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# Optimization Of Reaction Parameters For Biodiesel Production From ACPO Using Different Catalysts

Biodiesel Production

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***Abstract*— The alternative fuel Biodiesel though has enormous beneficial impacts, producing it economically is the greatest challenge. In the present study there has been an effort made to produce it economically. Here ACPO (Acidic Grade Crude Palm Oil) a waste was chosen as the feedstock using Sulphuric acid ($H_2SO_4$) as a catalyst for esterification followed by another catalyst Sodium Hydroxide (NaOH) for trans-esterification. Single parameter optimization technique is adopted towards biodiesel production. The operating parameters like oil to methanol, catalyst concentration and duration were varied in the range (5:0-5:1.8), (2-6%) and (60-120 minutes) respectively with other parameters like temperature and RPM at constant levels. And the derived optimized parameters were oil to methanol ratio - 5:1.6, catalyst ($H_2SO_4$) concentration - 2%, temperature - 60$^oC$, RPM - 400 for 90 minutes duration. With the adoption of optimized parameters the obtained yield was 80.3%. The produced biodiesel was tested for physico-chemical characterization. And the results obtained are comparable to the IS and ASTM standards shows the adoption of the biodiesel in the CI engines without any modifications.**

***Keywords*— *Biodiesel, ACPO, esterification, trans-esterification, optimization***

## I. INTRODUCTION

Biodiesel is a fuel of biological origin, an alternative or a substitute to presently using petroleum fuel broadly. Chemically it is the mixture of long chain fatty acids derived from a process said alcoholysis of triglycerides [5]. Indiscriminate usage, limited reserves of fossil fuels, increasing prises, to meet future demands and environment concern worldwide are the key driving factors towards the research and inventions on the alternative fuels.

Alternative new and renewable fuels like biodiesel can solve many socioeconomic problems and concerns, from global warming and air pollution to other environmental improvements and sustainability issues. All types of oils can be used for biodiesel production but edible are expensive and leads the food vs fuel debate. So, producing biodiesel in an economical way is the biggest challenge as discussed earlier. In this context non-edible oils and spent oil wastes from various sectors like hotels and oil milling units etc could be employed as a cheap feedstock for biodiesel production [1].

Generally biodiesel is produced by a method called 'Trans-esterification' for the oils with less FFA. It is the reaction between triglycerides and alcohol in the presence of alkaline catalysts like sodium hydroxide or potassium hydroxide. [11]. Trans-esterification is very sensitive to FFA content of oil. The feedstock with high FFA (>1%) leads to the formation of soap which reduces the catalyst efficiency and increases the viscosity of oil and makes the separation of glycerol very difficult. These all have direct impact and leads to less yield of esters. Oils used in trans-esterification have to be anhydrous (0.06%) as the presence of moisture leads to the hydrolysis process of some of the produced ester, with consequent soap formation. [1]

In our study we have utilized ACPO as a feed stock which is with high FFA level i.e.12.96%. So, the oil needs to be pre-treated (esterification) with catalysts (normally homogeneous acid catalyst) with methanol to reduce FFA level to < 1%. ACPO is a waste obtained in the oil milling process. Esterification is followed by alkaline catalysed trans-esterification process with methanol. Here the main objective of the study was to investigate the adoptability of ACPO as a low cost feedstock and optimization of operating parameters like oil to methanol ratio, catalyst concentration and duration for the reduction of %FFA level to less than 1% and so to produce biodiesel efficiently.

## II. MATERIALS AND METHODS

### *A. Materials*

ACPO, Methanol, Ethanol, Sulphuric Acid ($H_2SO_4$) and Sodium Hydroxide (NaOH) are some of the materials required for the process.

### *B. Method*

In the production of biodiesel two-step catalysis process has been followed i.e. both esterification and trans-esterification steps are followed. For these processes, parameters like catalyst concentration, oil to methanol ratio, and duration are optimized. A pre-treatment is done as the oil was with high %FFA (12.96%) level with $H_2SO_4$, a homogeneous acid catalyst followed by trans-esterification with NaOH, an alkaline catalyst with the adoption of optimized parameters in the presence of methanol.

Experimental setup:

The equipment has been fabricated to optimize the process conditions for biodiesel production. Batch stirred tank reactor of 1000 ml has been utilized for carrying out experimental trials where there was a provision to take out the sample during the process. It is equipped with a reflux condenser which are connected in a cascade format, a mechanical stirrer (200-5000 RPM), heating mantle by which the required temperature is maintained and a thermometer pocket to equip the thermometer. The utilization of chilled water increased the condenser efficiency (reducing the temperature of coolant for better reflux). Circulating pumps provides the constant discharge of coolant which is well regulated by providing the by-pass channel.

Pre-treatment of ACPO via Acid esterification:

ACPO usually exists in a semisolid phase at room temperature. So for moisture removal and for ease of handling it is preheated to around 70$^{o}$C, is the prior step of the process as adopted by [3]. After, preheated ACPO was poured into the three necked round bottom flask, a batch reactor for FFA to FAME conversion as a pre-treatment at different dosages using acid catalyst (esterification). Single factor optimization was followed for the process esterification to study:

1. Effect of catalyst concentration ranging (2- 6% w/w) of catalyst.
2. Ratio of ACPO to methanol (w/w) (5:1– 5:1.8).
3. Process duration (60- 120 min).

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## III. RESULTS AND DISCUSSIONS

Qualitative and quantitative analysis has to be conducted on the feedstock at room temperature that is selected for experimental trials. The Table 1 below reveals the detailed characteristics of the feedstock.

Table. 1. Characteristics of ACPO and their comparison with Palm Oil

| Parameters | ACPO | Std Palm Oil |
|---|---|---|
| Free Fatty Acid | 12.96% | 0.66 |
| Iodine Value | 65.04 | 10.8 |
| Saponification Value | 162 | 196.5 |
| Colour | Reddish brown | Straw colour |
| Specific Gravity | 0.97 | 0.86 |
| Acid number | 17.95 | < 1 |

As it is evident from Table 1, the key parameters like FFA, Iodine value and Acid value are found to be more and saponification value found to be lesser in the waste ACPO than the standard Palm oil, and so needs the pre-treatment to bring the FFA to less than 3% in the ACPO feedstock as advised by [6].

Optimization Steps:

Before stepping for the esterification process the process conditions/operating condition/reaction conditions for the production process was optimized by single parameter technique. The main objective of the process was to monitor the %FFA level. The major contributing factors which have direct effect on yield of biodiesel and quality of the biodiesel produced are oil to methanol ratio, reaction duration and catalyst concentration. However the other parameters like reaction temperature and RPM of stirring are kept as 60$^{o}$C and 400 RPM as most of the literature have opted for the similar conditions. For biodiesel production from pongamia pinnata temperature at 65$^{o}$C and 360 RPM was maintained by [10].

### *A. Optimization of Oil:Methanol molar ratio*

Here the main objective of the process is to obtain the optimal methanol to oil ratio towards biodiesel production per unit quantity of ACPO taken in reducing %FFA at 60 minutes duration.

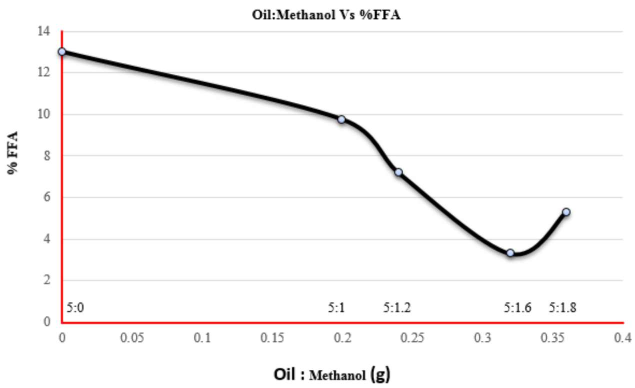


Fig. 1. Effect of Oil: Methanol on %FFA

The trials were conducted by varying the methanol amount from 10g to 18g for 50g of ACPO that is taken. From the above Figure 1, it is evident that at 16 units of methanol concentration the FFA reduction reached the saturation level. Therefore for every 5g of feedstock handled 1.6g of methanol is required to reduce %FFA to the maximum level. Several authors have reported the reduction of the FFA with different operating conditions. In such one study, oil to methanol ratio as 3:1 with 0.5% NaOH, 55$^oC$, and at 250 RPM operating parameters were optimized and adopted for the production of biodiesel from waste soybean oil in their study [2]. The quantity of the methanol consumption, all depends on the FFA content and rheology (Mass transfer between Methanol and oil) of the feedstock. Hence the difference exists.

*B. Optimization of Catalyst Concentration*

Here the effect of catalyst concentration on %FFA reduction was analyzed to get optimum catalyst concentration. This was performed by variation of the reaction duration along with the utilization of the optimized methanol concentration along with the constant parameter like temperature 60$^oC$ and RPM 400. The concentrations of the catalyst were varied in the range of 2 to 6% weight basis.

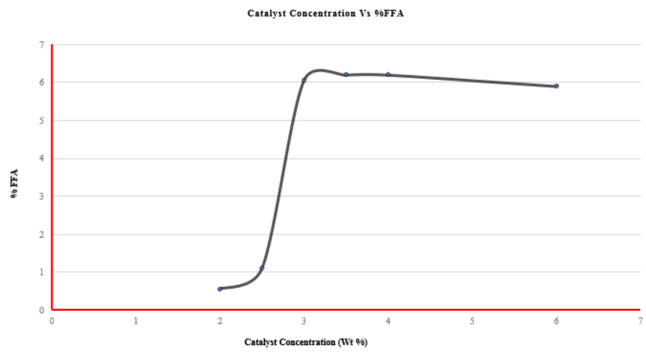


Fig. 2. Effect of $H_2SO_4$ (wt%) on %FFA

It was found from the experimental trials that, a catalyst ($H_2SO_4$) concentration of 2% (w/w) was the optimum dosage required to reduce %FFA effectively. Beyond 2% (w/w), the varied concentrations of the catalyst in FFA reduction was not significant. So with 2% (w/w) catalyst concentration the %FFA reduced significantly and is taken as the optimized parameter. By sulphuric acid catalyst the FFA was reduced from 12.96% to 0.56% which is within the acceptable limits. Several authors have reported that the permissible limit of FFA for the biodiesel production to give better yields with minimal soap formation is less than 1% [12]. Since the catalyst selected for the biodiesel production is satisfying the FFA limits, can be considered as the effective one for the biodiesel production from ACPO. Optimization of various acidic catalyst concentrations are reported in the survey of literature for the biodiesel production, found in the range of 1.43% to 10% (wt) for $H_2SO_4$. A catalyst concentration of 1.43% (wt) $H_2SO_4$ was utilized for esterification of Jatropha Curcas by [7] and with 10% (wt) $H_2SO_4$, [8] did the pre-treatment of waste vegetable oil.

*C. Optimization of Reaction time*

Prime objective of the present study conducted is to derive the optimal reaction duration for 2 % $H_2SO_4$. Here the effect of duration in reducing %FFA is investigated.

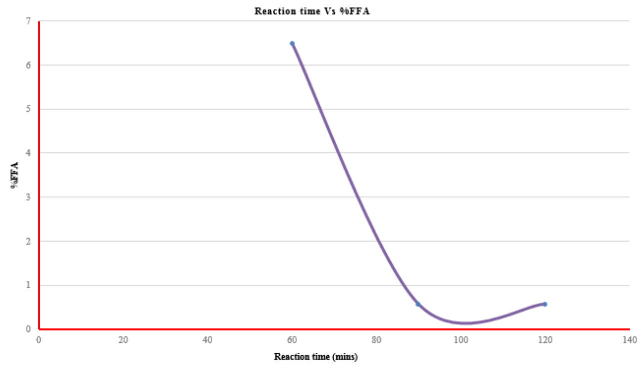


Fig. 3. Effect of Reaction time v/s %FFA for 2% $H_2SO_4$

From the Figure 3 it can be analyzed that, at 90 minutes reaction duration the reduction of %FFA reached the optimal level i.e. (0.564%) with 2% $H_2SO_4$ catalyst concentration. There was a saturation level in %FFA reduction there onwards. Hence, it is concluded that 90 minutes is the optimal reaction time for the process. Many authors have maintained different reaction duration such as 30 minutes during biodiesel production from LGCPO in biodiesel production [3]. It is done for %FFA reduction for better yield and also to reduce the viscosity. *The conversion rate depend on the reaction time [* 5].

*D. Trans-esterification with NaOH*

In our study NaOH is used as an alkaline catalyst for trans-esterification. Catalyst concentration of 3% alcoholic 1 N NaOH is used with above said optimized reaction conditions (5:1.6 oil to methanol ratio, 60$^oC$ , 400 RPM and 90 minutes reaction time) towards the better yield and conversion per cent as many of the literature surveys has opted for the similar conditions. The gravity settling of 24 hours lead to crude biodiesel, a product and glycerol by-product generation. Several authors chosen different alkaline catalysts like KOH, alkoxides etc. with different catalyst concentration with varied operating parameters. In a similar study, 1% wt KOH was utilized for trans-esterifying Jatropha oil by [4] and [9] used 1% wt NaOH catalyst concentration for trans-esterification process.

After trans-esterification the crude biodiesel was washed with warm distilled water, to drain out excess and unreacted catalyst, unreacted oil particles, dissolved glycerin, soaps and other impurities. After washing, biodiesel is heated to remove entrained water and excess methanol content.

Fig. 4. ACPO converted to Biodiesel

The highest yield in the process is obtained by adopting the derived optimized parameters towards the biodiesel production. The yield of biodiesel produced was around 80.3% for H2SO4 catalyzed process in our experiment. Several authors achieved different % yield from different feed stock. From Jatropha oil 99% yield was reported after the process [7]. When waste cooking oil was taken up for biodiesel production it has been reported that the obtained yield was around 90% [9].

### *E. Physico–chemical Characteristics of biodiesel from ACPO*

The physico- chemical properties of biodiesel produced were estimated as per IS (Indian Standards). And the test results obtained are compared with standard Biodiesel and Petro diesel in Table 2.

Table. 2. Physico- Chemical parameters of ACPO Biodiesel, Standard Biodiesel and Petro diesel as per ASTM standards.

| Parameters | Units | Results of ACPO Biodiesel as per IS: 1448 | Std Biodiesel (ASTM) | Petro Diesel (ASTM) | ASTM Standards |
|---|---|---|---|---|---|
| Calorific value | MJ/kg k | 38(P 6) | 37 to 42.5 | 43.5 | ASTM D 613 |
| Flash point | $^{o}C$ | 176 (P 66) | 130 | 54 | ASTM D 2500 ($\geq$130) |
| Cloud point | $^{o}C$ | 20 (P 6) | -3 to 12 | -28 to -7 | ASTM D 287 |
| Density at 15 $^{o}C$ | Kg/ $m^3$ | 0.865 (P 32) | 870-900 | 820 | ASTM D 445 |
| Viscosity at 40 $^{o}C$ | Cst | 4.7 (P 25) | 1.9 – 6.0 | 2.54 | ASTM D 97 |
| Pour point | $^{o}C$ | 10 (P 10) | -15 to 10 | -15 | ASTM D 613 |
| Fire point | $^{o}C$ | 186 (P 66) | | | ASTM D 613 |

## IV. CONCLUSION

The study conducted concludes that ACPO is a suitable low cost feedstock towards biodiesel production with pre-treatment using $H_2SO_4$ as a catalyst (acidic) using derived optimized parameters such as oil to methanol (5:1.6), $H_2SO_4$ catalyst concentration (2%) w/w, duration (90 minutes), temperature (60$^{o}$C), RPM (400). With the adoption of these parameters the %FFA of the feedstock reduced from 12.96% to 0.56%. The yield of the biodiesel was 80.3% and ester content was 95.32% (mol mol -1) with trans-esterification followed by further processing. The results obtained in the current study are comparably nearer to the standards set for it and hence produced biodiesel meets the standard specifications. Like the way different acidic catalysts could be explored in the esterification reaction. The comparative study may assists in highlighting the advantages and disadvantages of different catalysts used for the pre-treatment of acidic oils of various types.

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