Biodiesel production by transesterification of *jatropha curcas* oil using homogeneous acid catalyst

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Abstract

Biodiesel has become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources. Biodiesel is one of the new possible substitutes of regular fuel for engines. The main reaction involved is the transesterification of triglycerides into esters. The production of biodiesel by transesterification process employing alkali catalyst has been industrially accepted for its high conversion and reaction rates. Recently, acidic and enzymatic (bio-catalyst) transesterification has attracted much attention for biodiesel production as it produces high purity product and uses various feed stocks.

In this work, transesterification reaction via homogeneous acid catalytic was studied. Sulfuric acid (H_2SO_4) was used as homogeneous acid catalyst. Here the raw materials used were jatropha oil and methanol as an alcohol in the reaction and the effects of the main variables involved in the process, reaction temperature, amount of catalyst, the molar ratio alcohol/oil, speed of agitation were analyzed.

It was found that 5% (v/v) acid catalyst, 5 hr reaction time, 6:1 methanol to oil ratio, reaction temperature 60^{o} C and agitation speed 600 rpm are the optimum parameters for reaching higher conversion of jatropha oil to biodiesel. The results for quality check shows that the properties of blend (B20) and biodiesel (B100) meet the ASTM standards.

Keywords: Biodiesel, homogeneous, acid catalyst, jatropha curcas.

1. Introduction

Vegetable oils were initially tested by Rudolph diesel as possible fuel sources for the engine he developed in 1892. Today, because of the incitement from increasing petroleum prices, biodiesel (alkyl esters from vegetable oils or animal fats, defined by ASTM) is used as a substitute of the regular diesel. A great number of advantages are obtained by using biodiesel instead of normal diesel, namely, lower emission of CO due to a better combustion, a better lubricating effect on engines, non-sulfur emission and non-particulate matter pollutants.

The availability and sustainability of sufficient supplies of less expensive feedstock will be a crucial determinant delivering a competitive biodiesel to the commercials filling stations. Fortunately, inedible vegetable oils, mostly produced by seed-bearing trees and shrubs can provide an alternative. With no competing food uses, this characteristic turns attention to *Jatropha curcas*, which grows in tropical and subtropical climates across the developing world.

In many cases crude *jatropha curcas* oil quality deteriorate gradually due to improper handling and inappropriate storage condition. It was known that improper handling of crude *jatropha curcas* oil would cause the water content increase. In addition, exposing the oil to open air and sunlight for long time would affect the concentration of FFA increase significantly to high level of FFA above 1%. The FFA amount of crude jatropha curcas oil will vary and depend on the quality of feedstock.

The FFA and moisture contents have significant effects on the transesterification of glycerides with alcohol using catalyst. The high FFA content (>1% w/w) will happen soap formation and the separation of products will be exceedingly difficult, and as a result, it has low yield of biodiesel product. The acid-catalyzed esterification of the oil is an alternative.

This paper presents the development of one step process for the production of biodiesel from the raw *jatropha curcas* oil having the high FFA. The special attention was focused to optimize the parameters required to produce higher yields of biodiesel.

2. Experimental

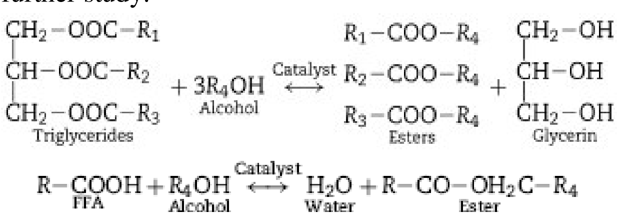
Raw *Jatropha curcas* oil was obtained from Gujarat Growell agro Forestry Private Limited, Ahmedabad. According to analysis jatropha oil had 185 mg KOH/g oil of saponification value, 25.320 g iodine/100 g oil of iodine value, 10.586 mg KOH/g oil of acid value and 5.29 % of FFA. The average molecular weight was

870 g/mol, calculated from the saponification value. The catalyst H_2SO_4 (98%) and methanol were obtained from local laboratory reagent distributor.

2.1 Transesterification reaction

For the reaction 50 Gms of jatropha oil was used as initial reactant. The raw jatropha oil was added to flat bottom flask and heated up to 60 ^oC for 10 minutes. Then acid catalyst H_2SO_4 was added into the flask and allowed to get reacted for 15 minutes. The quantity of catalyst was varied from 1 % to 6 % (v/v), to evaluate the optimum quantity of acid catalyst required. Then methanol as a second reactant was added to reaction mixture in the flask. The quantity of methanol was varied by varying oil to methanol molar ratio, to find out optimum methanol quantity required for this reaction. The time for reaction was also varied, to find out optimum reaction time which gives higher conversion of oil to biodiesel. The reaction temperature for the reaction was kept constant but varied for different batches from 50 ^oC to 70 ^oC, to find out optimum reaction temperature. The stirrer speed was kept constant but it was varied for different batches from 300 to 700 RPM.

Then reaction mixture was allowed to be cooled for 15 minutes. Then it was transferred to settling funnel, to separate out the biodiesel and glycerin layers. Then after 24 hrs of settling time the layers were separated and the samples collected in the sample bottles for further study.



Where R, R_1, R_2, R_3 and R_4 denotes any hydrocarbon chain.

2.2 Analysis Method

After transesterification is over, the reaction mixture was cooled and was allowed to settle down to separate into two layers. The oil phase consisted of methyl esters and unreacted triglycerides, while the aqueous phase mainly contained methanol and glycerol. The residual methanol was separated from the liquid phase by distillation. Glycerol formed after the reaction was weighted and mole was to be calculated. This mole value of glycerol is compared with theoretical value. And based on this difference conversion of triglyceride was found out.

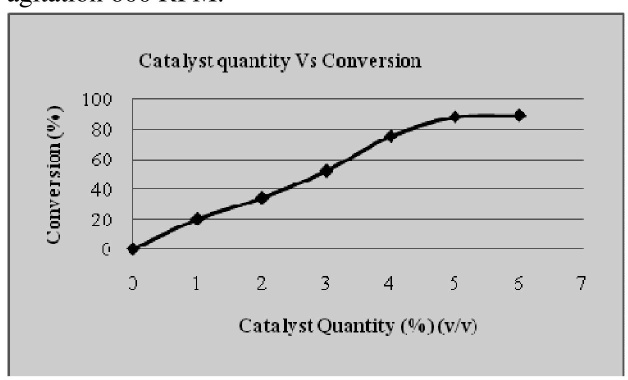
3. Results and Discussions

As given in experimental section the most relevant variables for the reaction which were studied were:

- Catalyst Quantity.
- Methanol to oil molar ratio.
- Reaction time.
- Reaction temperature.
- Speed of agitation.

3.1 Catalyst Quantity

The effect of the quantity of catalyst on the conversion was checked in this part. The catalyst amount was varied in the range of 1.0 % – 6.0 %. These percentages were volume fractions of the oil supplied for this reaction. As shown in Figure, the conversion was increased firstly with the increase of catalyst amount from 1 to 5%. But, with further increase in the catalyst amount the conversion was remained as it was. Therefore 5 % v/v quantity of acid catalyst is optimum for the jatropha oil used. Addition of further catalyst showed decreased conversion of oil. The conditions were: reaction time 6 hours, methanol to oil molar ratio 6:1, reaction temperature 60 ^oC and speed of agitation 600 RPM.

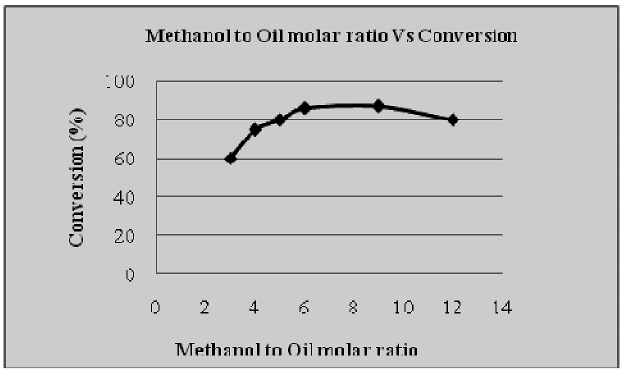


The effect of catalyst quantity on the conversion

3.2 Methanol to Oil molar ratio

One of the most important variables affecting the yield of ester is the molar ratio of alcohol to triglyceride. The stoichometric ratio for transesterification requires three moles of alcohol and one mole of triglyceride to yield three moles of fatty acid alkyl esters and one mole of glycerol. However, transesterification is an equilibrium reaction in which a large excess of alcohol is required to drive the reaction to the right. The molar ratio has no effect on acid, saponification and iodine value of methyl esters However, the high molar ratio of alcohol to vegetable oil interferes with the separation of glycerin because there is an increase in solubility. When glycerin remains in solution, it helps drive the equilibrium to back to the left, lowering the yield of esters.

As is evident from Figure, when the methanol loading amount was increased, the conversion was increased considerably. The maximum conversion was obtained when the molar ratio was very close to 6:1. However, with further increase in the molar ratio there was only little improvement in the conversion. Therefore, it can be could concluded that to elevate the conversion, an excess methanol feed was effective to a certain extent. For a molar ratio of 12:1 the separation of glycerin is difficult and the apparent yield of esters decreased because a part of the glycerol remains in the biodiesel phase. Therefore, molar ratio 6:1 seems to be the most appropriate.



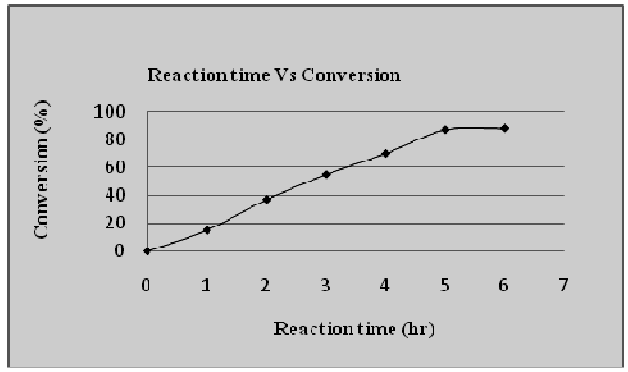
The effect of methanol to oil molar ratio on the conversion

3.3 Reaction Time

For every reaction, the reaction time is the most important parameter, because it affects the overall cost of production. So it is required to evaluate the optimum reaction time. In this study the effect of reaction time on the biodiesel reaction was studied. In Figure below, the conversion versus reaction time observed during experiments are shown. During all batches the catalyst quantity was kept 5 % (v/v), reaction temperature at 60^{o}C, speed of agitation was 600 RPM with methanol to oil ratio of 6:1. It is obvious that the conversion increases as the reaction time for transesterification increases. But after some time it reaches to its equilibrium condition and conversion cannot go beyond that. It can be seen that the conversion increased in the reaction time range between 1 and 5 h, and thereafter it remained nearly constant. The maximum conversion it could reach was 87% in 6 hr of operation for used raw materials. Therefore the reaction time, 5 hr is the optimum time to achieve highest conversion of oil to biodiesel.

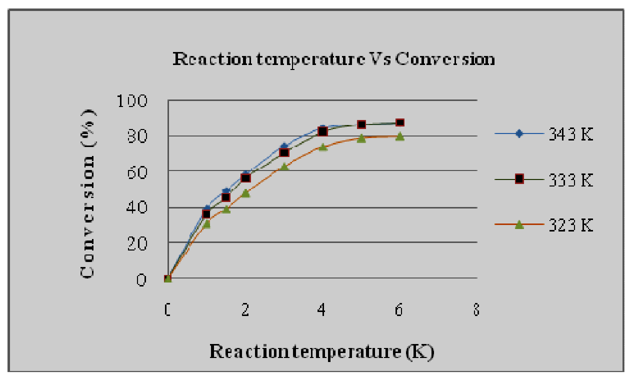
3.4 Reaction Temperature

Transesterification can occur at different temperatures, depending on the oil used. For the transesterification of jatropha oil with methanol to oil molar ratio (6:1) and 5% H_2SO_4 (v/v), the reaction was studied with three different temperatures. Other parameters like reaction



The effect of reaction time on the conversion

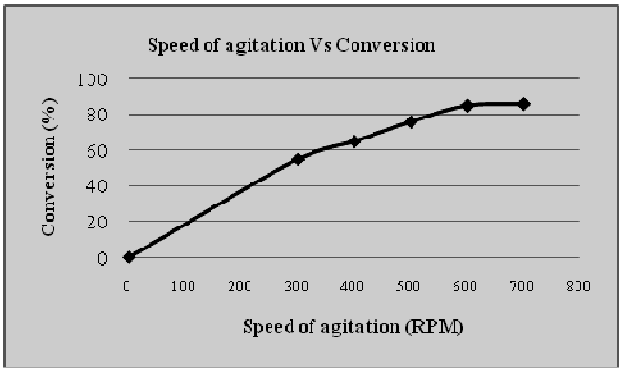
time 5 hr and speed of agitation 600 RPM was kept constant. Temperature clearly influenced the reaction rate and yield of esters. For the temperature 323 K reactions occurred well but in 333 K reactions it gave higher conversion. Further increase in reaction temperature by 10 K gave higher conversion initially, but in the end, it gave the same conversion as 333 K. Further increase in temperature shown lesser conversions because methanol has boiling point of 343 K to 348 K. From all this reaction temperature vs. conversion data the kinetic study has been done. The order of reaction was found out by integral method and From Arrhenius' law activation energy of reaction was calculated.



The effect of reaction temperature on the conversion

3.5 Speed of Agitation

Mixing is very important in the transesterification reaction, as oils or fats are immiscible with methanol solution or catalyst No reaction was observed without mixing. Thus, the methanolysis reaction was carried out at different stirring speeds for 6 hr. As shown in figure at lower stirring speed, the oil conversion reached only 55%, whereas at 600 rpm the oil conversion reached 85% at the same reaction conditions. These results showed that an efficient mixing of the reagents is important for higher conversions.

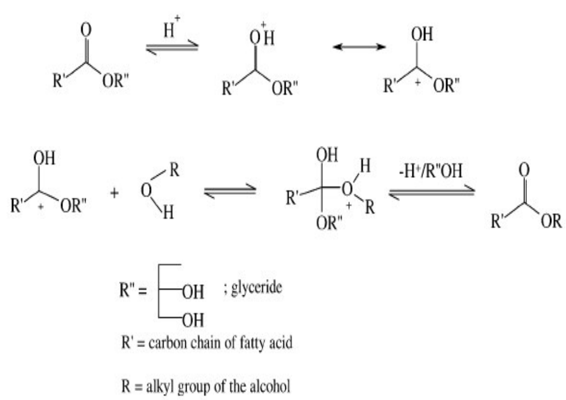


The effect of speed of agitation on the conversion

4. Kinetics study

The rate of a reaction depends on the reaction temperature. As the temperature increases, the molecules move faster and therefore collide more frequently. The molecules also carry more kinetic energy. Thus, the proportion of collisions that can overcome the activation energy for the reaction increases with temperature.

The only way to explain the relationship between temperature and the rate of a reaction is to assume that the rate constant depends on the temperature at which the reaction is run.



Acid catalyzed reaction mechanism

The initial step is protonation of the acid to give an oxonium ion (1), which can undergo an exchange reaction with an alcohol to give the intermediate (2), and this, in turn, can lose a proton to become an ester (3). Each step in the process is reversible, but in the presence of a large excess of the alcohol, the equilibrium point of the reaction is displaced so that esterification proceeds virtually to completion.

Temperature	**Order of reaction n**	**Rate constant K (hr^{-1})**
70 °C	0.958	0.948
60 °C	0.952	0.812
50 °C	1.007	0.751

Order of reaction and rate constant for different temperatures

From these values activation energy was found out by Arrhenius' law:

Rate constant $k = k_o\ e^{(-E/RT)}$

Activation energy E = 2561 cal and

Frequency factor K_O = 40.08

5. Conclusions

Experiments on the effects of variations in parameters shown that the acid catalyst quantity required is 5 % (v/v), which is optimum for the transesterification reaction of used raw jatropha oil. The other values of parameters like, reaction time is 5 hr, reaction temperature 60 ^oC, oil to methanol molar ratio of 1:6, agitation speed of 600 RPM are optimum for the raw jatropha oil used for biodiesel reaction at laboratory scale. And the order of reaction is one and activation energy of the reaction is about 2561 calories and frequency factor is 40.06.

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