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Synthesis of biodiesel from pongamia oil using heterogeneous ion-exchange resin catalyst

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ABSTRACT

Biodiesel is a clean-burning renewable substitute fuel for petroleum. Biodiesel could be effectively produced by transesterification reaction of triglycerides of vegetable oils with short-chain alcohols in the presence of homogeneous or heterogeneous catalysts. Conventionally, biodiesel manufacturing processes employ strong acids or bases as catalysts. But, separation of the catalyst and the by-product glycerol from the product ester is too expensive to justify the product use as an automobile fuel. Hence heterogeneous catalysts are preferred. In this study, transesterification of pongamia oil with ethanol was performed using a solid ion-exchange resin catalyst. It is a macro porous strongly basic anion exchange resin. The process parameters affecting the ethyl ester yield were investigated. The reaction conditions were optimized for the maximum yield of fatty acid ethyl ester (FAEE) of pongamia oil. The properties of FAEE were compared with accepted standards of biodiesel. Engine performance was also studied with pongamia oil diesel blend and engine emission characteristics were observed.

1. Introduction

Diesel and petrol are considered as main commodities; they play a dynamic role in the socio-economic development of India. Uncertainty about their resources can influence the economy. In order to decrease this uncertainty it is essential to plan and use the resources judiciously. Diesel was mainly consumed for the road transport, agriculture, industry and power generation sectors. India is the fourth largest crude oil consumer among the world countries in 2013. In 2012–2013 India consumed 157.1 MMT which was 6.0% higher than the 2011–2012 consumption. Net oil import dependency rose from 43% in 1990 to an estimated 71% in 2012. In the year 2012–2013 India imported 184.8 MMT of crude oil as against 171.7 MMT during 2011–2012. Among all the crude oil products diesel was consumed more than of 50% when compared with the other crude oil products. The total consumption of diesel accounted for 43.98%. India's diesel demand is likely to grow by about 5.5% for every year. Diesel accounts for about 40% demand of all refined oil products in India.

In India, fuel consumption is doubled in every ten years, since 1980. India is one of the major emitters of atmospheric pollutants. These days clean fuel technology is being given more impetus owing to the prevailing fuel crisis and related pollution (Singh et al., 2012a, 2012b 2012c, 2014a, 2014b, 2013a, 2013b, in press). Recent survey reveals that by 2017, 20% of energy needs of India should be met by biodiesel (Das and Priess 2011). To meet this expectation it would require 12–13 million ha of biodiesel feed stock plantation.

As per the government policy of India, biodiesel is to be produced using non-edible oil only (MNRE, 2011). Oil of *Pongamia pinnata* (Legumnosae; Pappilonaceae) is one of the promising non-edible oil of Indian origin. It is found mainly in the native Western Ghats in India, northern Australia, Fiji and in some regions of Eastern Asia (Srinivasa, 2001). The oil content of the kernel is 30–40%. The oil contains primarily eight fatty acids *viz.* palmitic, stearic, oleic, linoleic, lignoceric, eicosenoic, arachidic and behenic (Karmee and Chadha, 2005). Of these, the four which are commonly found in most oils, including pongamia are the saturated acids, palmitic (Hexadecanoic acid) and stearic (Octadecanoic acid) and the unsaturated acids, oleic (Octadec-9-enoic acid) and linoleic (9,12-Octadecadienoic acid). This dark brown oil has a repulsive odour and possesses fungicidal properties.

Biodiesel is usually obtained from transesterification of triglycerides with methanol or ethanol in the presence of an activated catalyst to improve the reaction rate. Homogeneous base catalysts such as potassium hydroxide, sodium hydroxide, potassium methoxide and sodium methoxide are most frequently used in the industrial process to produce biodiesel due to their high catalytic activities (Kucek et al., 2007). Homogeneous acid catalysts such as strong mineral acids or p-toluene sulphonic acids are used (Liu

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and Wang, 2009). However, in the transesterification catalyzed by homogeneous catalyst, the vegetable oil should have an acid value less than one and all the materials should be substantially anhydrous (Sasidharan and Kumar, 2004). Furthermore, undesired side reaction, saponification occurs and an extra step is adopted to remove the homogeneous catalysts, thus resulting in high cost of production. The use of heterogeneous catalysts such as zeolites and ion-exchange resins, on the other hand, have clear advantages as they are non-corrosive and are easily separated from the reaction mixture and no washing of the ester is required (Hamer and Sun, 2001).

Ion-exchange resins are convenient catalysts for etherification, esterification, and transesterification reactions and have a large number of applications (Kitakawa et al., 2007). They have a greater potential than the lipase enzyme and supercritical alcohol from the economic point of view. Symmetrical dicarboxylic acids with 4–14 carbon atoms gave selective monoesters in high yields in esterification reactions catalyzed by strongly acidic ion-exchange resins (Kafuku and Barawa, 2010). The anionic basic resins are active at low temperatures and owing to their molecular sieve action, produce fewer by-products (Sun et al., 2014). It has been reported that anion-exchange resins exhibit much higher catalytic activities than the cation-exchange resin in the transesterification of triolein with ethanol (Noureddini et al., 1998).

The objective of this work is to conduct the transesterification of pongamia oil with ethanol using a strongly basic anionic resin Indion 810 at optimum reaction conditions. The properties of resulting fatty acid ethyl ester were compared with diesel fuel. Performance of pongamia oil diesel blend (PO10D) was studied in a 4 stroke diesel engine along with its emission characteristics.

2. Materials and methods

2.1. Catalyst

Indion 810 was used as a catalyst. It is a macro porous strongly basic anion exchange resin. It has a high capacity with a cross linked polystyrene matrix and quaternary ammonium functional groups. It gives a higher operating exchange capacity due to greater utilization of the exchange sites as compared to other conventional macro porous resins. This feature combined with its high basicity, permits adsorption of large sized soluble organic molecules and their subsequent elution during regeneration. Table 1 shows the important characteristics of this anionic resin (Oguzhan, 2011).

2.2. Transesterification

The anionic resin was in the chloride form and it was pretreated with 1 M Sodium hydroxide solution to displace chloride ions with hydroxyl ions and then washed with distilled water followed by ethanol. All the experiments were performed in a 250 ml three-necked round bottom flask heated on a thermostat equipped with a reflux condenser and a digital speed controlled mechanical stirrer. The oil sample was taken in the round bottomed flask and preheated to remove the water present in the oil. It is then cooled to room temperature. A mixture of ethanol and oil in a specific molar ratio was weighed and poured into the reactor (Feng et al., 2010). The mixture was heated to the required temperature then a known amount of catalyst was charged and stirring was started to initiate the reaction. After several hours, the reaction mixture was cooled and the catalyst was separated by filtration. The filtrate was allowed to settle down and kept overnight for the separation of biodiesel and glycerol layer. The oil phase consisted of ethyl esters and unreacted triglycerides, while the aqueous phase mainly contained ethanol and glycerol (Encinar et al., 2010).

Table 1
Characteristics of anion-exchange resin.

Characteristics	Indion 810
Appearance	Opaque beads
Matrix	Styrene divinyl benzene copolymer
Functional groups	$-N^+ (CH_3)_3$
Ionic form as supplied	Chloride
Total exchange capacity	1.0 meq/ml, minimum
Moisture holding capacity	56–63%
Shipping weight	640–700 kg/m^3
Particle size distribution	0.3–1.2 mm
Uniformity coefficient	1.7 maximum
Effective size	0.40–0.50 mm
Reversible Swelling	Cl^- to OH^- 15% to 20%

2.3. Fuel analysis

A JEOL Gas Chromatograph system equipped with double-focusing mass spectrometer, JMS-700 (JEOL ltd., Tokyo, Japan) was used for the analysis of sample to determine the composition of the fatty acid ethyl esters. The column was CP-Sil88 capillary column (60 m × 0.25 mm, 0.1 μm) with Helium at 1.5 ml min^{-1} as carrier gas. Samples (1 μl) were injected by a sampler at an oven temperature of 160°C. After an isothermal period of 2 min, the system oven was heated at 5–240 °C and held for 10 min to ensure that all material had eluted from the column. The injection temperature was 250 °C. The mass range of the spectrometer was set to 10–500 amu. Quantitative analysis was realized by external calibration using standard solutions of fatty acid ethyl esters (Dos Reis et al., 2005). The important fuel properties of biodiesel were determined using ASTM (D6751) (Selvan et al., 2013).

2.4. Performance of pongamia oil 100 (PO10D) in four stroke diesel engine

The experimental set up consists of a single cylinder four-stroke, water-cooled and constant-speed (1500 rpm) compression ignition engine. The detailed specification of the engine is given in Table 2a. The engine is equipped with a DC swinging field generator and a salt-water rheostat in order to apply the required load. An exhaust gas analyser, model DIGAS 444 is coupled to this engine for measuring the various emission parameters. The detailed specification of the analyser is given in Table 2b. During each trial, the engine was allowed to attain stable condition, and the readings were measured and the engine emission parameters like N_2, CO_2, CO, NO_x, C_xH_y and SO_2 from exhaust gas analyzer were recorded (Sureshkumara et al., 2008).

Table 2a
Diesel engine specifications.

Engine parameter	Specification
Make	Kirloskar
Engine type	4 stroke, CI, water cooled engine
Bore	8 mm
Stroke	140 mm
Compression ratio	18:1
Rated power @1500 rpm	3.75 KW
Loading type	Electrical dynamoter