Methanolysis of High FFA Mahua Oil in an Oscillatory Baffled (Batch) Reactor

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Abstract

Today about 80% of world energy requirement is provided by petroleum products. Its, extensive utilization has led to climate change, environmental pollution, and health problems. To reduce these effects, it is necessary to enhance the use of renewable energy sources. Among many renewable energy sources biodiesel is one such alternative. An oscillatory baffled reactor has been designed and fabricated to produce Mahua oil methyl esters from high FFA Mahua oil. In our present study the production of Biodiesel was carried out in two steps. The highest biodiesel yield was obtained (95%) under conditions of reaction temperature of 25 degree celcius, reaction time of 10 minutes, oil to methanol molar ratio of 1:12 and 4 v/v % sulfuric acid in the first step and 0 .3 weight % of potassium hydroxide in second step as catalysts.

Keywords: Transesterification, Biodiesel, Mahua Oil, Methanol, Oscillatory Baffled Reactor

Introduction

Presently the world's energy needs are met through nonrenewable resources such as petroleum products, and coal. Since the demand of petroleum based fuel is increasing rapidly particularly in developing countries like India and China, generated interest of researchers in the field of renewable energy led to a huge increase in energy demand [1-2].

The Primary energy sources can be divided into non-renewable and renewable [3]. The renewable sources of energy include solar energy, wind energy, geothermal energy, tidal energy, ocean thermal energy, hydropower and biofuels. Fossil Fuels are non renewable energy resources. Although, fossil fuels are contributing largely to the world energy supply, their production and use have raised environmental concerns. The effects of burning of fossil fuels have caused an increase in the percentage of carbon dioxide (CO_2) enrichment of the atmosphere, and is the primary contributor to the generally accepted phenomenon called global warming [4]. Global warming and climate change are visible in the form of dwindling freshwater supplies, increase pollution, drastic changes in seasonal temperatures and precipitation, increase intensity of hurricanes and extreme weather conditions, depletion of the ozone layer, melting of glaciers, and the rise of sea level, shrinking of forest cover, loss of species. To reduce these effects, it is necessary to enhance the use of renewable energy sources.

Among many renewable energy resources biodiesel is one alternative. Biodiesel is a fatty acid methyl ester (FAME) formed from renewable sources (vegetable oils) with short carbon chain alcohols in the presence of some catalyst (acid/alkali). The name Biodiesel was introduced in the United States during 1992 by the National Soy diesel Development Board (presently national biodiesel board) which has pioneered the commercialization of Biodiesel in the United States [5].In this paper Mahua oil is used as feedstock for the preparation of biodiesel. Currently biodiesel is mostly produced from edible and nonedible vegetable oils as shown in table 1 [5].

Table 1 Source of Oil

Vegetable oils	Non-edible oils	Animal Fats
Soybeans	Almond	Lard
Rapeseed	Abutilon muticum	Tallow
Canola	Andiroba	Poultry fat
Safflower	Babassu	Fish Oil
Barley	Brassica carinata	
Coconut	B. napus	
Copra	Camelina	
Cotton Seed	Cumaru	
Groundnut	Cynara cardunculus	
Oat	Jatropha nana	
Rice	Jojoba oil	
Sorghum	Pongamiaglabra	
Wheat	Laurel	
Winter rapeseed oil	Lesquerellafendleri	
	Mahua	
	Piqui	
	Palm	
	Karang	
	Tobacco seed	
	Rubber plant	
	Rice bran	
	Sesame	
	Salmon oil	

Feedstock

Madhuca longifolia, commonly known as mahwa or Mahua, is an Indian tropical tree found largely in the central and north Indian plains and forests. The two major species of genus Madhuca found in India are Madhuca Indica (latifolia) and Madhuca longifolia (longifolia). The seed potential of this tree in India is 500,000 tons and oil potential is 180,000 tons. It is a fast-growing tree that grows to approximately 20 meters in height, possesses evergreen or semi-evergreen foliage, and belongs to the family Sapotaceae. It is found in India in the states of Chhattisgarh, Jharkhand, Uttar Pradesh, Bihar, Maharashtra, Madhya Pradesh, Kerala, Gujarat and Orissa. Oil content in latifolia is 46% and 52% in longifolia. In seeds oil content is 35% and protein at 16% [6].

Fatty acid profile of Mahua Oil is given in Table 2 [7].

Table 2 Properties: the Average Fatty Acid Composition of Mahua Oil

Fatty Acid	Systemic Name	Formula	Structure	Wt%
Palmitic	Hexadecanoic	$C_{16}H_{32}O_2$	16:0	16.0–28.2
Steric	Octadecanoic	$C_{18}H_{36}O_2$	18:0	20.0–25.1
Arachidic	Eicosanoic	$C_{20}H_{40}O_2$	20:0	0.0–3.3
Oleic	cis-9-Octadecenoic	$C_{18}H_{34}O_2$	18:1	41.0–51.0
Linoleic	cis-9,cis-12-Octadecadienoic	$C_{18}H_{32}O_2$	18:2	8.9–13.7

Apparatus and experimental setup

Oscillatory baffled reactor (OBR reactors) is a novel type of reactor, consisting of tubes containing equally spaced orifice plate baffles. 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 cylinder. The Oscillatory baffled reactor is a new relatively mixing device, based upon superimposing periodic fluid oscillations within a cylindrical column containing equally spaced orifice baffles [8]. Experiments were conducted in a laboratory- scale setup of Oscillatory Baffled Reactor as shown in figure 1.

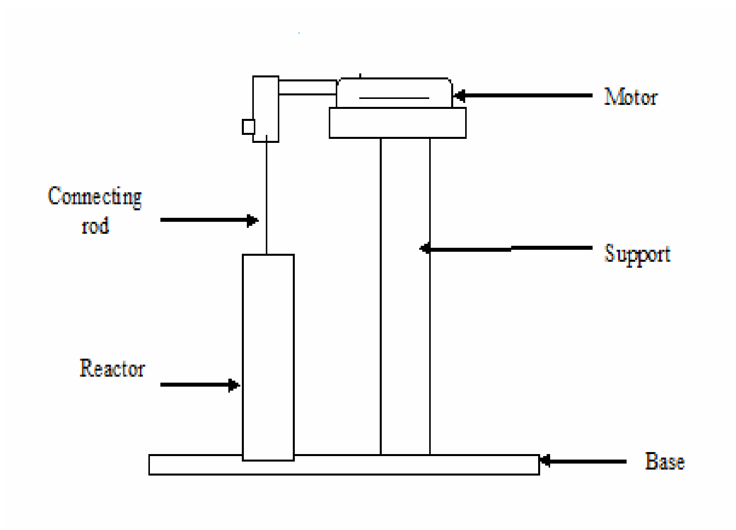

Figure 1 Oscillatory Baffled Reactor

The constructional details

The oscillatory Baffled reactor is a 7 cm diameter Stainless Steel pipe (to avoid corrosion due to sulfuric acid) consisting of a support plate at the bottom. The reactor is 46 cm long, with a maximum capacity of 2.0 liters. The reactor consists of a cap at the top, which can be opened to feed the reactor for a batch operation. The reactor is provided with an outlet at the bottom so as to avoid the use of any pump for product withdrawal, the product discharge is purely due to gravitational effects.

An oscillatory motion is superimposed upon the net flow of the process fluid, creating flow patterns conducive to efficiently heat and mass transfer, while maintaining plug flow. That's why in an oscillatory baffled reactor the reaction time is less that is 10 minutes at a temperature in the range of 20^0C-25^0C compared to conventional batch reactor which takes minimum 1 hour and temperature of 50^0C - 55^0C for reaction under similar conditions [8].

Some advantages of oscillatory baffled reactors, such as

i)Enhanced heat and mass transfer.

ii)Efficient dispersion of immiscible fluids.

iii)Uniform particle suspension.

Materials and Methods

Mahua Oil was obtained from District Gadchiroli, Maharashtra, India. Mahua Oil was contaminated with water and solid particles. So Solid particles of Mahua oil were removed by filtration using a Whatman 40 filter paper. It was found that the initial acid value of Mahua Oil 21.34 mg KOH/gm of oil which was very high. Therefore to convert Mahua oil into Mahua oil methyl esters two steps were necessary.

Step 1: Esterification of Mahua Oil (Pretreatment)

The pretreatment process comprised of two steps. In each step, different methanol-to-oil ratios (1:9, 1:12, 1:15) and sulfuric acid as a catalyst (4, 5 v/v %) at reaction time 10 min and temperature 25^0C - 30^0C were used to investigate their influence on the acid value of crude Mahua oil. Then, the mixture was left overnight to settle into two layers. The lower layer was removed while the upper layer which contained fatty acid methyl ester and un-reacted triglycerides were subjected to the second step of transesterification process.

Step 2: Transesterification

In the second stage, treated Mahua oil obtained from first stage was trans esterified in an Oscillatory Baffled Reactor by varying the oil–methanol molar ratio (1:9, 1:12, 1:15) with Potassium Hydroxide (0.3-0.4 weight %) as alkaline catalyst having reaction time of 10 min and temperature 25^0C to produce methyl ester. It was observed that the yield of biodiesel maximum 95% at 1:12 molar ratio, 0.3 weight % of KOH as a catalyst, reaction time of 10 min and temperature 25^0C. Finally, the mixture was left overnight to settle into two distinct layers i.e. glycerol layer and methyl ester Layer. Upper layer of methyl ester is separated and is preserved for analysis.

Analysis of reaction product

The fuel properties namely, density, kinematic viscosity at 40^0 C, flash point, pour point, cloud point, acid value and of Mahua oil and Mahua oil methyl ester were determined in the laboratory, which summarized in Table 3. Gross Calorific Value of Mahua oil methyl ester was 7564.08 kcal/kg which tested by method IS: 1350 (Part 2): 1970 and the fatty acid composition was analyzed using GC-MS/MS instrument which is authentic standards in Anacon Laboratories Pvt. Ltd, Nagpur. It can be seen that Mahua oil methyl ester (biodiesel had) comparable fuel properties with those of diesel and was within the limits prescribed in the latest standards for biodiesel. The average fatty acid composition of Mahua Oil Methyl Ester is summarized in Fig.2.

Table 3 Fuel Properties of Mahua Oil, Mahua Biodiesel and Diesel

Properties	Unit	Mahua Oil	Mahua Oil Biodiesel	Diesel [7]
Color	-	Slight greenish yellow	Dark yellow	Light yellow
Kinematic viscosity	cst	38.4	5.04	2.60
Acid value	mg of KOH / gm of oil	21.34	0.8194	0.35
Density	gm/ml	0.945	0.8812	0.850
Flash Point	^{0}C	232	204	68
Fire Pont	^{0}C	239	230	
Pour Point	^{0}C	15	1	-20
Cloud Point	^{0}C	14	6	
Calorific Value	Kcal/kg	-	7564.08	10031.04

Results and Discussion

Esterification

The variables affecting esterification such as catalyst concentration (4 – 5 Vol %) and oil to alcohol molar ratio (1:9, 1:12, 1:15) at a temperature (25-30°C), reaction time of 10 minutes were studied to get higher conversion under optimal reaction condition. Graph 1, 2, 3 shows the effect of the amount of sulfuric acid on viscosity, acid value and density respectively. It was observed that as the mole ratio increases since 1:9 to 1:15 specific gravity, viscosity and acid value decreases. And also it was observed that specific gravity, viscosity and acid value are less when 4 Vol % of catalyst used as compared to when 5 Vol % of catalyst.

Transesterification

The variables affecting transesterifcation such as catalyst concentration (0.3 and 0.4 weight %) and oil to alcohol molar ratio (1:9, 1:12, 1:15) at a temperature (25-30°C), reaction time of 10 minutes were studied to get higher conversion under optimal reaction condition.

Influence of catalyst concentration

Methanolysis of Treated oil was carried out with KOH as a catalyst at a concentration of 0.3 - 0.4 weight % with oil to alcohol molar ratio. Graph 4, 5, 6 shows the oil to alcohol molar ratios versus viscosity, acid value and density at different catalytic concentrations. The higher catalytic concentration i.e. 0.4% of KOH was insignificant to catalyze the reaction to completion. However, 0.3% KOH was optimal in the reaction. With the increase in the concentration of the catalyst, there was an increase in the viscosity, acid value and density of methyl esters.

Influence of oil/methanol molar ratio

The alcohol to oil molar ratio is one of the important factors that affect the reaction. In the present work, the average molecular weight of oil from its composition was calculated as 899gm and accordingly the amount of methanol was taken in the reaction so that the oil to alcohol molar ratio varied from 1:9 to 1:15. The yield of methyl esters versus catalyst concentration at different molar ratio of oil to methanol, such as 1:9, 1:12, 1:15, are shown in graph 7. The yield of methyl esters of oil to methanol molar ratio of 1:12 was 93.25%. From the graph 8 it was observed as for mole ratio is concerned 1:12 appears to be optimum value. Hence this mole ratio was to be chosen for study of catalyst concentration on viscosity of biodiesel.

Influence of catalyst concentration on properties of bio-diesel at mole ratio 1:12

When the catalyst concentration varied from 0.3 weight % to 0.4 weight% at oil to the alcohol molar ratio 1:12 at room temperature viscosity increases from 5.04 cst to 5.32 cst. The viscosity of biodiesel is low at the 0.3 weight % of catalyst concentration as compared to the 0.4 weight %. When the catalyst concentration varied from 0.4 weight % to 0.3 weight% at oil to the alcohol molar ratio 1:12 at room temperature acid value decreases from 0.9485 to 0.8194 mg of KOH/gm oil. When the catalyst concentration varied from 0.4 weight % to 0.3 weight% at oil to the alcohol molar ratio 1:12 at a room temperature density decreases from 0.8884 to 0.8812 gm/cc.Similar observations can be seen when the molar ratio has increased from 1:9 and 1:15.

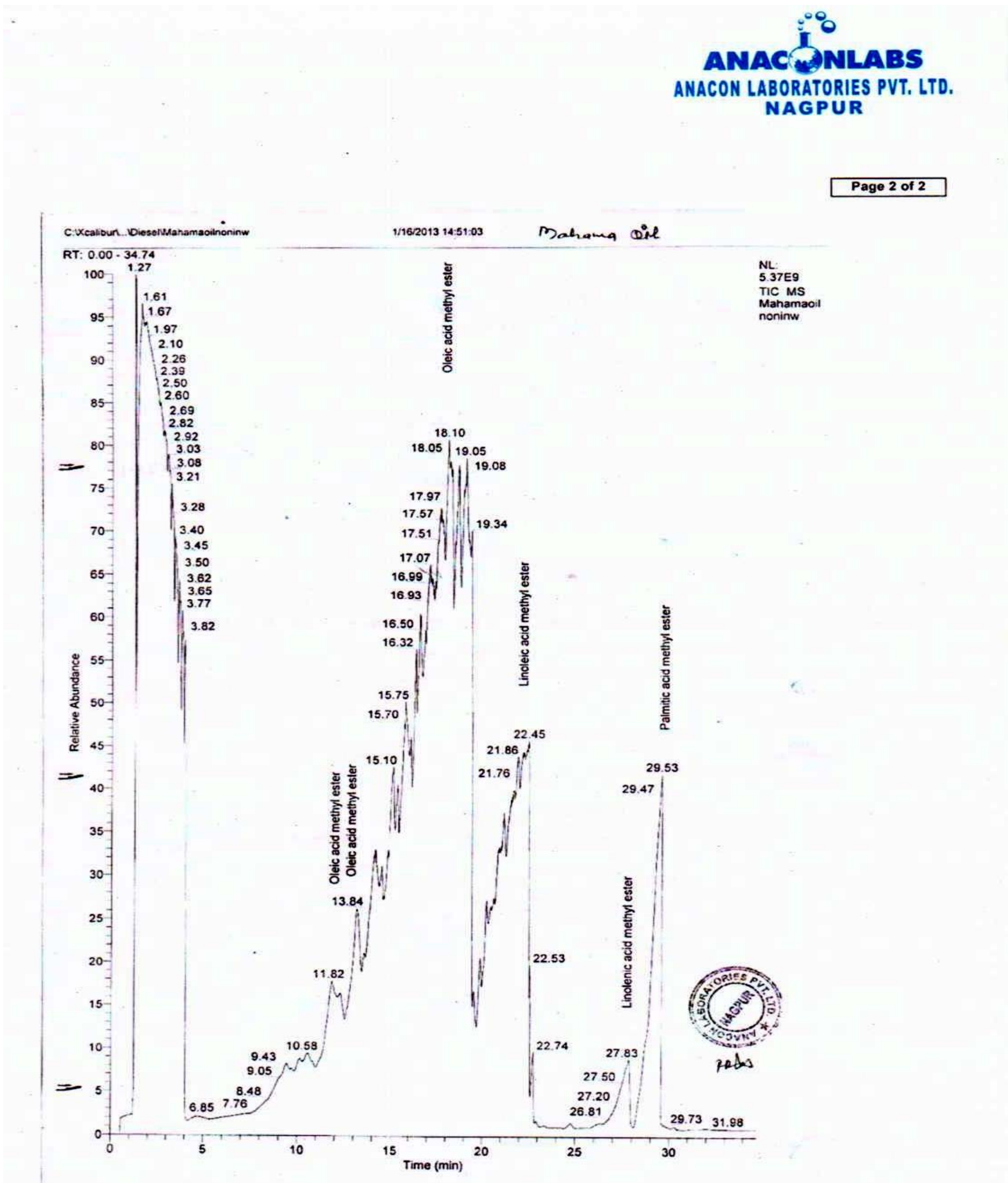

Figure 2 Average fatty acid composition of Mahua Oil Methyl Ester

Conclusions

The Transesterification of high FFA Mahua oil in an Oscillatory Baffled reactor is carried out. Oil to alcohol mole ratio, Catalyst (H_2SO_4) concentration for First Stage and Catalyst (KOH) concentration for Second Stage are the three parameters were chosen to study the influence of variables on the properties of biodiesel. The following conclusions may be drawn from the present work in the transesterification of Mahua performed in an oscillatory flow reactor operated under batch mode.

i) In an oscillatory flow reactor at lower oil to methanol mole ratios gave biodiesel with highest viscosity. When oil to alcohol mole ratio was increased from 1:9 to 1:12 the viscosity was found to decrease from 5.69 cst to 5.32 cst.
ii) When the catalyst concentration varied from 0.4 weight % to 0.3 weight% at oil to the alcohol molar ratio 1:12 at room temperature acid value decreases from 0.9485 to 0.8194 mg of KOH/gm oil.
iii) When the catalyst concentration varied from 0.4 weight % to 0.3 weight% at oil to the alcohol molar ratio 1:12 at a room temperature density decreases from 0.8884 to 0.8812 gm/cc.
iv) In the Oscillatory flow reactor the reaction time is less that is 10 minutes.
v) The oscillatory flow reactor can be operated at low temperature (25-300C)
vi) The optimum conditions for biodiesel production in 1st stage from Mahua oil in a batch oscillatory flow reactor appears to be, oil to the methanol mole ratio 1:12, catalyst concentration (H2SO4) 4 Vol%, reaction time of 10 minutes at room temperature of 250C.
vii) The optimum conditions for biodiesel production in 2nd stage of Mahua oil in a batch oscillatory flow reactor appears to be, oil to the methanol mole ratio 1:12, catalyst concentration (KOH) 0.3weight%, reaction time of 10 minutes at room temperature of 250C.

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