaction, the mixture was cooled to the room temperature and transferred into a separating funnel. The crude fatty acid methyl esters (FAME) and glycerol was allowed to settle for overnight. The top layer of crude biodiesel was separated and the excess methanol was removed using rotary vacuum evaporator (Model No.IKV RV-10 automatic)

2.4 Characterization of vegetable oil and biodiesel: Fourier Transform Infrared Spectroscopy (FTIR) was carried out using PERKIN – ELMER instrument to identify the functional groups of castor oil and biodiesel. The following physico-chemical properties including specific gravity (Hydrometer), kinematic viscosity (Oswald U-tube viscometer), flash point (AutomaticFlash point open cup apparatus), cloud point (Cloud point apparatus), carbon residue (Muffle furnace),refractive index (Refractometer) and calorific value (IKA : C200-Bomb calorimeter)were performed for the castor oil and produced biodiesel. In addition, acid value and saponification values were analyzed for the castor oil using standardized potassium hydroxide solution. Copper strip corrosion test was carried out for obtained biodiesel. All the physico-chemical properties were determined as per the methods of American Standards for Testing Material (ASTM) and the obtained values were compared with the biodiesel specification as per ASTM D6751.

3. RESULTS AND DISCUSSION

3.1 Fourier Transform Infrared Spectroscopy (FTIR) Analysis: The observed bands in both castor oil and biodiesel spectra are hydroxyl group (OH), C-C and vC (=O)-O. The band at 3396 cm^{-1}in castor oil and 3395 cm^{-1} in biodiesel represent the hydroxyl group (OH). The bands at 1400and1572cm^{-1} in castor oil and 1403and 1575 cm^{-1}in biodiesel indicate the presence of C-C stretching. The band at 1263 cm^{-1} in castor oil and 1244cm^{-1}in biodiesel represent the presence of υC(=O)-O. The observed band at 1457 $cm^{-1}$for methyl group and 1162 $cm^{-1}$for ester group revealed the formation of biodiesel (Figure.1). Similar peak was also observed by Yab et al., (2011).The presence of two groups namely methyl (CH_3) and ester (C-O ester) in biodiesel indicated that the transesterification of castor oil occurred due to the addition of methanol and iron nanoparticles.

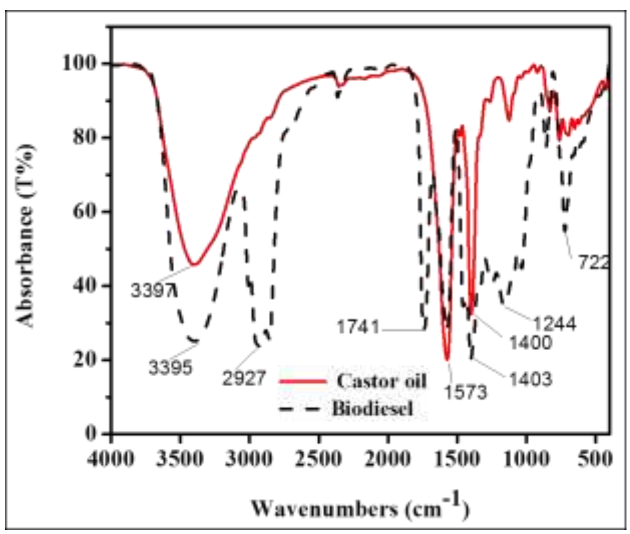

Figure.1. FT-IR Spectra for Castor oil and produced Biodiesel

3.2. Physico-chemical properties of vegetable oil and biodiesel: The measured physio-chemical properties including acid value, saponification value, specific gravity, kinematic viscosity, flash point, cloud point, carbon residue, refractive index and calorific value are used to express the quality of the castor oil and biodiesel. Table.1. represents the properties of the castor oil determined as per ASTM standards. The fuel properties of produced biodiesel (castor 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. Also, the results obtained in this study were compared with the biodiesel produced by conventional acid/base catalyst and the results are tabulated in Table 3. It was noted that the quality of produced biodiesel was superior in terms of specific gravity, kinematic viscosity, flash point, calorific value and carbon residue when compared to the literature values.

Table 1. Physical and chemical properties of castor oil

Sl.No	Physico-chemical properties	Units	ASTM test method	Castor oil
1	Color	-	Visual	Light Reddish Yellow
2	Specific gravity at 40ºC	-	D 1298	0.960
3	Kinematic viscosity at 40°C	mm^2/s	D 445	224
4	Acid value	mg KOH/gm	D 93	2.63
5	Sponification value	mg KOH/gm	D 94	173.4
6	Flash point	°C	D 92	286
7	Cloud point	°C	D2709	14
8	Carbon residue	% mass	D130	-
9	Refractive index	-	-	1.479
10	Calorific value	cal/gm	P6	7686

Table. 2. Fuel properties of produced biodiesel from castor oil using iron nanoparticles and ASTM specification

Physico-chemical properties	ASTM test method	Biodiesel specification as per ASTM D6751	Values of produced biodiesel
Specific gravity at 40 °C	D4052	0.81-0.90	0.914
Kinematic viscosity at 40 °C (mm^2/s)	D445	1.9-6.0	9.8
Flash point (°C)	D93	≥ 130	185
Cloud point (°C)	D 97	-3 to 12	6
Water content (% vol)	D2709	≤ 0.05	0.17
Carbon residue (% mass)	D 524	≤ 0.05	0.042
Refractive index	-	-	1.46
Copper strip Corrosion	D 130	No.3 max.	1a
Calorific value (cal/gm)	P 6	-	9295

Table 3, Comparison of fuel properties of produced castor oil biodiesel using iron nanocatalyst with the conventional catalysts

Type of catalyst	Specific gravity at 40 °C	Kin.visco at 40 °C (mm^2/s)	Flash point (°C)	Cloud point (°C)	Calorific value MJ/Kg (cal/gm)	Ref
CH_3OH	0.917	14.85	205	-	-	Encinar et al., (2010)
KOH	0.910	10.75	160	-13	(7074)	Okullo et al., (2012)
NaOH	0.888	4.74	147.4	-1.7	-	Efeovbokhan et al., (2012)
NaOH	0.925	24	200	-	37500 (8963)	Sreenivas et al.,
NaOH	0.927	15.98	190.7	-45	37908 (9060)	Ingle et al., (2010)
NaOH	0.928	13.75	120	3	-	Mohamed et al., (2008)
Acid +Base	0.94	26	191	-	38500 (9202)	Babu PS et al., (2011)
Iron Nanoparticles	0.914	9.8	185	6	(9295)	Present study

3.2.1. Specific gravity: The specific gravity is a key fuel property, which affects the mass of fuel injected into the combustion chamber. This property directly affects the engine performance characteristic because the fuel injection pump meter works on by volume not by mass. The specific gravity of castor oil was found to be 0.960 (Table 1). After transesterification process, the specific gravity was reduced to 0.914. The obtained value is slightly greater than the specification of biodiesel standard ASTM D6751 (Table 2). A similar result was observed by Encinar et al., (2010) who found that, the specific gravity of castor oil biodiesel was 0.917 (Table 3) with 1 wt% of potassium methoxide as catalyst. 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.

3.2.2. Kinematic viscosity: Kinematic viscosity is the most important property of biodiesel because it affects the fluidity, lubricity and atomization of the fuel. Fuels with low viscosity may not provide sufficient lubrication resulting in wear and high viscosity causes poor combustion and increases exhaust emission. The kinematic viscosity of the castor oil was about 224 mm^2/s at 40 ^oC (Table 1), whereas the viscosity of produced biodiesel was about 9.8mm^2/s. After 95.6% reduction achieved in kinematic viscosity by transesterification reaction, the obtained results are not matched with the limits as per standard (1.9-6.0 mm^2/s, Table 2). The similar kinematic viscosity values of 14.85 and 24.0mm^2/s were observed by Encinar et al., (2010) and Sreenivas et al., (2011) respectively (Table 3). Besides, the kinematic viscosity of the conventional diesel ranges from 2 to 4.5 mm^2/s at 40 ^oC. Thus it can be concluded that the viscosity of produced biodiesel is not similar to both the conventional diesel and biodiesel standard ASTM D6751. The reason for the higher viscosity of the castor oil biodiesel is due to the presence of hydroxyl group in its 12^{th} carbon molecular structure, as reported by Deshpande, (2012).Hence, the produced biodiesel may be used as fuel by adding additives in existing diesel engine without any design modification.

3.2.3. Flash point: The flash point is the minimum temperature at which fuel gives momentary flash on ignition under specified test conditions. It is an important parameter for storage, handling and safety of the fuel. The flash point of the produced biodiesel was about 185°C (Table 2), whereas the flash point of castor oil was about 286°C (Table 1). This value is much higher than that of the minimum requirement of 130 ^oC as indicated in the ASTM standard. The similar flash point values of 205^oC and 200^oC were obtained by Encinar et al., (2010) and Sreenivas et al., (2012) respectively (Table 3). The minimum value of flash point for conventional diesel fuel is about 35 ^oC. Based on the results, the produced biodiesel was considered to be safe for storage and handling purposes when compared to the conventional diesel.

3.2.4. 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 under prescribed conditions. The cloud point of vegetable oil and biodiesel produced in the present study was about 14^oC and 6^o C, respectively (Tables 1 and 2). The observed value of biodiesel matches with the specifications of ASTM. Mohamed, (2008) observed that the cloud point for castor oil biodiesel produced using acid/ base catalyst was3 ^oC. The cloud point of conventional diesel fuel is between -10 and -15 ^oC. 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. To overcome this problem, the suitable additives can be used.

3.2.5. Carbon residue: Carbon residue is an indication of carbon depositing tendencies of the fuel in diesel engine. The carbon residue of castor oil and biodiesel produced in the present study was about 0.095 and 0.042wt%, respectively (Tables 1 and 2). The obtained result agrees well with the specifications of biodiesel standard ASTM D6751. The carbon residue 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 castor 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.

3.2.6. Calorific value: Calorific value is the ability of heat generated by the unit mass of fuel. The calorific value of castor oil and the produced biodiesel were reported as 7686 cal/gm and 9295cal/gm respectively. The similar result was observed by Babuand and Mamila, (2008) and Ingle, (2012) for calorific value of biodiesel from castor oil.

3.2.7. Copper strip corrosion: The copper corrosion test was carried out at 50 ^oC for a period of 3 hrs. The value of copper corrosion test for the produced biodiesel was found to be 1a (Slightly Tarnish). The results revealed that the quality of obtained biodiesel was observed to be superior, when compared to the conventional diesel and hence, it may lead to good resistance for copper corrosion. The refractive index of the produced biodiesel and castor oil was 1.460 and 1.479, respectively. The similar result was observed by Mohamed, (2008) for refractive index.

4. CONCLUSIONS

The production of biodiesel from castor oil with methanol was successfully conducted using iron nanoparticles as catalyst. The properties of resulting castor oil biodiesel agree well with the specifications of biodiesel standards ASTM D6751 except for specific gravity kinematic viscosity. Most of the physico-chemical properties of castor oil biodiesel match well with the normal diesel. The use of iron nanoparticles as catalyst showed more advantageous than the conventional acid/base catalyst for the production of biodiesel. Hence, the produced biodiesel can be considered as an alternative to the conventional diesel.

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