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Optimization of Biodiesel (MOME) Using Response Surface Methodology (RSM)

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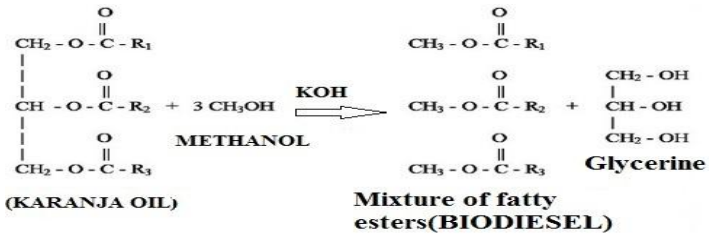
Abstract
Today about 80% of world energy requirement is provided by petroleum products. Its, extensive utilization has led to climate change, environmental pollution, and health problems. To reduce these effects, it is necessary to enhance the use of renewable energy sources. Among many renewable energy sources biodiesel is one such alternate. Biodiesel is produced by reacting oil (mahua oil) with alcohol in present of base catalyst such as (NaOH, KOH) by a process known as trans-esterification. For the optimization of biodiesel production, various parameters have to be considered such as oil/alcohol ratio, temperature, reaction time, catalyst, nature of catalyst (homogeneous, heterogeneous), and type of process (single, two step process). This can be achieved with experience and research in the corresponding field but these things require enamors time. There is a method based on statistics and mathematics which can optimize the process parameters in very short time, called RESPONSE SURFACE METHODOLOGY (RSM). The optimum condition for the biodiesel production using RESPONSE SURFACE METHODOLOGY (RSM) is 92.7 ml mahua oil with 1:12 methanol/oil molar ratio, 0.4wt of catalyst and 10 minute reaction time in an oscillatory baffled reactor (OBR).

Keywords: *biodiesel, mahua oil, trans-etherification, response surface methodology (RSM), oscillatory baffled reactor (OBR).*

INTRODUCTION

The world energy requirement is mainly provided by non renewable resources such as petroleum products, and coal. Since the demand of petroleum based fuel is increasing rapidly, there is need to replace these conventional (non renewable) source of energy with the renewable energy sources. Among many renewable energy sources, biodiesel is one such alternate. Biodiesel is produced by trans-esterification reaction where vegetable oils react with alcohol in present of catalyst such as (NaOH, KOH).

Biodiesel is produced through a trans-esterification reaction as shown below,



Where R_1, R_2, and R_3 are long hydrocarbon chains; sometimes called fatty acid chains.

Through previous researches and patents, we have following observations about the trans-etherification process:

1. Excess alcohol of more than 1.6 times the stoichiometry amount is required for complete reaction.
2. The amount of alcohol used can be reduced by conducting the reaction in steps, where part of the alcohol and catalyst are added at

the start of each step, and the glycerol is removed at the end of each step.

3. Besides methanol, other alcohols can be used including ethanol, propanol, isopropanol, butanol, pentanol.
4. Water and free fatty acids inhibit the reaction. Higher alcohols are particularly sensitive to water contamination.
5. Free fatty acids in the oils or fats can be converted to alkyl esters with an acid catalyst.
6. This can be followed by a standard alkali-catalyzed trans-esterification to convert the triglycerides.
7. Acid catalysts can be used for the trans-esterification of oils to alkyl esters, but they are much slower than alkali catalysts.

BASE MATERIAL FOR BIODIESEL

Biodiesel can be produced from vegetable oils or animal fats. Basically, vegetable oil is used for biodiesel production. The reason is that in compared with animal fats, they are easy to use and do not have bad odour. Various raw materials used for biodiesel production are edible oils (such as Soybeans, Cotton seed, Sunflower, etc), non-edible oils (Mahua, Jatropha, Karanja, Neem oil) and Animal fats (Fish oil, Poultry fats, Tallow, Lard). Among many non-edible oil mahua oil, karanja oil and jatropha oils are basically used for Biodiesel in India. But, the biodiesel produced from jatropha oil has corrosive effect on engine piston. So, Mahua oil and karanja oil is used to produce Biodiesel.

MAHUA OIL

The Madhuca Indica oil is commonly known as mahua oil, which are an Indian tropical tree found largely in the central and north Indian plains and forests. The two major species of madhuca found in India are Madhuca Indica (latifolia) and Madhuca longifolia (longifolia). The seed potential of this tree in India is 5,00,000 tons and oil potential is 1,80,000 tons. It is fast growing tree that grows to approximately 20 meters in height. It is found in India in the states of Chhattisgarh, Jharkhand, Uttar Pradesh, Bihar, Maharashtra, Madhya Pradesh, Kerala, Gujarat and Orissa.

Table 1. Fatty acid profile of Mahua oil

Fatty Acid	Formula	Structure	Wt %
Palmitic	$C_{16}H_{32}O_2$	16:0	16.0-28.2
Stearic	$C_{18}H_{36}O_2$	18:0	20-25.1
Arachidic	$C_{20}H_{40}O_2$	20:0	0.0-3.3
Oleic	$C_{18}H_{34}O_2$	18:1	41.0-51.0
Linoleic	$C_{18}H_{32}O_2$	18:2	8.9-13.7

Table 2. The physico-chemical properties of Mahua oil Parameter Value

Acid value (mg of KOH/g)	20
Iodine value (gram of iodine /100g)	78.12
Saponification value (mg of KOH/g)	196
Viscosity @40^{0}c (mm^2/s)	55.03
Density @ 30°C (kg/m3)	912
Flash point (°C)	186
Pour point (°C)	11

APPARATUS AND EXPERIMENTAL SETUP

Oscillatory baffled reactors are a novel type of reactor, consisting of tubes containing equally spaced orifice plate baffles. These 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. Effective and energy efficient heat transfer can be obtained by oscillatory flow mixing for both the batch fluid oscillation situation and for the batch baffle oscillation, due to the mechanisms of vortex interaction. The Oscillatory baffled reactor is schematically shown below.

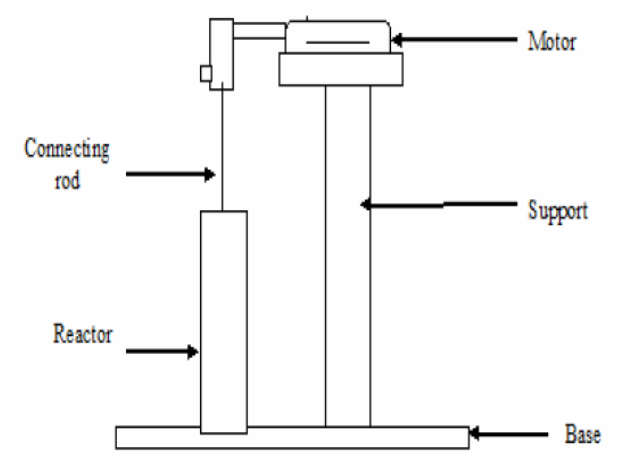


Fig 1: Oscillatory baffled reactor

The mechanism of mixing in the OBR is illustrated 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 eddies. 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. The mechanism of mixing in OBR is shown below:

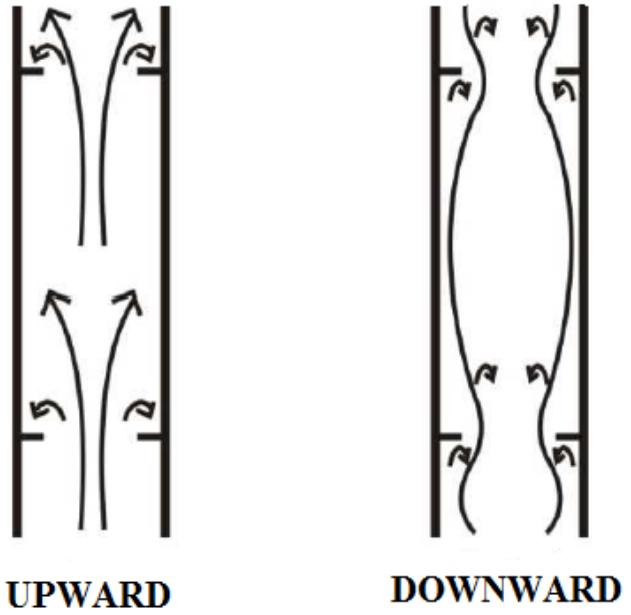


Fig 2: Mechanism of mixing in an oscillatory baffled reactor

PROCEDURE

Biodiesel production (trans-esterification reaction):

Free fatty acid (FFA) value of oil plays key role in the trans-esterification process. If free fatty acid content of the oil is less than 1, single stage process (alkali trans-esterification) is will be carried out. If it is greater than 1, double stage process (acid esterification and alkali trans-esterification) will be carried out. Since, the acid value of mahua oil is more than 1, so it processed through two stage processes.

A. TRANS-ESTERIFICATION OF MAHUA OIL

1. Acid catalyzed esterification process

100ml of Mahua oil (FFA>1) is taken in an oscillatory baffled reactor (OBR). Then, 30ml of methanol and sulphuric acid was added (volume of H2SO4 = FFA value * 0.05). The process is continued for 10 min at room temperature. This mixture was separated for overnight. Top layer consisting of acid esterified oil and bottom layer known as residues were found. The bottom residues layer was separated out from acid esterified oil and used it for biodiesel production.

2. Alkali catalyzed trans-esterification process

The bottom layer product of acid esterification reaction is again taken in an oscillatory baffled reactor (OBR). The alkali methanol mixed solution was added to the product of the acid esterification. The reaction was conducted again at room temperature for 10 min. The resulted product was allowed to settle down under gravity for 8h in a separating funnel. The products of the alkali trans-esterification process result in the formation of two layers viz., an upper layer containing biodiesel (methyl ester) and lower layer containing glycerol. . The upper layer is washed with water till neutral water is obtained after washing. And then different properties of biodiesel were analysed as per ASTM.

CHARACTERISTICS OF BIODIESEL:

The fuel properties namely, density, kinematic viscosity, flash point, pour point, cloud point, acid value and of Pongamia pinnata (Karanja oil) and karanja oil methyl ester were determined in the laboratory. It can be seen that Karanja oil methyl ester (KOME) had more comparable fuel properties than Mahua oil methyl ester (MOME) with those of petroleum diesel and was within the Limits prescribed in the latest standards for biodiesel. The various properties are summarized below:

Table 5: Fuel Properties of MOME, KOME and Diesel

Properties	Unit	Biodiesel (MOME)	Biodiesel (KOME)	Diesel
Colour		Dark yellow	Dark yellow	Light yellow
Kinematic viscosity	Cst	5.60	5.04	2.06
Acid value	mg of KOH/g m of oil	0.896	0.8194	0.35
Density	gm/ml	0.887	0.881	0.850
Flash point	^{0}C	117	96	68

OPTIMIZATION (USING RESPONSE SURFACE METHODOLOGY (RSM)):

Response surface methodology (RSM) provides superb static tools for design and analysis of experiments aimed at process optimization. At the final stages of process development, RSM illuminates sweet spot where high yield of in-specification products can be achieved at lowest possible cost. It produces statically-validated predictive models and with the aid of specialized software, response surface map that point the way to pinnacles of process performance.

The most expensive application of RSM are in the industrial world, particularly in situations where several input variables potentially influence some performance or quality characteristic of the product or process. This performance measure or quality characteristics is called response. It is typically measured on a continuous scale, although attribute responses, ranks and sensory response are not unusual. The input variables are sometimes called independent variables, and they are subjected to the control of the engineer or scientist, at least for the purposes of a test or an experiment.

The experimentation plays an important role in science, engineering and industry. The experimentation is an application of treatments to experimental units, and then measurement of one or more responses. With the increasing competition and existence in market, the manufacturer needs to produce the product (both quality and quantity) with least cost. The process yield and quality which depends on certain operating parameters can be optimized using various mathematical models. This is possible by optimizing each step in manufacturing line i.e. process and operations. This can be achieved with experience and research in the corresponding field but these things require enamors time. There is a method based on statistics and mathematics which can optimize the process parameters in very short time, called response surface methodology (RSM). It is a part of scientific method. It requires observing and gathering information about how process and system works. In an experiment, some input X's transform into an output that has one or more observable response variables Y. Therefore, useful result and conclusion can be drawn by experiment. In order to obtain an objective conclusion, an experimenter needs to plan and design the experiments and analyze the results.

In the mathematical analysis, Quadratic models were established by using methods of least square. Firstly we will develop the linear equation by using the curve fitting software i.e. LAB FIT. The predicted pre- treatment product viscosity is shown in eq. 1

$$Y_{viscosity} = 5.58574 + 1.48357*X1 - 0.144833*X2 - 0.386333*X3. \quad (1)$$

Where R2 = 0.87756.

Here, $Y_{viscosity}$ stands for predicted pretreatment product viscosity value and X1, X2, X3 are the coded values for the factor value (Reaction Time, Catalyst concentration and Methanol- oil ratio, respectively).

We will repeat the above procedure to find the value of Viscosity (Y) using Cross equation.

$$Y_{viscosity} = 9.41739 - 1.118860*X1 - 0.988760*X2 - 1.089045*X3 - 0.0782427*X1*X2 - 0.06822124*X1*X3 + 0.0068333*X2*X3. \quad (2)$$

Where R2 = 0.878084.

Similarly, we will repeat the above procedure to find the value of Viscosity (Y) using Square equation.

$$Y_{viscosity} = 4.9341 - 0.565494*X1 - 0.483244*X2 - 0.899795*X3 - 0.0237625*X1*X2 - 0.01790364*X1*X3 + 0.00683331*X2*X3 +$$

0.12862740*X1^2 – 0.00654761*X2^2 -0.0373332 *X3^2. (3)

Where R2 = 0.901681.

Here we will select the equation among linear, cross and square whose value of R2 is near to 1. Here the value of Regression correlation R2 for square equation is 0.901681 is nearer to 1.0 compare to cross and linear equation value.

Now we will use the software Design Expert 7.0 to analysis the variance in order to check that the experimental data is adequate and fits the mathematical model.

The relationship between reaction time and catalyst concentration at molar ratio 1:09 is shown in Fig 2.

The Figure 1 shows that for high molar ratio pre-treatment product viscosity increases with increasing amount of methanol. The pre-treatment product viscosity decrease when the reaction time is less and viscosity increases with increase in reaction time. Similarly, with increase in catalyst concentration the viscosity of the pre treatment product increases and with less catalyst concentration the viscosity decreases.

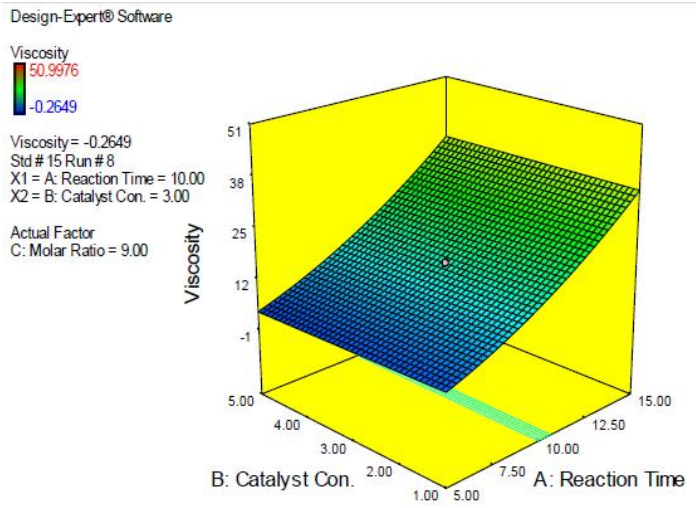


Figure 1: 3 D Graph for Catalyst Conc. Vs Reaction Time for Viscosity

Figure 2 shows the response surface plot of viscosity as a function of reaction time and molar ratio. As the reaction time increases the viscosity of pre-treated product increases and with less time the viscosity also decreases. Similarly the response plot shows that as the molar ratio does on increasing the viscosity of pre-treated oil decreases.

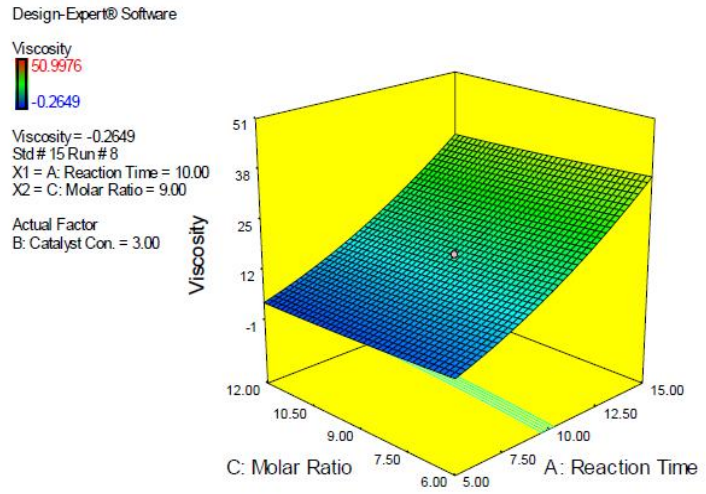


Figure 2: 3D Graph for Molar Ratio vs. Reaction Time for Viscosity

Figure 3 shows the various effects of catalyst concentration and molar ratio on the viscosity of pre-treatment product. As the molar ratio increases the viscosity of the pre-treated product increases. Similarly as the catalyst concentration goes on increasing the viscosity of the pre-treated product goes on decreasing.

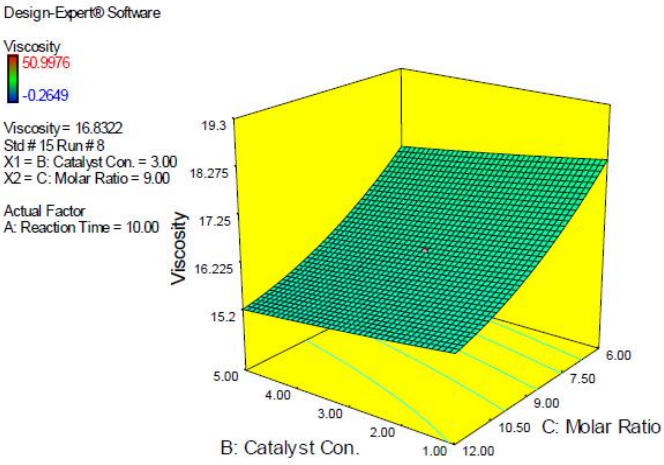


Figure 3: 3D Graph for Catalyst Conc. Vs Molar Ratio for Viscosity

CONCLUSIONS

Central Composite Design was used for optimization of methanol/oil ratio, Catalyst loading, reaction temperature and time on the Transesterification of mahua oil.

Thus, research work gave an optimal value of 95% biodiesel at 60 °C, in 90 minutes of reaction time with 0.3 wt % of catalyst loading and methanol/oil ratio of 1:5. Quadratic polynomial models were

obtained to predict yield of biodiesel. The result showed that the predicted value was in agreement with the experimental value, which was established with additional experiments to confirm the optimized parameters. Therefore production of biodiesel from mahua oil is a feasible process.

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