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BIOLUBRICANTS FROM JATROPHA CURCAS SEED OIL AND SIMAROUBA SEED OIL --1 ESTERIFICATION

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ABSTRACT

In all types of machines moving parts rub against each other and cause friction. A substance which is introduced in between the moving parts in order to reduce friction is the lubricants. The increase in the environmental pollution and the diminishing reserves of petroleum has brought the attention towards the bio-lubricants, an alternative source to the conventional petroleum oil based lubricants. The major advantage of the biolubricant being the biodegradability, non toxic and zero green house gases. This paper gives an insight into the advantages of the biolubricant derived from bio source. In this project the Jatropha curcas oil and Simarouba oil was used as a feedstock for producing biolubricant. A two step process for lubricant production was assisted by acid esterification to reduce the free fatty acid content and co-solvent transesterification. The total reaction time was shorter than previous studies. Therefore the two step catalyzing process has a potential application in producing biolubricant from seed oils.

INTRODUCTION

Biolubricant is an alternative to the petroleum based lubricants have received attention in recent years. The most important reason for this being the renewability, non-toxic and the bio-degradability.

Jatropha curcas is an oil rich, drought resistant shrub which originated in the central america and can be easily grown in the tropical and the sub-tropical regions of the world[8]. Today the interest in this oil has increased due to their high oil content which on transesterification yields a methyl ester with competing properties than most of the other seed oils[2][13][14][15][16].

Simarouba glauca, a multipurpose tree that can grow well under a wide range of hostile ecological conditions, offers a great hope. It is found in the rainforests and savannahs of South and Central America and the Caribbean. However, in our present context, the seeds are the most important part as they contain 60-75% oil. The potential impact of bio based lubricant is immense in countries with no indigenous fossil fuel and for regions remote from source of supply. One of the advantage of biolubricant being the absence of sulphur which is environmentally friendly since it emits zero sulphur based greenhouse gases.

Biolubricant production through transesterification[4] involves reaction of methanol with oil. The primary problem with the transesterification is the presence of free fatty acid in the oil. Another with the methanol and oil is their immiscibility. Hence the surface of contact of the reacting molecules is very less. This lowers the rate of reaction leading to low reaction rates, longer reaction times and hence higher operating costs.

The oil rich in free fatty acid cannot be taken up for co-solvent transesterification since it leads to a lesser yield. Hence the Jatropha and the Simarouba oil was initially taken up for acid esterification process. This reduced the free fatty acid content to less than 0.5%[1][2]. Later it was mixed with the co-solvent tetrahydrofuran as proposed by Boocock et al., 1998[5][6]. This yielded a single layer of solution facilitating the mixing of molecules and hence enhanced reaction rate. The reaction took place in less than half an hour. Tetrahydrofuran(B.P -65.8°C) is chosen because of its closeness of the boiling point to that of methanol (B.P-64.4 °C) [12]. By this both the solvents can be recovered at a time and sent for recycling[7].

The objective of this work is to optimize some of the parameters in the acid esterification and the transesterification steps[19][20].



EXPERIMENTAL PROCEDURE

A. Materials:

The Jatropha and Simarouba seed oil in this study was supplied by GKVK, Bangalore and the chemicals used in the synthesis and testing were of reagent grade. The reactions were carried out in a 2000 ml three-necked flat bottom flask to facilitate the use of magnetic stirrer.

The flask was fitted with a reflux condenser, thermometer and a stopper to enable the addition of feed and reactants. The reaction mixture was heated through a heating mantle.



Figure 1: Experimental setup

B. Experimental Methods:

1) Pre-treatment:

The oil was heated to 110°C for half an hour in an oven and cooled in the Dessicator with silica gel crystals.

2) Acid based esterification:

The free fatty acid (FFA) if not reduced will lead to saponification reaction in the transesterification step [9][11]. The Jatropha oil and Simarouba oil had an FFA content of 9.8% and 19.6% respectively. The reduction of this was accomplished by reacting it with methanol in the presence of concentrated sulphuric acid. The methanol along with sulphuric acid (2% w/w with oil) was heated to 60°C. 100 g of oil is weighed and transferred to the flask. The temperature was maintained between 60-65°C. The Methanol:Oil ratio used was 6:1 by volume. The flask was fitted with the reflux condenser and the thermometer. A pipette was used to draw the samples at the interval of 10 minutes and was titrated to determine the % FFA level and acid value.

3) Oil Transesterification:

The pretreated oil was transesterified using methanol and THF for half an hour. The methanol to oil molar ratio and methanol to THF ratio was 3:1 and 1:1 respectively (by volume). Reaction was catalysed with 1% potassium hydroxide and the temperature of the reaction bath was maintained at 40°C. The reaction was carried out in the same setup used for acid esterification step (Figure 1).

4) Purification:

The resulting methyl ester was next distilled in a simple round bottom distillation flask with two neck. To one neck was connected the thermometer and the other to a simple condenser circulated with water to condense the contents hence removing the methanol and cosolvent mixture. The heat to the flask is supplied and regulated

from a heating mantle. After this the contents in the flask was separated from glycerol in the separating funnel. The pure methyl ester layer was washed with hot distilled water and dried in a desiccator. The optimized method from Jatropha oil in the discussion was used for the conversion of fatty acids in Simarouba oil by two step method and finally simple distillation to remove methanol and THF.

RESULTS AND DISCUSSION

Various factors affecting the reaction was checked and few of them was taken for optimization[3]. Initial acid value of Jatropha oil and Simarouba oil are 26.8% and 39.22% respectively.

A. Acid catalyzed esterification:

On the first step of pretreatment of crude Jatropha and Simarouba oil, the objective is to reduce the Free Fatty Acid content to less than 0.5%.

1) Effect of Temperature during Acid esterification

The effect of Temperature on FFA is shown in Figure 2.

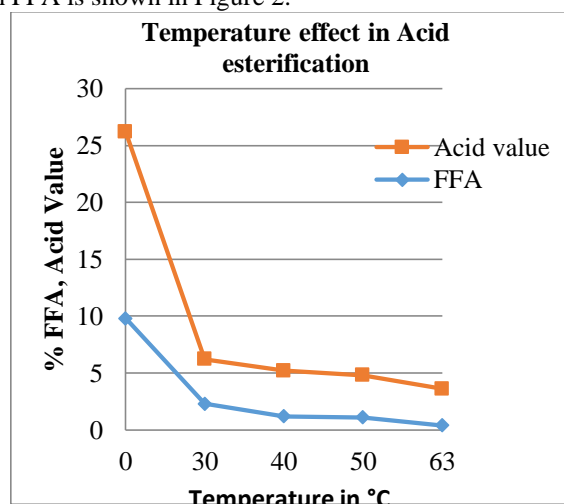


Figure 2: Temperature Vs FFA and Acid value in the acid transesterification step

Temperature is one of the vital factor which affects the conversion of the fatty acid. Reaction temperature should be preferably lower than the boiling point of methano, to ensure that methanol will not leak out through vaporization. The temperature was varied from 30 to 65°C.

In all the experiments the catalyst concentration was 2% w/w sulphuric acid with oil, Methanol : Oil ratio of 6:1 and duration of one hour. From the figure it can be seen that FFA had reduced to 2.3% at 30°C and decreased gradually to less than 0.5% at around 65°C. In conclusion and considering the objective of the experiment, 63-65°C was selected as optimum temperature for acid esterification reaction of Jatropha oil.

2) Effect of Reaction Time during Acid esterification

In order to optimize the reaction time the different reaction time selected was 10, 20, 30, 40, 50 and 60 minutes. The catalyst concentration was 2% w/w sulphuric acid to sample, temperature maintained at 63°C and Methanol to Oil ratio of 6:1 by volume were maintained. Figure 3 shows the reaction time variation with acid value and FFA.

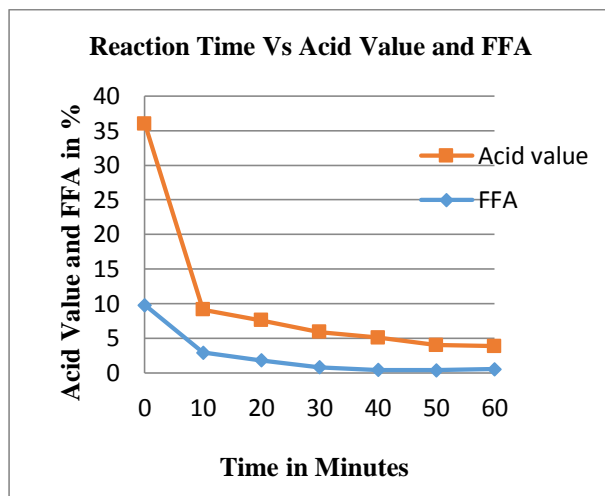


Figure 3: Reaction time Vs FFA and Acid value in the acid transesterification step

As observed in the figure the FFA values decreases sharply to 2.9% at 10 minutes and decreases gradually to less than 0.5% at 40 minutes. Increasing the reaction time further did not have any effect on the conversion of FFA. Hence the optimum Reaction time was chosen as 40 minutes.

3) Effect of Catalyst concentration on Acid esterification reaction

The effect of catalyst that is sulphuric acid concentration in the acid esterification reaction was investigated with concentration varying from 0.5% to 2% w/w with oil sample. The operating condition for the reaction was fixed at temperature of 63°C, Reaction time of 1 hour and volume ratio of methanol to oil of 6:1. Figure 4 shows the change in FFA and Acid Value with the variation in catalyst concentration.

The FFA was found to be decreased from an initial value of 9.8% to 0.44% in 40 minutes. The FFA content reduced sharply to 2.6% at a catalyst concentration of 0.5% but would reach below 0.5%, our set objective only at 2%.

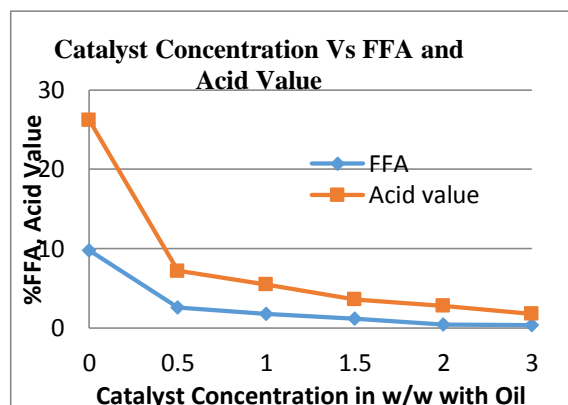


Figure 4: Catalyst concentration Vs FFA and Acid value in the acid transesterification step

The increase in catalyst concentration however did not have significant effect on the conversion of FFA. Hence the optimum quantity of sulphuric acid catalyst was chosen as 2% for this reaction.

B. Base catalyzed cosolvent transesterification reaction

The pretreated oil with acid esterification step was further transesterified to methyl ester catalysed by potassium hydroxide in the presence of Tetrahydrofuran as cosolvent. The set objective was to reduce the acid value to less than 0.5% in this reaction.



1) Effect of Reaction temperature

The effect of Reaction temperature is investigated at first to understand the optimum temperature for the reduction of acid value in the transesterification reaction. The temperature was varied between room temperature (27°C) to 65°C which is the boiling point of methanol. In all the experiments the methanol to oil ratio was taken as 3:1 by volume, KOH concentration of 1% and the reaction time of 30 minutes. The cosolvent used was 1:1 with methanol by volume.

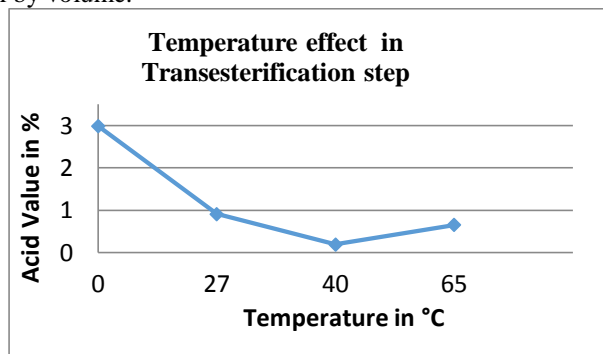


Figure 5: Temperature effect in the base transesterification step

The Acid value measured at 40°C was 0.19% and later increased to 0.65% at 65°C. The experimental result indicates temperature higher than 40°C had negative impact on methanolysis of oil to ester. At higher temperature chances of loss of methanol may also lead to negative impact. Hence the optimum temperature was chosen to be 40°C for cosolvent transesterification.

2) Effect of Catalyst concentration

The variation in the catalyst concentration adopted in this study was 0.5%, 1% and 1.44%. The temperature was maintained at 40°C, methanol to oil ratio of 3:1 and cosolvent to methanol ratio of 1:1 was maintained during all the above studies. The reaction was conducted for 30 minutes.

Figure 6 shows the reduction in acid value with different concentration of catalyst.

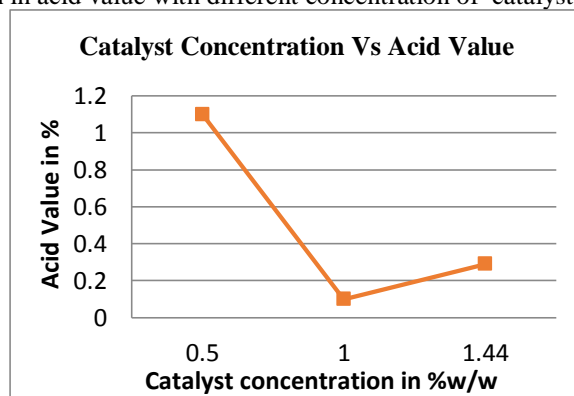


Figure 6: Catalyst concentration Vs Acid value in the base transesterification step

It was observed that maximum conversion of acids occurred at catalyst concentration of 1% KOH. With the increase in catalyst concentration there was a slight decrease in conversion of acid to esters since the acid value was 0.29% however within our set objective. This could be because of the saponification as the side reaction with the KOH catalyst. Hence 1% KOH was taken as the optimum catalyst concentration for the effective transesterification using cosolvent method.

3) Effect of Reaction time

The experiment was conducted for 50 minutes and the acid value was checked at the time interval of 10 minutes.

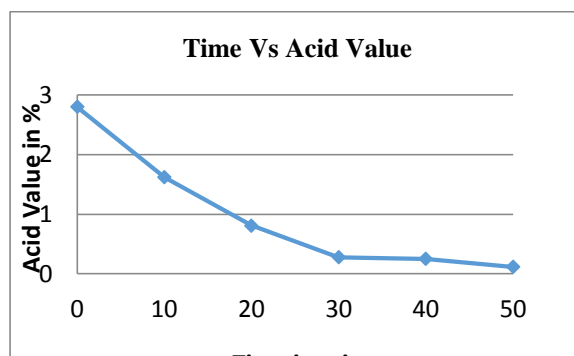


Figure 7: Reaction time Vs the Acid value in the base transesterification step

This experiment was carried out with the reaction temperature of 40°C, catalyst concentration of 1% KOH and methanol : oil ratio by volume at 1:3. The cosolvent to methanol ratio was 1:1. From the above figure we can observe that the reaction proceeds very fast and the conversion of fatty acid is below 0.5% at 30 minutes. As the time proceeds the conversion does not vary much. Although a considerably good conversion is obtained at 20 minutes, the optimum reaction time is taken as 30 minutes as it achieves the set objective.

CONCLUSION

In conclusion the two step method coupled with cosolvent in the second step is an efficient method and saves time for the production of methyl ester from *Jatropha* oil with high free fatty acid. The two step method optimized was selected to increase the conversion of fatty acid and is also cost effective. The first step, acid esterification or the pretreatment step reduced the free fatty acid content to a stringent limit of less than 0.5% under the optimized conditions discussed above. The second step base transesterification using cosolvent gave a better yield more than 95% conversion of the fatty acids present in the oil sample. The total time consumed in both the steps was below two hours compared to conventional method of two step esterification which is around four hours. This will give a more economical process although there is an addition of simple distillation operation to remove the solvent mixture. Overall the above two step method offers an avenue for reduction in cost of material and energy in biofuel production.

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