Research Journal of Recent Sciences ______________________________ ISSN 2277-2502
Vol. **2(ISC-2012),** 223-228 **(2013)** *Res.J.Recent.Sci.*

Production of Neem Oil Methyl Ester (NOME) from Oscillatory Baffled Reactor

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Available online at: www.isca.in
Received 6th October 2012, revised 26th December 2012, accepted 18th January 2013

Abstract

The depleting petroleum reservoir, concern for environment or climate leads to many researches to search for renewable alternative source of energy. These renewable sources of energy include solar energy, Tidal energy, wind energy, Hydropower, Biomass and Biofuels. Among the different possible renewable sources one such alternative is produced by transesterification of vegetable oil with methanol in presence of catalyst (alkali and acid) in Convensional Batch Reactor. In our study the preparation of Neem Oil Methyl Ester (NOME) were carried out by varying different parameters like oil/alcohol molar ratio, reaction time, concentration of acid and base catalysts. Fatty Acid Methyl Ester produced by using Oscillatory Baffled Reactor 1-2% H_2SO_4, 1:9 oil/alcohol ratio, 10-15min reaction time, 25-30ºC temperature.

Keywords: Transesterification, Biodiesel, Neem Oil, Methanol, Oscillatory Baffled Reactor.

Introduction

Biodiesel is a liquid fuel similar to petroleum diesel in combustion properties, but essentially free of sulphur, making it a cleaner burning fuel than diesel. Biodiesel is derived from renewable energy sources, such as vegetable oils and animal fats. It has similar physical and chemical properties with petro-diesel fuel. However, biodiesel properties can sometimes be superior to that of petrodiesel fuel because the former has higher flash point, ultra-low sulphur concentration, better lubricating efficiency, and better cetane number.

The depletion of world petroleum reserves, the instability of petroleum sources, recent increase in petroleum prices and uncertainties concerning petroleum availability have generated interest in vegetable oil fuels for diesel engines. Biodiesel is a promising non-toxic and biodegradable renewable fuel comprised of mono-alkyl esters of long chain fatty acids, which is produced by a catalytic transesterification reaction of vegetable oils with short-chain alcohols. Biodiesel has become an interesting alternative to diesel, because it has similar properties to the traditional fossil diesel fuel and may thus substitute diesel fuel with none or very minor engine modification. Biodiesel is oxygenated and essentially free of sulfur making it a cleaner burning fuel than petroleum diesel with reduced emissions of SOx, CO, unburnt hydrocarbons and particulate matter.

Biodiesel is gaining more and more importance as an attractive fuel due to the depleting fossil fuel Resources. The use of vegetable oils as alternative fuels has been around for 100 years when the inventor of the diesel engine Rudolph Diesel first tested peanut oil, in his compression ignition engine. The renewable energy sources such as biomass, hydro, wind, solar, geothermal, marine, and hydrogen will play an important role in the future. Table1 shows potential and production of renewable energy sources in India.

In the U.S., research in biodiesel has taken place at various laboratories and universities. Some of the defining work on biodiesel kinetics took place at US Department of Agriculture. Iowa State University has led in establishing production standards and methods especially for methyl esters, while the production and testing of ethyl esters has been the province of Idaho State University.

Mostly biodiesel is prepared from edible oil soybean, rapeseed, palm; few attempts have been made of producing biodiesel from non edible oil such as neem oil, karanja, babssu, jatropha and tobacco seed oil. Jatropha curcus and pungama pinnata, (karanja) can be cultivated on any type of soil. The cultivation of these plants is easier and plants have high oil content (25-30%).

Most biodiesel is produced by the transesterification of triglycerides of oils using methanol and an alkaline catalyst (NaOH, NaOMe). The reaction is normally performed at 60–80 °C. The glycerol and FAME are separated by settling after catalyst neutralization. The crude glycerol and biodiesel obtained are then purified.

The production of biodiesel is greatly increasing due to its environmental benefits. However, production costs are still rather high, compared to petroleum-based diesel fuel[1]. Ecological, political and economic concerns over petro diesel, which is the single largest industry in terms of dollar value on earth, are the drivers behind biodiesel production from edible/

non-edible oils and fats. Although the growth rate of plantations for vegetable oil is expanding, much of it is due to oil palm at 5% per year. The reactions for direct transformation of vegetable oils into methyl esters and glycerol have been known for more than a century.

Biodiesel (a mixture of fatty acid methyl esters, FAMEs) has become very attractive as a biofuel because of its environmental benefits as it has less air pollutants per net energy than diesel and is nontoxic and biodegradables because it is produced from renewable sources with high energetic efficiency, biodiesel yields from an estimated 90% to 40% more energy than the energy invested in producing it.

In this paper discussion is made on production of biodiesel in oscillatory baffled reactor. Oscillatory baffled reactors are used in biodiesel production, it consisting of tube containing equally spaced orifice plate baffles. An oscillatory motion is superimposed upon the net flow of the process fluid, creating flow patterns conducive to efficient heat and mass transfer, whilst maintaining plug flow.

Material and methods

Apparatus and experimental setup: Oscillatory baffled reactors (OBR reactors) are a novel type of reactor, consisting of tubes containing equally spaced orifice plate baffles (Figure 10). OBR reactors exploit the uniform and efficient vortex mixing that can be achieved when an oscillatory fluid motion interacts with orifice plate baffles in a tube.

Many advantages have been characterized for oscillatory baffled reactors, such as enhanced heat and mass transfer, efficient dispersion for immiscible fluids, uniform particle suspension, Gas-in-liquid dispersions and multiphase mixing, both batch and continuous modes of operation are accommodated.

An oscillatory motion is superimposed upon the net flow of the process fluid, creating flow patterns conducive to efficient heat and mass transfer, whilst maintaining plug flow.

Unlike conventional plug flow reactors, where a minimum Reynolds number must be maintained, the degree of mixing is independent of the net flow, allowing long residence times to be achieved in a reactor of greatly reduced length-to-diameter ratio.

Many long residence time processes are currently performed in batch, as conventional designs of plug flow reactor prove to be impractical due to their high length-to-diameter ratios, which lead to problems such as high capital cost, large "footprint", high pumping costs and, also control is difficult. The OFR allows these processes to be converted to continuous, thereby intensifying the process.

The transesterification of various natural oils to form biodiesel is a long reaction, usually performed in batch. Conversion to continuous processing should improve the economics of the process, as the improved mixing should generate a better product (rendering the downstream separation processes easier), at lower residence time (reduction in reactor volume). These improvements can decrease the price of biodiesel, making it a more realistic competitor to petro-diesel.

The mechanism of mixing in the OFR is illustrated (figure 11) in which shows two half cycles over an oscillation period. Vortices are formed behind baffles on an upstroke, drawing fluid from near the walls into the Eddie . On the reverse stroke, the vortices formed are pushed into the central region of the device while new vortices are generated at the same time behind the opposite baffles, and the cycle repeats. This provides an effective way to move fluid from the wall of the device to the centre, and leads to the axial velocity components being of the same order of magnitude as the radial ones.

Experimental Procedure: The acid value of Neem oil is very high, a two step process, i.e., acid catalyzed esterification followed by based- catalyzed transesterification process is needed for converting it into methyl ester. The first step is acid catalyzed esterification is for the reduction of acid value, which is mainly a pretreatment process. The process used sulphuric acid as acid catalyst. Once the acid value of Neem oil reduces to the base catalyst transesterification is applied to get biodiesel.

Neem oil is contaminated with water and solid particles. Solid portion and water content of Neem oil is removed by filtering using a filter paper. This step is conducted twice to ensure complete removal of water. Then the Neem oil is processed through two step process.

Pre-treatment Step: Esterification- First the oil and methanol are reacted in molar ratio of 1:9 with sulfuric acid as a catalyst. After reaction mixture is settled for 6-8 hours, two layers are formed and the layers are separated, the upper layer is treated oil which is tasted for its acid value, after separating the layers, acid value of treated layer is measured, it comes out to be considerable. Otherwise further esterification is to be carried out with sulfuric acid. Now oil was ready for transesterification.

Transestrification: The treated oil is reacted with methanol in presence of base catalyst NaOH by varying the oil–methanol molar ratio and catalyst concentrations. The mixture of NaOH with methanol is added into the reactor along with the oil and oscillations are started. The transesterification reaction takes place giving two distinct layers i.e. glycerol layer and methyl ester Layer. Upper layer of methyl ester is separated and is preserved for further treatment. Two layers are formed.

Physicochemical analysis: The oil was analyzed for some physicochemical properties like iodine value, saponification value, acid value.

Characterization of biodiesel: The characterization of the biodiesel was carried out[7]. The density and the viscosity were measured at room temperature using the density bottle and the

Ostwald Direct Flow (BS/U), respectively. The parameters are determined with the standard methods. Table 2 shows the Physicochemical Properties of Neem Oil.

Results and Discussion

Neem oil batch oscillatory flow reactor: In this topic, effect of various parameters like feed to methanol ratio, concentration of catalyst on quality of biodiesel produced in terms of kinematic viscosity, density and acid value are discussed for feedstock namely Neem oil in a oscillatory flow reactor operated in a batch mode.

Effect of molar ratio on properties of bio-diesel: Runs carried out with increasing mole ratio of oil to alcohol from 1:6 to 1:12 at catalyst concentration 1.0 to 3.0 vol% for 10 minutes are given. From the graph 1 it can be seen that as the mole ratio increases specific gravity decreases. In the range of mole ratio 1:6 to 1:12 gave biodiesel of decreasing viscosity from figure 2. And as the mole ratio increases acid values decreases. From the graph it was observed as for mole ratio is concerned 1:9 appears to be optimum value. Hence this mole ratio was to be chosen for study of catalyst concentration on viscosity of biodiesel.

Effect of catalyst concentration on properties of bio-diesel at mole ratio 1:9: Increasing catalyst concentration from 1 to 3 wt % at oil to alcohol mole ratio 1:9 and reaction time for 10 minutes shows variation in viscosity of biodiesel. Thus increasing catalyst concentration from 1 to 3 vol% increases the viscosity of biodiesel from 31.340 cSt to 34.595 cSt at first stage. At the second stage viscosity was decreased from 31.340 cSt to 4.260 cSt for 1 vol% catalyst concentration.

For acid value when catalyst concentration increases from 1 to 3 wt% acid value shows increasing order from 1.569 to 2.164 (mg of NaOH/gm of sample) at first stage and decrease to 0.713 (mg of NaOH/gm of sample) in the second stage for concentration 1% for oil to alcohol mole ratio 1:9 and reaction time for 10mins.

Increasing catalyst concentration from 1 to 3 wt % at oil to alcohol mole ratio 1:9 and reaction time for 10 minutes shows slight variation in density of biodiesel. In the first and second stage specific gravity shows slight increase.

Similar observations can be seen when molar ratio is increased from 1: 6 to 1 : 9 and 1 : 12.

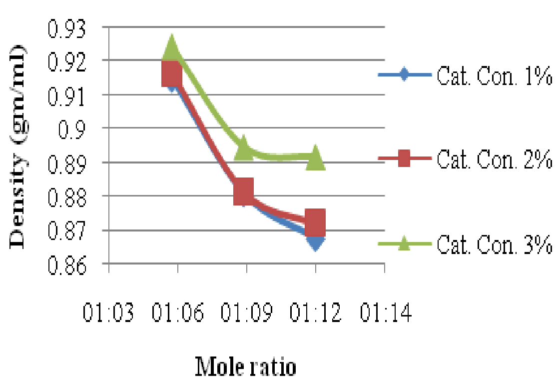

Figure-1
Effect of Density vs Molar Ratio at 1st stage

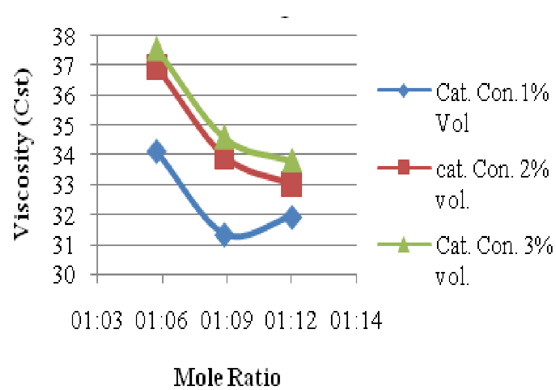

Figure -2
Effect of Viscosity vs Mole ratio at 1st stage

Table-1
Various properties of Biodiesel at first stage

Property	Oscillatory flow reactor	Batch reactor	Petroleum Diesel
Kinematic viscosity (cSt)@ (40 ^{0}C)	31.34	25.822	3.600
Density @ (30 ^{0}C)	0.8808	0.874	0.841
Acid value mg KOH /gm	1.569	2.580	___

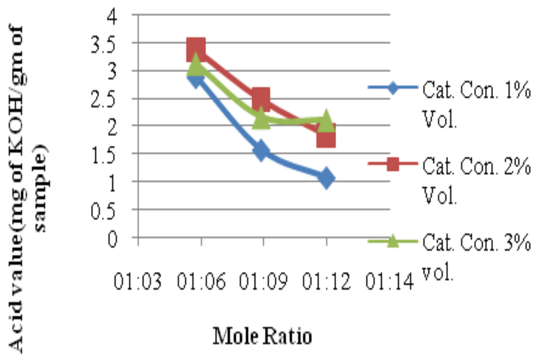

Figure-3
Effect of Acid value vs Mole Ratio 1st stage

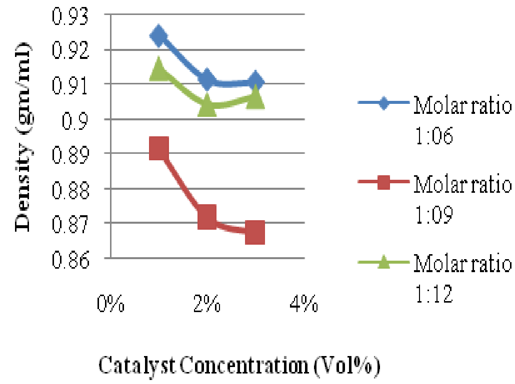

Figure-4
Effect of Density vs Cat. Con. 1st stage

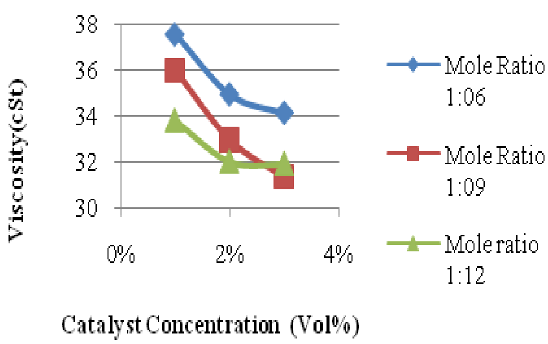

Figure-5
Effect of Viscosity vs Cat. Con. 1st stage

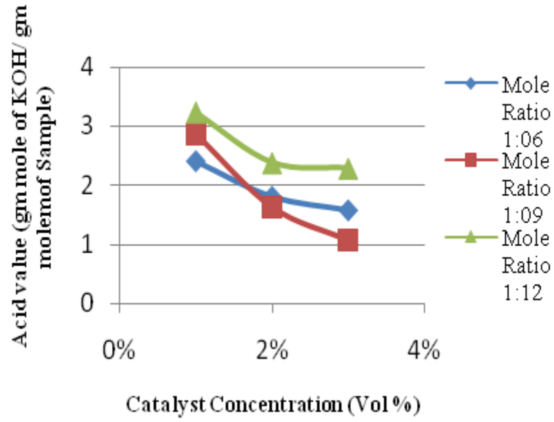

Figure-6
Effect of Acid Value vs Cat. Con. 1st stage

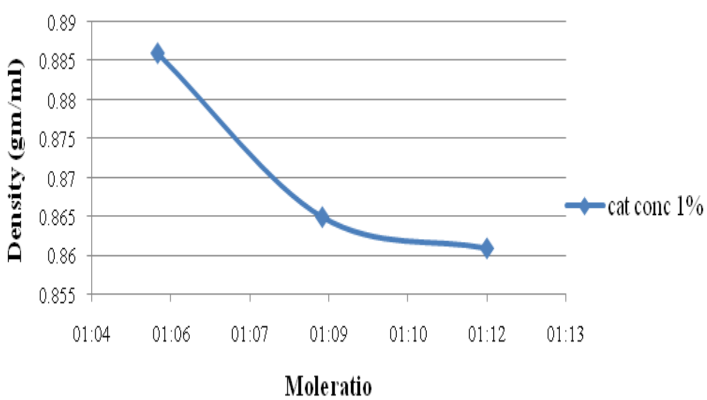

Figure-7
Effect of Density vs Mole Ratio at 2nd stage

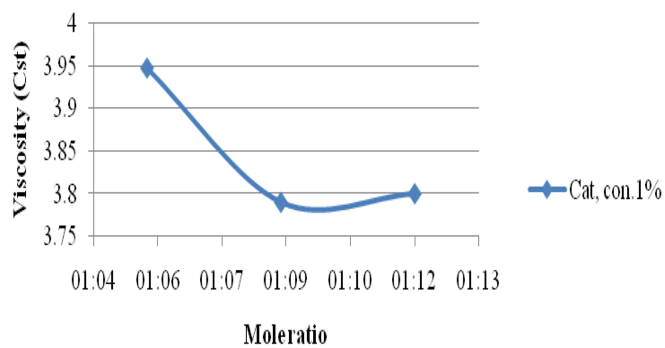

Figure-8
Effect of Viscosity vs Mole Ratio at 2nd stage

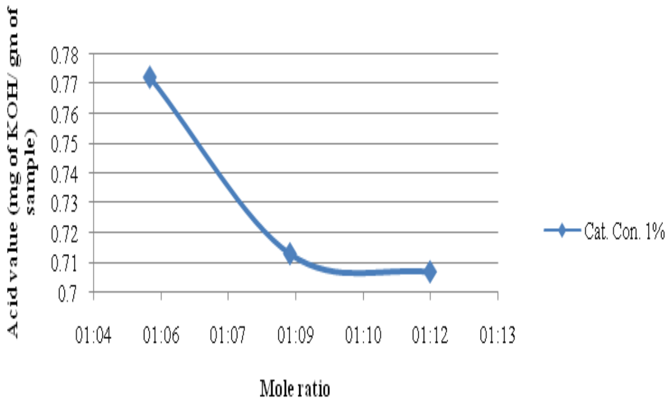

Figure-9
Effect of Acid value vs Mole Ratio at 2nd stage

Table-2
Various properties of biodiesel at second stage

Property	Oscillatory flow reactor	Batch reactor
Kinematic viscosity (cSt)@ (40 ^{0}C)	4.26	5.321
Density @ (30 ^{0}C)	0.865	0.864
Acid value mg KOH / gm	0.713	0.648

Conclusions:

The following conclusions may be drawn from the present study in the transesterification of Neem performed in an oscillatory flow reactor operated under batch mode.In oscillatory flow reactor at lower oil to methanol mole ratios gave biodiesel with highest viscosity. With increasing mole ratios viscosity decreases. In Oscillatory flow reactor the reaction time is less that is 10 minutes compared to batch reactor. Oscillatory flow reactor can be operated at room temperature. The optimum conditions for biodiesel production from Neem oil in a batch oscillatory flow reactor appears to be, oil to methanol mole ratio 1:9, catalyst concentration (H_2SO_4) 1 wt% and reaction time of 10 minutes. Biodiesel production from Neem needs less catalyst concentration and requires more mole ratios of oil to alcohol. The transesterification reaction carried out in a batch operation is a long reaction involving immiscible liquid phases, thus the product yield is greatly dependant on effective mixing and agitation. This is efficiently achieved in the oscillatory flow reactor under study to give the product in much less periods of time. Non edible oils like Neem, Karanja, Mahua, Jatropha are easily available in many parts of the world and are very cheap compared to edible oils in India.

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Table-3
Potential and production of renewable energy sources in India

Source / system	Estimated Potential (MW)	Cumulative installed capacity (MW)
Solar Photovoltaic	20 MW/km^2	2.80
Wind power	45000	3595.0
Biomass power	16000	302.53
Bagasse co generation	3500	447.0
Waste to energy (a) Municipal solid waste (b) Industrial waste	1700 1000	 17 29.5
Small hydropower (Up to 25mw)	15000	1705.63
TOTAL		6099.46

Table-4
The Physicochemical Properties of Neem Oil

Property	**Value**	**Reference Value[7]**
Acid Value (mg KOH/g)	10.92	44
Iodine Value	81.28	82-98
Viscosity (cSt)	@27^0 C 36.12	@40^0 C 35.83
Saponification	185.13	191-202
Physical state at room temperature	Liquid (Golden Yellow)	-
Cloud Point	11	19
Pour Point	7	10
Density	0.9733	0.92

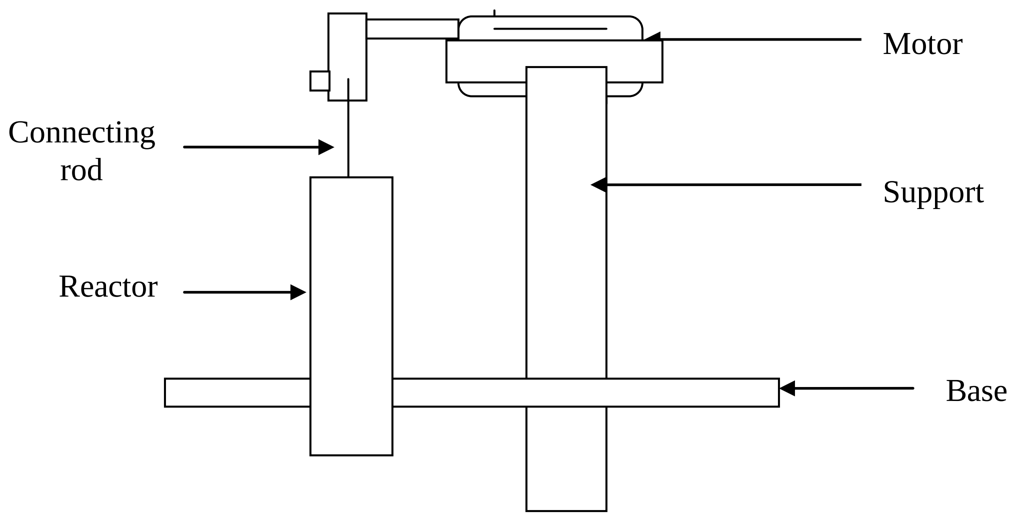

Figure-10
Assembly of the Oscillatory Flow Mix Reactor for Biodiesel Production

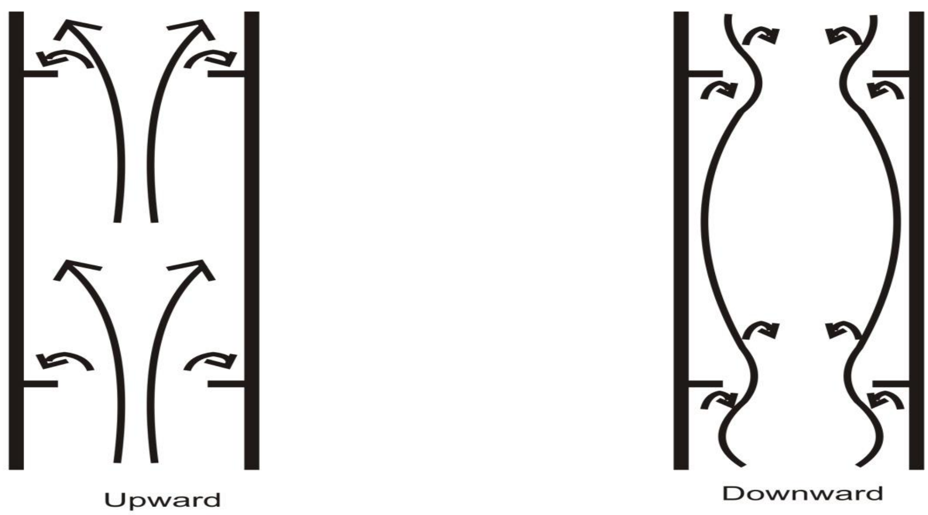

Figure-11
Mechanism of mixing in an oscillatory baffled column