Journal of Scientific and Innovative Research 2015; 4(3): 127-130
Available online at: www.jsirjournal.com

Research Article

ISSN 2320-4818
JSIR 2015; 4(3): 127-130

Received: 29-04-2015
Accepted: 16-07-2015

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Biodiesel Conversionionof high FFA Neem oil by blending it with low FFA Sesame oil

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Abstract

Biodiesel is a clean, renewable fuel and may be considered as a potential option to supplement fossil-based fuels. It is deduced from a variety of edible and non-edible vegetable oils, animal fats, waste cooking oil and animal fat, etc. Non-edible vegetable oils are second generation feedstocks and a better alternative to edible feed crops for biodiesel production.This paper deals with production of Biodiesel from the oils of Sesame (*Sesamum indicum* L.) and Neem (*Azadirachta indica*) which are available in India and other parts of the world. Neem oil is non edible oil having very high free fatty acid (FFA) content. It requires pre-treatment neutralization step before undergoing the alkali catalyzed transesterification process, very high alcohol to oil molar ratio and comparatively larger reaction time needed to obtain sustainable yield of biodiesel. Sesame oil is an edible oil mainly used in pharmaceuticals due to its medicinal properties and has low FFA content. These two oils, one having very high FFA content and other having low FFA content are mixed in suitable proportions and this mixture is transesterified without the pre-treatment process at a molar ratio of 6:1. A significant conversion yield is achieved by mixing the feedstocks before transesterification reaction.

Keywords: Neem oil, Sesame oil, Free Fatty Acid, Transesterification

Introduction

The scarcity of world petroleum reserves, their uneven distribution, growing emissions of combustion-generated pollutants, uncertainties in its supply, rising prices and dramatic increase in an energy demand due to rapid industrialization may lead to severe energy crisis in near future[1]. A major part of the energy demand (about 88.6%) is fulfilled by fossil fuels, in which crude oil accounts for 33.7% [2]. With consumption rates of 4 billion tonnes a year, the oil deposits will be exhausted by 2052[3]. Biodiesel is the mixture of mono alkyl esters of long chain fatty acids, suitable for use in compression ignition engines[4]. The plant oils usually contain free fatty acids, phospholipids, sterols, water, odorants and other impurities. Due to these the oil cannot be used as fuel directly. To overcome these problems the oil requires slight chemical modification through transesterification, pyrolysis and emulsification[5]. Unlike fossil fuel, biodiesel contains a significant amount of oxygen in its molecular structure which helps in speeding up the combustion of fuel in compression ignition engines, resulting decrement in the emission of carbon monoxide (CO), soot etc[6]. Presently, more than 95% of biodiesel production feedstocks comes from edible oils since they are mainly produced in many regions. The properties of biodiesel produced from these oils are much suitable to be used as a diesel fuel substitute[6-7]. However the use of edible vegetable oils may jeopardize food supplies and biodiversities. Thus, non-edible oils are considered potential substitutes of edible food crops for biodiesel production[8]. A two-step transesterification process and longer time are required for transesterification of nonedible oils containing high FFA content.

Transesterification reaction is shown in Eq. (1). The catalysts used in transesterification reaction are mainly of three types: alkalis, acids and enzymes[9-11]. Due to faster transesterification reaction, less corrosive action of an alkaline catalyst to industrial equipment and requirement of low methanol to oil molar ratio, most commercial transesterification reactions are carried with alkali catalyst[12-13]. However, alkali catalysts have limitation for high FFA containing oils leading to soap formation, higher consumption of the catalyst and reduction in biodiesel yield[14]. The typical soap formation (saponification) reaction with alkali catalyst NaOH is shown in Eq. (2). Moreover, the alkali catalysts are highly hygroscopic and absorbs water from air during storage. Water is also formed during the

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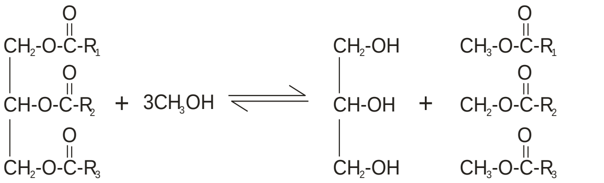
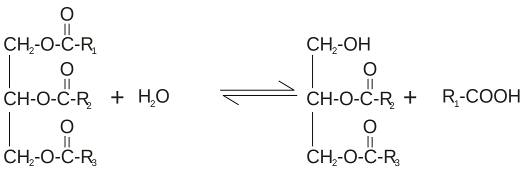
saponification reaction. Water retards the transesterification reaction through the hydrolysis reaction. It can hydrolyze the triglycerides to diglycerides and forms more FFA[14-15]. The typical hydrolysis reaction is shown in Eq. (3). Acid catalyst directly converts free fatty acid present in raw vegetable oils into biodiesel avoiding undesirable saponification reaction as shown in Eq. (4).

Non edible oil (containing high fatty acids more than 2.5%) is first neutralized in the presence of an acid and then undergoes alkali catalyzed transesterification reaction. Even after pre-treatment or neutralization of free fatty acids, the yield of biodiesel produced from high FFA oils is comparatively much less than that for biodiesel produced from oils with low FFA content. Figure 1 shows the flowchart of a commonly used alkali catalyzed transesterification process.



(Triglyceride) (Alcohol) (Glycerol) (Methyl esters) (1)

$$R_1COOH + NaOH \rightarrow R_1COONa + H_2O$$
(FFA) (Sodium hydroxide) (Soap) (Water) (2)



(Triglyceride) (Water) (Diglyceride) (FFA) (3)

$$R_1 - COOH + ROH \xrightarrow{H^+} R_1COONa + H_2O$$
(FFA) (Alcohol) (Soap) (Water) (4)

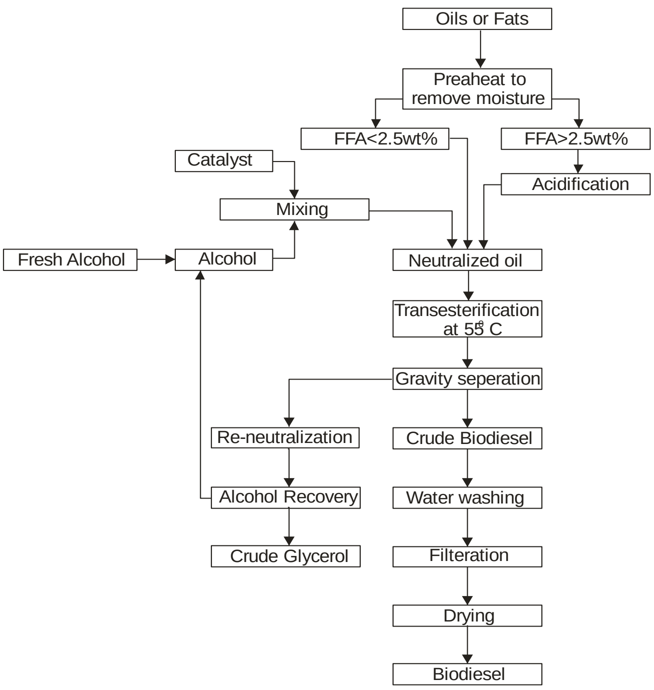


Figure 1: Process flow chart of alkali catalyzed biodiesel production

Material and Methods

Neem (*Azadirachta indica*) is a medium sized evergreen tree from the *Meliaceae* family. Neem trees are usually grown in several Asian countries and thrive well in areas with sub-arid to sub-humid conditions and with an annual rainfall of 400-1200 mm. Oil is extracted mainly from seeds. Neem seeds contain 20-30 wt. % oil, and its kernel contains 40-50% brown oil[8]. Neem oil is having very high FFA content. Neem seeds are available in huge quantity, which are mainly used for medicinal purposes and a large part of it remain untapped which can be utilised for biodiesel production.

Sesame is an oilseed herbacaceous crop of the Pedliaceace family, which is widely cultivated in many parts of the world, primarily in tropical and sub-tropical parts of the world and has recently been adapted to semi arid regions [15-16]. Sesame seeds contains 57-63 wt. % oil [17]. Neem oil and Sesame oil are extracted by mechanical pressing. The fruits are collected in a drum, and the kernels are separated to obtain the seeds. The crude oil is filtered to remove impurities and obtain pure oil. The various properties of Neem oil and sesame oil were analysed by the methods described by the association of Official Analytical Chemists [18]. These properties are given in Table 1. The densities of two oils are similar and their mixture can be formed by simple mechanical stirring for 2-3 minutes.

The FFA value of oil is calculated similarly to the basis of acid-base-titration neutralization reaction except that the base is titrated against oil, instead of an acid against the base. The FFA content of neem oil and sesame oil were found to be 15.4 and 0.28 respectively. Sesame oil contains sesamin and sesaminollignans in its nonglycerol fraction, which are known to play an important role in the oxidative stability [16].

Experimental work

Experiments were carried out for molar ratio of 6:1 for 1%, 1.5% & 2% catalyst KOH by weight of oil. Each catalyst is used with 3 mixtures of Neem and sesame oil taken in ratios of 30:70, 50:50 and 70:30. The three oil mixture are heated upto 120-130 ℃ and kept at this temperature for about 5-7 minutes to remove moisture present in oil to avoid soap formation and allowed to cool upto 65°C. 22 gm methanol and KOH (1%, 1.5% and 2% weight of oil) are mixed and stirred until entire Potassium hydroxide dissolves in methanol. This liquid mixture is then mixed with oil in a beaker placed on a hot plate of mechanical stirrer and the temperature of sample is maintained around 550C during the reaction time period of 30 min, 45min, 60 min and 75 min. A magnetic capsule is dipped in the mixture and rotated with the help of mechanical stirrer. After completing the process of mechanical stirring, the sample is poured into a separation flask for 2-3 hour for the separation. Methyl esters were separated from glycerol by means of gravity separation and finally water washed to remove soap and residual catalyst to obtain pure biodiesel. The properties of biodiesel so obtained for different mixture ratios along with properties of diesel are given in table 1.

Table 1: Properties of Raw oil, Biodiesel and Diesel

Property	Neem oil	Seasme oil	Acceptable limit for diesel engine	Diesel	Biodiesel N:S(30:70)	Biodiesel N:S(50:50)	Biodiesel N:S(70:30)
Fuel standard	ASTM D 6751	ASTM D 6751	-	ASTM D 975	ASTM D 6751	ASTM D 6751	ASTM D 6751
Density at 15°C(kg/m^3)	961	923	860-900	830	889	894	898
Viscosity at 40°C x10^{-6} (m^2/s)	22.75	39.97	2.5-6	2.86	4.56	4.64	4.78
Calorific value (MJ/kg)	35.90	40.20	-	42	38.20	37.98	37.85
Sulphur content (ppm)	88	75	Max 350	350	86	82	76
Flash Point (°C)	259	230	Min 100	51	208	204	202

Results

Figure 2 shows biodiesel yield from neem oil, sesame oil and their mixtures in different proportions at 2%, 1.5 % and 1 % catalyst concentration. The yield of biodiesel from these samples were calculated at reaction time periods of 30 min, 45min, 60 min and 75 min at 6:1 alcohol to oil molar ratio.

2% Catalyst

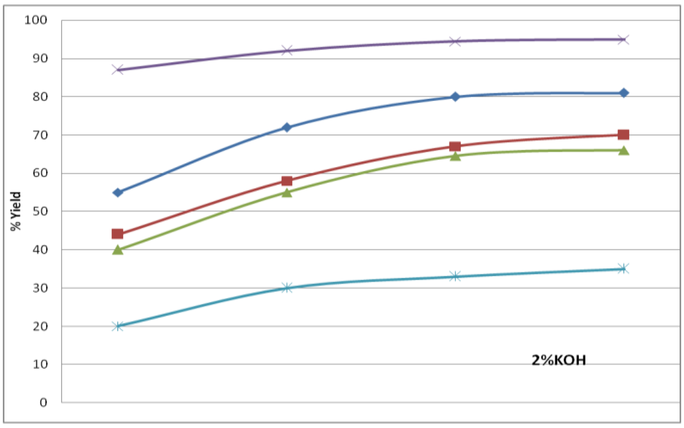
Variation of % yield achieves a linear trend with increase in reaction time and almost maximum yields were obtained at 75 minutes of reaction time for all blends. Biodiesel yield for pure sesame oil (95%) was approximately 63% higher than that for pure neem oil, 30.5 % than that for 70:30 mixture of Neem and Sesame oil, 26.3% than that for 50:50 mixture of Neem and Sesame oil and 14.7% than that for 30:70 mixture of Neem and Sesame oil.

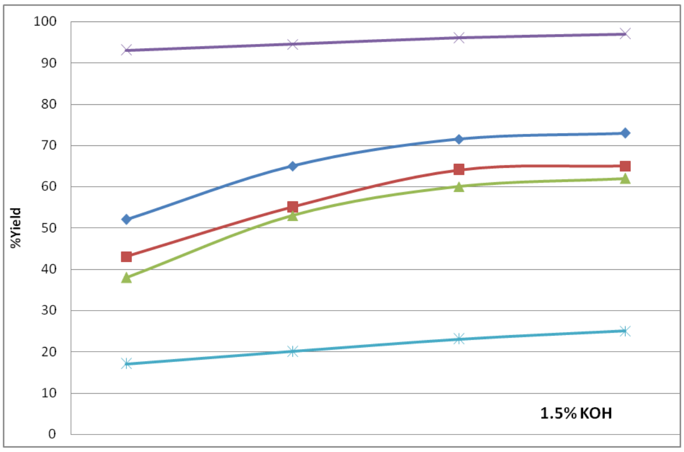
1.5 %Catalyst

Variation of % yield achieves a linear trend with increase in reaction time and almost maximum yields were obtained at 75 minutes of reaction time for all blends. Biodiesel yield for pure sesame oil (97%) was approximately 74.2% higher than that for pure neem oil, 36 % than that for 70:30 mixture of Neem and Sesame oil, 33% than that for 50:50 mixture of Neem and Sesame oil and 23.1% than that for 30:70 mixture of Neem and Sesame oil.

1% Catalyst

Variation of % yield achieves a linear trend with increase in reaction time and almost maximum yields were obtained at 75 minutes of reaction time for all the blends. Biodiesel yield for pure sesame oil (99%) was approximately 52.5% higher than that for pure neem oil, 30.5 % than that for 70:30 mixture of Neem and Sesame oil, 44.4% than that for 50:50 mixture of Neem and Sesame oil and 30.3% than that for 30:70 mixture of Neem and Sesame oil.





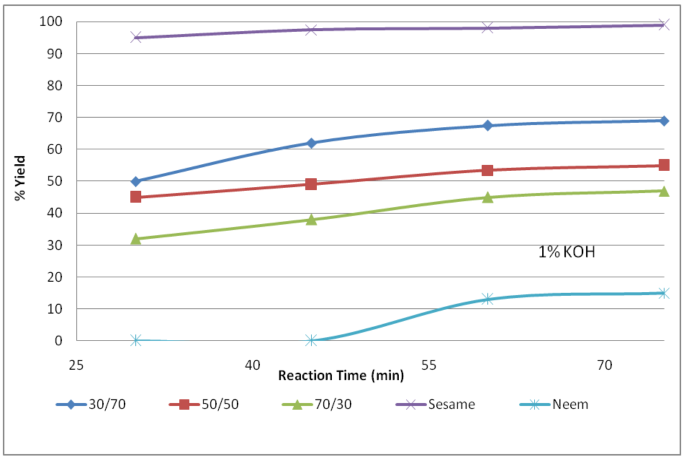


Figure 2: % yield of Biodiesel Production

Discussion

Neem oil and the 3 oil mixtures have high FFA content and the yield of biodiesel produced from the blends increases with increase in catalyst concentration. However Sesame oil has very low FFA content its biodiesel obtained is maximum (upto 99%) for 1 % catalyst and the yield progressively decreases with increase in catalyst concentration. A maximum of 81 % yield is obtained with 30:70 Neem and Sesame oil mixture in single step transesterification reaction with 2% catalyst concentration as shown in figure 3. This is well above 50.78% yield obtained for pure neem oil in two step transesterification rection carried by Mazloom Shah[19]. A statistical model predicted the highest conversion yield of sesame oil to biodiesel as 99.71% and actual yield was 98.36% in an experiment conducted by Eriola Betiku[20].

Conclusion

Mixing of two oils, one with low FFA content (Sesame) and one with high FFA content (Neem) results in a mixture of moderate FFA content. Appreciable yields of biodiesel is obtained from the mixture in one step transesterification reaction. Approximately 81 % biodiesel was obtained with 30:70 ratio of Neem and Sesame oil at 75 minute reaction time with 2 % catalyst concentration at 6:1 alcohol to oil molar ratio. Thus, high FFA non edible oils can be easily converted into biodiesel with a Low FFA oil. This method may prove to be economic and environmental friendly, requiring lower reaction time and low catalyst concentration and simultaneously eliminating the need for pre-treatment process.

Acknowledgment

Authors are thankful to the Delhi Technological University and Goverment of Delhi for financing the lab infrastructure and materials.

Conflict of interest

There is no conflict of interest involved in this work.

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