PRODUCTION OF BIODIESEL USING PALM OIL

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Abstract - *Due to the increase in price of petroleum and environmental concerns, the search for alternative fuels has gained importance. Biodiesel can be used as a substitute for fossil diesel. Biodiesel is mainly produced by a transesterification reaction where the oils or fats react with a short chain alcohol, usually methanol, in the presence of a catalyst. However, it is not used on a large scale because of its high price mainly due to the costs associated to feedstock and to the production process. In this work, biodiesel production by transesterification of palm oil with methanol has been studied in the presence of NaOH as catalyst. Moreover, the dependence of the conversion of palm oil on the reaction's variables such as the molar ratio of methanol/oil, the amount of catalysts used, reaction temperatures and reaction times were performed. The results show that using palm oil as feedstock it is possible to produce a biodiesel with fatty acids methyl esters content higher than 96.5%, which is the minimum values imposed by the international standards. Its use has several environmental benefits related to the decrease of CO2 emissions as well as several other air pollutants.*

Key Words: *Biodiesel, petroleum, palm oil, fatty acids, air pollutants.*

1. INTRODUCTION

Biodiesel is the name of a cleaner burning renewable fuel for diesel engine. It is produced from domestic, agriculture co-products such as soyabean oil, palm oil or other fats and vegetabl oils. Biodiesel contains no petroleum, but it can be blended at any level with petroleum diesel. Blends upto 20% (B20) can be used in diesel engine with no modification. Higher blends are also possible, all the way upto B100 in some cases. Biodiesel are sustainable and renewable energy sources derived from biological materials wastes. The production and consumption of biodiesel continues to increase as more attention is paid to the environment protection, the rapid rate of growth in world energy requirements mainly in developing countries and the depletion of conventional fossil-fuel resources. Biodiesel, a fuel produced from natural/virgin edible and non-edible vegetable oils including used cooking oils or animal fats like tallow and fish oil, is a good substitute for petroleum- diesel fuel representing an alternative source of energy, which can supplement or totally replace fossil fuels in diesel engines without any major modification. According to the United States Environmental Protection Agency (EPA), biodiesel may be blended with conventional diesel to obtain different blends such as B20 (20% biodiesel) or it can be used as 100% biodiesel (B100). Biodiesel is technically defined as a mixture of long-chain fatty acid methyl esters (typically C14-C22). Biodiesel is non-toxic, biodegradable and significantly reduces pollutant emissions such as carbon monoxide (44%), particulate matter (40%), and sulphur dioxide (100%).

1.1 Biodiesel Synthesis Process

Biodiesel is a clean burning alternative fuel that comes from 100 % renewable resources such as natural vegetable oils and fats. Biodiesel is made through a chemical process which converts oils and fats of natural origin into fatty acid methyl esters (FAME) that can be used in any diesel engine without modifications. Chemically, it is defined as mono alkyl esters of long chain fatty acids derived from renewable lipid sources. In words, the reaction is:

Oil + Alcohol → Biodiesel + Glycerine

The biodiesel is the lighter-coloured layer at the top of the interface. The darker-coloured crude glycerine always settles to the bottom of the reactor vessel. It is important to realize that unmodified vegetable oil, sometimes called straight vegetable oil (SVO) or waste vegetable oil (WVO), is not biodiesel. Some people have used SVO or WVO in diesel engines with varying degrees of success. The primary problem is the high viscosity and low volatility of the unmodified vegetable oils. Without exception, U.S. engine manufacturers have recommended against the use of SVO and WVO. Biodiesel is usually preferred over SV and WVO because the chemical reaction converts the oil or fat into compounds that are closer to the hydrocarbons found in regular diesel fuel.

1.2 Processes used in Biodiesel Production
1.2.1 Transesterification Process:

Transesterification process, as showed in Fig.(2.1) is a conventional and the most common method for biodiesel production. In transesterification reaction homogeneous catalysts (alkali or acid) or heterogeneous catalysts can be used. The catalysts split the oil into glycerine and biodiesel and they could make production easier and faster.

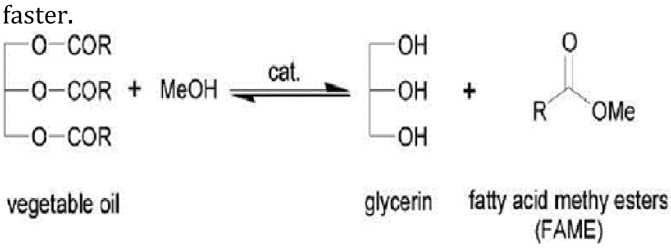


Fig.1 Biodiesel production via transesterification reaction

In this method, fatty acid alkyl esters are produced by the reaction of triglycerides with an alcohol, especially ethanol or methanol, in the presence of alkali, acid or enzyme catalyst etc. The sodium hydroxide or potassium hydroxide, which is dissolved in alcohol, is generally used as catalyst in transesterification reaction. The products of the reaction are fatty acid methyl esters (FAMEs), which is the biodiesel, and glycerine. Ethanol can be also used as alcohol instead of methanol. If ethanol is used, fatty acid ethyl ester (FAEE) is produced as product. Methyl ester rather than ethyl ester production was preferred, because methyl esters are the predominant product of commerce, and methanol is considerably cheaper than ethanol. However, methanol usage has an important disadvantage, it is petroleum based produced. Whereas ethanol can be produced from agricultural renewable resources, thereby attaining total independence from petroleum-based alcohols. Ethanol is also preferred mostly in ethanol producing countries. Propanol and butanol have been also used as alcohols in biodiesel production.

1.2.2 Supercritical Process

Supercritical method is one of the novel methods in biodiesel production. Biodiesel production can be easily achieved by supercritical process without catalysts. A supercritical fluid is any substance at a temperature and pressure above its critical point. It can diffuse through solids like a gas, and dissolve materials like a liquid. These fluids are environment- friendly and economic. Generally, water, carbon dioxide and alcohol are used as supercritical fluids. Supercritical fluids have different application areas. One of these applications is the biodiesel production that is firstly achieved by Saka and Kusdiana in 2001. And many studies on biodiesel production in supercritical conditions were made since 2001. In Saka's study, rapeseed oil was converted to methyl esters with supercritical methanol (molar ratio of methanol to rapeseed oil: 42 to 1) at temperature of 350°C in 240 s.

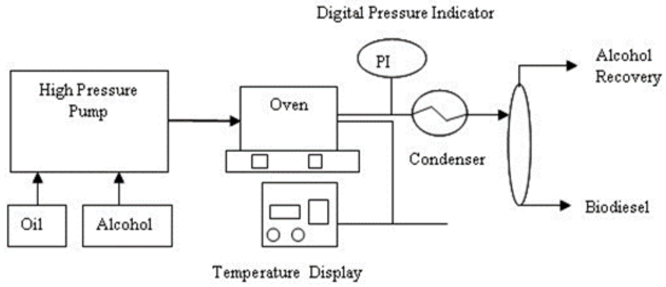


Fig.2 Biodiesel Production by Continuous Supercritical Alcohol Process.

The methyl ester yield of the supercritical methanol method was higher than those obtained in the conventional method with a basic catalyst. Liquid methanol is a polar solvent and has hydrogen bonding between OH oxygen and OH hydrogen to form methanol clusters, but supercritical methanol has a hydrophobic nature with a lower dielectric constant, so non-polar triglycerides can be well solvated with supercritical methanol to form a single phase oil/methanol mixture. For this reason, the oil to methyl ester conversion rate was found to increase dramatically in the supercritical state.

2. Raw Materials and Methodology

Materials required for different synthesis reaction include: Palm oil, Methanol, Enzyme, Water, NaOH

Table -1 Enlists the raw material specifications.

Component	Molecular Weight (g/mol)	Density (Kg/L)	Purity	Viscosity (cp)
Oil	872	0.92	100	57
Methanol	32	0.790	99	-
Enzyme	-	1.018	100	-
Water	18	0.9433	100	0.8

2.1 Method Used for Synthesis

The method used for biodiesel production in this project is Enzyme catalyzed or Lipase catalyzed method. Large amounts of research have focused recently on the use of enzymes as a catalyst for the transesterification. Researchers have found that very good yields could be obtained from crude and used oils using lipases. The use of lipases makes the reaction less sensitive to high free fatty-acid content, which is a problem with the standard biodiesel process. One problem with the lipase reaction is that methanol cannot be used because it inactivates the lipase catalyst after one batch. However, if methyl acetate is used instead of methanol, the lipase is not in-activated and can be used for several batches, making the lipase system much more cost effective. Optimization of various parameters in order to get 100% conversion was carried out in this project. Five main parameters were optimized in this project. They are as follows: Reaction Time, reaction temperature, molar ratio of methanol: oil, enzyme conc., water content. The above parameters were varied with every new reaction and hence the optimized results were found out at a particular parameter value. Hence in this manner all the parameters were studied carefully to reach optimized production.

3. Experimental Setup

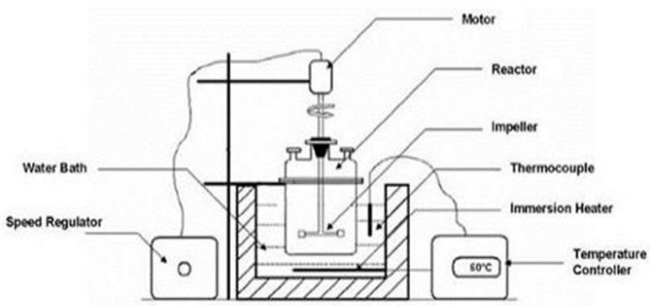
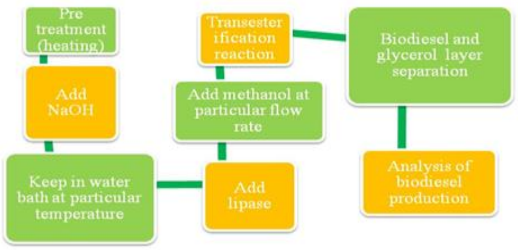
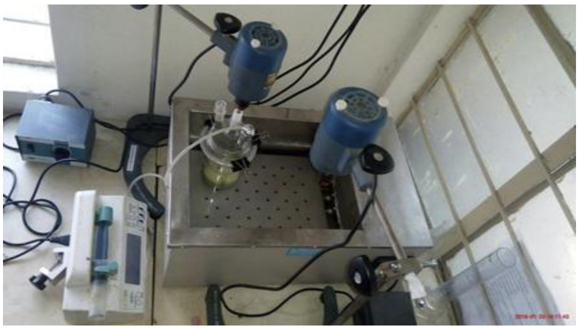


Fig 3 Schematic Diagram for Experimental Setup

Flowchart for Experimental Procedure





3.1 Analytical Methods

3.1.1 Gas Chromatography

A gas chromatograph (GC) is an analytical instrument that measures the content of various components in a sample. The analysis performed by a gas chromatograph is called gas chromatography. Principle of gas chromatography: The sample solution injected into the instrument enters a gas stream which transports the sample into a separation tube known as the "column." (Helium or nitrogen is used as the so-called carrier gas.) The various components are separated inside the column. The detector measures the quantity of the components that exit the column. To measure a sample with an unknown concentration, a standard sample with known concentration is injected into the instrument. The standard sample peak retention time (appearance time) and area are compared to the test sample to calculate the concentration.

3.1.2 Percent Conversion

The Percent Conversion is the calculation for the overall reaction of the soybean oil with the lipase catalyst.
Formula:

$$\% \text{ Conversion} = \frac{\text{Initial mass of oil} - \text{unreacted mass of oil x 100}}{\text{Initial mass of oil}}$$

4. Results

Five main parameters were optimized in this project. They are as follows:

4.1.1 Effect of Molar Ratio of Methanol to Oil on Biodiesel Synthesis

One of the most important variables affecting the yield of ester is the molar ratio of alcohol to triglyceride. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of glyceride to yield three moles of fatty acid ester and one mole of glycerol. The molar ratio is associated with the type of catalyst used. For example, a reaction conduced with an acid catalysed needed a 30:1 ratio of BuOH to palm oil, while a alkali catalysed reaction required only a 6:1 ratio to achieve the same ester yield for a given reaction time. Higher molar ratios result in greater ester conversion in a shorter time. During the ethanolysis of peanut oil with a molar ratio alcohol:oil of 6:1 the amount of glycerin liberated was more than did a 3:1 molar ratio. In this point is important to consider the type of alcohol that is been used. This is because during ethanolysis, as this alcohol has chemical affinity for both glycerine and ester, the higher the molar ratio is more difficult to separate the both phases. The stoichiometric ratio for transesterification requires 3 moles of methanol for each mole of oil to yield 3 moles of fatty acid methyl ester and 1 mole of glycerol. Since the transesterification reaction is reversible reaction, excess methanol is required to drive the reaction towards product. Effect of varying ratio with each different batch can be seen in the below table 4.1.

Table 4.1 Effect of varying Molar Ratio of Methanol: Oil

Batch No.	Oil (ml)	Oil:Methanol	Enzyme (ml)	NaOH (ml)	Reaction temperature (°C)	Reaction time (hrs)	% Conversion
1	150	1:1	1.07	4	30	3.5	98.61
2	150	1:2	1.07	4	30	3.5	98.02
3	150	1:3	1.07	4	30	3.5	99.10
4	150	1:4	1.07	4	30	3.5	97.00
5	150	1:5	1.07	4	30	3.5	98.5
6	150	1:6	1.07	4	30	3.5	98.1

From the above table 4.1 we can see that all other parameters are kept constant except the molar ratio of oil: methanol parameter. The ratio is varied so that study can be made to find out the optimized batch at which the conversion is at its most. From the table 4.1 it can be seen that the batch no. 3 is the optimized batch with 99.10% conversion and least density of the biodiesel as needed. This batch at many points matches the factors to be a stable biodiesel. Even it can be seen that after batch 3 there is a sudden decrease in conversion; hence, we can say it as a critical point of the synthesis.

4.2 Effect of Enzyme Concentration on Biodiesel Synthesis

The catalysts for biodiesel can be separated into two major groups: homogeneous & heterogeneous. Homogeneous type forms a single-phase mixture when added to oil and alcohol while the heterogeneous do not mix in the reaction medium. The group of homogeneous catalysts is divided into acid and basic and heterogeneous into metal oxides, metal complexes, active metals loaded on supports, zeolite, resins, membranes, and lipases The criterion for choosing which type of catalyst use should take into account firstly, the quality of raw material, but also the type of alcohol, the costs of the catalysts and technological route to be used for biodiesel production. Addition to the batches were done according to table 4.2.

Table 4.2 Batches for enzyme concentration

Batch No.	Oil (ml)	Oil:Methanol	Enzyme (ml)	NaOH (ml)	Reaction Temperature (°C)	Reaction time (hrs)
1	150	1:3	1.0	4	30	3.5
2	150	1:3	1.7	4	30	3.5
3	150	1:3	1.5	4	30	3.5
4	150	1:3	2	4	30	3.5
5	150	1:3	3	4	30	3.5

In table 4.2 the enzyme concentration parameter were changed with each upcoming batch to find out the optimized value at which the conversion is utmost.

4.2.1 Effect of Enzyme Concentration

It can be seen that the batch no. 3 is the optimized batch with 100% conversion.

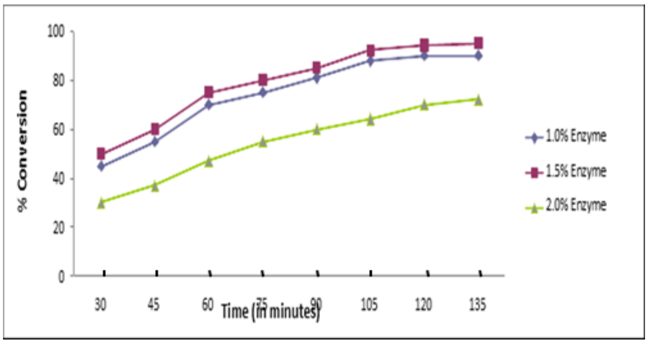


Fig 4. Effect of Enzyme Concentration on Biodiesel Synthesis

4.3 Effect of Reaction Temperature on Biodiesel Synthesis

Transesterification can occur at different temperatures depending on the types of catalyst and alcohol used. The influence of reaction temperature on conversion of palm oil to biodiesel was investigated with four different temperature. All other parameters are kept constant except the reaction temperature parameter. The temperature is varied so that study can be made to find out the optimized batch at which the conversion is at its most. From the result shown in Figure 3, the conversion increased as the reaction temperature increased and give the highest conversion of 97% at 40°C.

Table 4.4 Batches for reaction temperature

Time(Min)	Temperature (˚C)				
	30	35	40	45	
30	56	55	60	45	% Conversion
60	63	68	71	53	
90	75	80	85	62	
120	80	90	96	77	
135	85	93	97	84	

Transesterification can occur at different temperatures depending on the vegetable oil used, taking care not to exceed the boiling point of the alcohols used. In methanolysis of castor oil to methyl ricinoleate, with a molar ratio of 6:1-12:1 and 0.005-0.35% (by weight of oil) of NaOH catalyst, the reaction proceeded most satisfactorily at 20-35°C. For the transesterification of refined soybean oil with methanol, molar ratio alcohol:oil of 6:1 and 1% NaOH of catalyst, three different temperatures were used [5]. After 0.1 h, ester yields were 94, 87 and 64% for 60, 45 and 32°C, respectively. After 1 h, ester formation was identical for the 60 and 45°C runs and only slightly lower for the 32°C run.

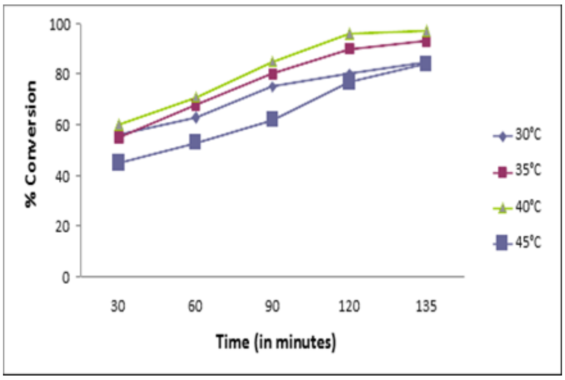


Fig 5. Effect of Reaction Temperature on Conversion.

4.4 Effect of Reaction Time on Biodiesel Synthesis

The conversion rate of vegetable oils into biodiesel increases with reaction time. Transesterified palm, cottonseed, sunflower and soybean oils under the condition of methanol to oil ratio of 6:1, 0.5% sodium methoxide catalyst and 60°C. After 1 minute, a yield of 80% of biodiesel was observed for soyabean and palm oils, and after 60 minutes, the conversions were almost the same for all four oils. During the transesterification of beef tallow with methanol the reaction was very slow during the first minute due to the mixing and dispersion of methanol into beef tallow. In the next five minutes, the reaction proceeded very fast [5]. The production of beef tallow slowed down and reached the maximum value at about 15 min. The di- and monoglycerides increased at the beginning and then decreased. At the end, the amount of monoglycerides was higher than that of diglycerides.

Table 4.4 Batches for Reaction Time

Batch No.	Oil (ml)	Oil:Methanol	Enzyme (ml)	NaOH (ml)	Reaction Temperature (°C)	Reaction time (hrs)
1	150	1:4	1.07	4	30	2.5
2	150	1:4	1.07	4	30	3.5
3	150	1:4	1.07	4	30	4.5
4	150	1:4	1.07	4	30	5.5
5	150	1:4	1.07	4	30	6.5

From the above table 4.4 we can see that all other parameters are kept constant except the reaction time parameter. The time is varied so that study can be made to find out the optimized batch at which the conversion is at its most. Thus batch no. 2 is optimized batch.

4.5 Effect of Methanol on Biodiesel Synthesis

Table 4.5 Batches for Method Concentration

The influence of catalyst (methanol) amount on the conversion of biodiesel was investigated. Methanol has an very important impact on the overall process of biodiesel production. Methanol was fed into the reactor by means of a syringe pump. Pumping of methanol helps to keep track on amount of methanol being added into the reactor to react with oil and carry out the conversion. Specific feed rate is set as per process requirements. Methanol feed rate of 12.5ml/hr was set throughout all the batches. The catalyst amount was varied in the range of 1-5 wt.%. The conversion was increased with the increased of catalyst amount from 1 to 3 wt.%.

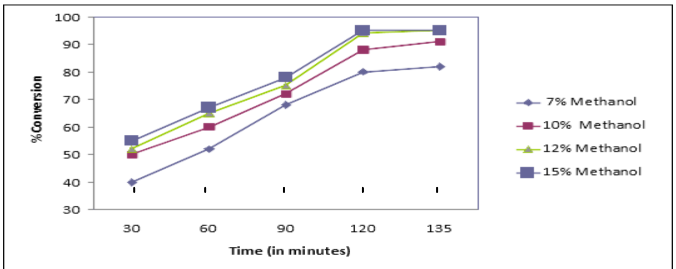


Fig 6. Influence of Methanol Conc. on Conversion

The lipase catalytic transesterification of vegetable oils is a promising method to obtain a substitute fuel for diesel engines. Lipase catalytic transesterification yield is often better when employing a basic catalyst, like sodium methoxyde, although acid catalysis might give better results, provided that free fatty acid content is high. Reaction parameters are strongly influenced by the type of oil employed, and a case to case optimization is required. The results have been verified with various analytical methods which showed satisfactory results. The parameters affecting the synthesis reaction were optimized at its best. The relationship between the various parameters has been successfully studied. The effects of the parameters like methanol/oil ratio, enzyme concentration, reaction temperature, reaction time, and water content were studied and optimized successfully. At different concentrations of enzymes of 1%, 1.5% & 2 %, highest conversion is obtained at 1.5% of enzyme. Enzyme concentration increases as % conversion increases. At different concentration of methanol 7%,10%,12%,15% highest conversion is observed at15%. At different temperature of 30,35,40,45 highest conversion is observed at 40˚C. Also we have studied effect of water content. The starting materials used for alkali-catalyzed transesterification of glycerides must meet certain specifications. The presence of water during alkali catalyzed transesterification causes a partial reaction change to saponification, which produces soap. For that reason, the glycerides and alcohol must be substantially anhydrous. A small amount of soap favors the consumption of catalyst and reduces the catalytic efficiency, as well as causing an increase in viscosity, the formation of gels, and difficulty in achieving separation of glycerol. The free fatty acid content of the refined oil should be as low as possible, below 0.5%, and it also stressed the importance of oils being dry and free of free fatty acids.

Time(Min)	%Conversion Methanol Concentration (in %)			
	7	10	12	15
30	40	50	52	55
60	52	60	65	67
90	68	72	75	78
120	80	88	94	95
135	82	91	95	95

5. Conclusion

The lipase catalytic transesterification of vegetable oils is a promising method to obtain a substitute fuel for diesel engines. Lipase catalytic transesterification yield is often better when employing a basic catalyst, like sodium methoxyde, although acid catalysis might give better results, provided that free fatty acid content is high. Reaction parameters are strongly influenced by the type of oil employed, and a case to case optimization is required. The results have been verified with various analytical methods which showed satisfactory results. The parameters affecting the synthesis reaction were optimized at its best. The relationship between the various parameters has been successfully studied. The effects of the parameters like methanol/oil ratio, enzyme concentration, reaction temperature, reaction time, and water content were studied and optimized successfully. At different concentrations of enzymes of 1%, 1.5% & 2 %, highest conversion is obtained at 1.5% of enzyme. Enzyme concentration increases as % conversion increases. At different concentration of methanol 7%, 10%,12%,15% highest conversion is observed at15%. At different temperature of 30,35,40,45 highest conversion is observed at 40˚C. Also we have studied effect of water content. The starting materials used for alkali-catalyzed transesterification of glycerides must meet certain specifications. The presence of water during alkali catalyzed transesterification causes a partial reaction change to saponification, which produces soap. For that reason, the glycerides and alcohol must be substantially anhydrous. A small amount of soap favors the consumption of catalyst and reduces the catalytic efficiency, as well as causing an increase in viscosity, the formation of gels, and difficulty in achieving separation of glycerol. The free fatty acid content of the refined oil should be as low as possible, below 0.5%, and it also stressed the importance of oils being dry and free of free fatty acids.

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