

# Esterification Of Crude Cotton (*Gossypium Hirsutum*) Seed Oil As Feedstock For Biodiesel Production

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## Abstract

*Esterification of crude cottonseed oil was conducted in place of edible-oil refining to reduce the Free Fatty Acid (FFA) of the oil and make it more suitable for transesterification of the triglycerides. The esterification process has been found to have an advantage in comparison to Edible-oil refining process as it does not require neutralization, bleaching and deodorization of the oil. In this study, the effect of methanol to oil ratio and catalyst loading and temperature on FFA conversion has been investigated using a Batch reactor. The highest conversion of 96.7% is achieved, and the optimum methanol to oil molar ratio was found to be 7:1, using catalyst concentration of 1% by weight, a reaction temperature of 60°C and an agitation speed of 464rpm. The FFA content of the Crude Cottonseed Oil was reduced from 5.2% to 0.9%.*

**Key Words:** Esterification, Sodium hydroxide, Free fatty acid and Crude cottonseed oil.

## 1. Introduction

Diesel is the major fuel used in transportation especially for heavy duty vehicles such as trucks and trains. It is also used as fuel for heavy machinery such as Agricultural and Construction machineries. Today in Nigeria however, as a result of insufficient energy from the two major energy sources (Hydro and Gas), diesel fuel is not only used as transportation or heavy machinery fuel but also as energy generating plants fuel. This has put so much pressure on diesel supply thereby resulting in the instability of retail diesel fuel prices in our markets. Biodiesel which is easy to make for diesel engines is a promising diesel fuel alternative, produced mainly from agricultural feedstock (Vegetable oils and animal fats). Nigeria being an agricultural based country, production of such diesel fuel substitute is not only feasible but will also create employment for majority of the unemployed people. Even though

biodiesel is not the total solution to our present energy crisis, it certainly is an important component of a combined strategic approach to stabilize diesel fuel price and ultimately decrease our current dependence on fossil fuels which has its own contribution to environmental pollution.

Presently, production cost of biodiesel has become the primary barrier to its commercialization. The conventional method of biodiesel production is alkaline catalyzed transesterification process [11][14], which currently requires mainly high-quality food-grade vegetable oils as feedstock [8]. The use of high-quality food grade vegetable oil contributes to the high cost of biodiesel production and in addition, comes into direct competition with food, thus disturbing the balance in the distribution chain of edible vegetable oils. Conversion of oil into biodiesel by direct transesterification is complicated if it contains higher amount of free fatty acid (FFA) >4 mg KOH/g [16]. Free fatty acid form soap, making separation of products exceedingly difficult, resulting in low biodiesel yield. The acid-catalysed esterification of vegetable oils is an alternative [7], but it is much slower than the base-catalysed transesterification reaction. One way of reducing the biodiesel production costs is to use the less expensive feedstock containing fatty acids such as crude vegetable oils, inedible oils, animal fats, waste food oil and by products of vegetable oil refining [18]. The production of biodiesel from these low-cost raw materials which generally contain high amounts of FFA is a valuable alternative that would make their production costs more competitive than petroleum derived fuel. Currently, the production of biodiesel from these kinds of raw materials comprise of a two-stage process that was developed by Canakci [5], which requires an initial acid-catalyzed esterification of the FFA, followed by a base-catalyzed transesterification of the triglycerides. The two-stage process has been applied by quite a number of

investigators on different low-grade oils [9][18][17][2][15]. Despite the fact that the two-step process showed promising result, investigators were mostly interested in the conversion and yield of the second stage of the process (transesterification), which produces the biodiesel.

This paper presents the conversion using different methanol to oil ratio and different catalyst loading, in the first stage (esterification) of the two-stage process using crude cottonseed oil, processed in Yola, North East Nigeria. Cottonseed oil has unique minor components, such as natural anti-oxidants gossypol [13] and carotene [4] which played an important role in retarding the oil oxidation, since the properties of biodiesel are in large part correlated with the parent oil [6], biodiesel produced from cottonseed oil may exhibit appreciable oxidative stability.

## 2. Materials and Methods

Crude cottonseed oil derived from expeller (i.e. screw pressed cottonseed oil) was purchased from Yola Oil mill, Yola, Adamawa state, Nigeria and used as such for this study. Methanol, Sulfuric acid and all other reagents were purchased from BDH Chemicals limited Poole England. Methanol and Sulfuric acid were of 95% and 99% purity respectively, the other reagents were also of 99% purity. All the reagents were used without further purification.

The initial triglyceride content and the free fatty acid content of the oil were analysed by using High Performance Liquid Chromatography (HPLC) (Shimadzu, LC-10AT) which consisted of the column (Capcell Pak C18, 25 cm in length and 4.6 mm in inner diameter) and ultraviolet detector at 220 nm (Tosoh, UV-8024) operated at 30°C with 0.7 ml/min flow rate of 80% acetonitrile solution containing 20% of 0.1% H<sub>3</sub>PO<sub>4</sub> as a carrier solvent. The sample volume was 20 µl and the percentage of a compound in the sample was made by comparing it with a standard compound. The initial acid value which is a measure of the FFA content of the oil was found by an acid-base titration technique. The titration was done with a 0.1N alkaline solution of

KOH. Treatment (Esterification) of the FFA in the crude cottonseed oil was carried out with methanol and concentrated sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) as the catalyst. The reactions were conducted in a laboratory scale set-up, which consisted of a 50 ml round bottom flask as a batch reactor. The reactor consists of spherical flask, which was immersed inside a water bath equipped with temperature controller to maintain the temperature of the water and in turn the temperature of the reactants at a desired value. The spherical flask consisted of three openings. The centre one was used for putting stirrer in the reactor. The speed controller motor propelled the stirrer at a desired speed. Thermometer was immersed inside the second opening to continuously monitor the temperature of the reaction. Samples were taken during the reaction through the third opening. The oil fed into the reactor was preheated to 55°C before the catalyst and the alcohol mixture was added. The progress of the FFA reduction during the reactions was monitored by measuring the acid value at every 20 min. interval. The acid value is defined as the amount of KOH necessary to neutralize 1g of the oil sample. The decrease in the acid value showed the forward progress of the esterification process. Different methanol to oil ratio between 4:1 and 10:1 were employed, catalyst amount was varied between 0.5 to 2% by weight. In all the experimental runs, excess methanol was used to overcome equilibrium limitations.

At the specified times, a sample was withdrawn quickly from the reactor. The sample was washed with distilled water to stop the reaction. A weighted amount of the samples were prepared to make titration analyses, which determines the remaining FFA. Phenolphthalein was used as indicator. The amount of KOH consumed was registered and the acid value (A) was calculated using equation 1:

$$A = \frac{1000VMC}{W} \quad (1)$$

Where A is the acid value (mg KOH/g), C is the concentration of KOH (mol/l), W is the weight of the sample (mg), M is the molecular weight of the solution (g/mol), and V is the volume of solution employed for titration (ml).

The final triglyceride content, the free fatty acid and the methyl ester formed during the esterification process were analyzed for the optimum condition.

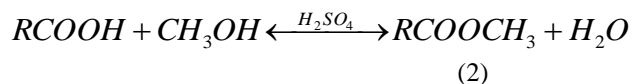
### 3. Results and Discussion

The results obtained from the analysis of the crude cottonseed oil before and after the esterification reaction are presented in Table 1.

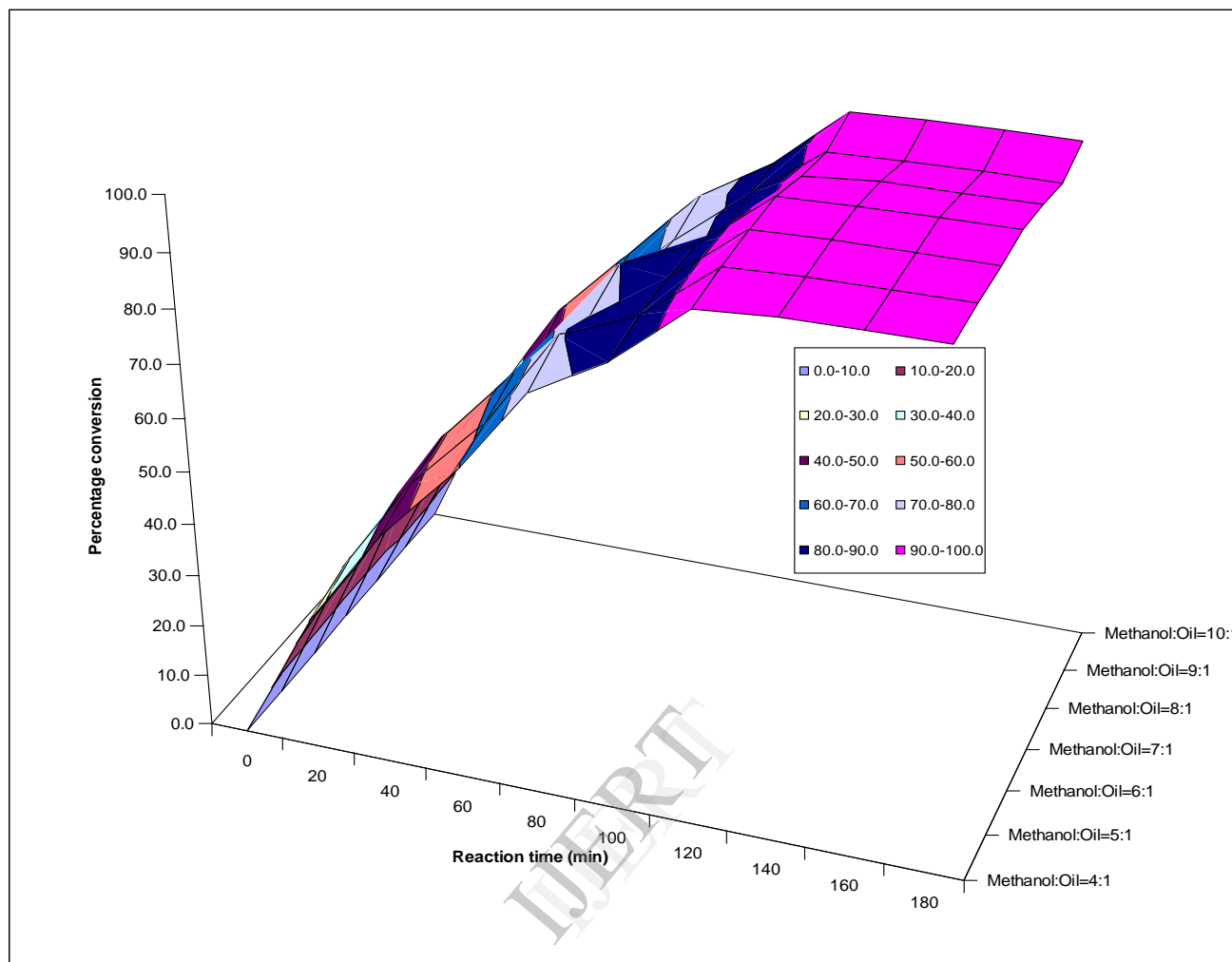
**Table 1:** Analysis of oils

	Method	Crude Cotton Seed Oil	Esterified Crude Cotton Seed Oil
Triglyceride (%)	HPLC	92.5	91.6
FFA (%)	HPLC	5.2	0.9
Methyl Ester (%)	HPLC	-	3.1
Acid Value (mg KOH/g)	Titration	10.2	1.81
FFA (%)	Titration	5.1	0.9

The methanolysis of FFA is a typical acid-catalyzed and an equilibrium reaction that produces ester and water as by-product:



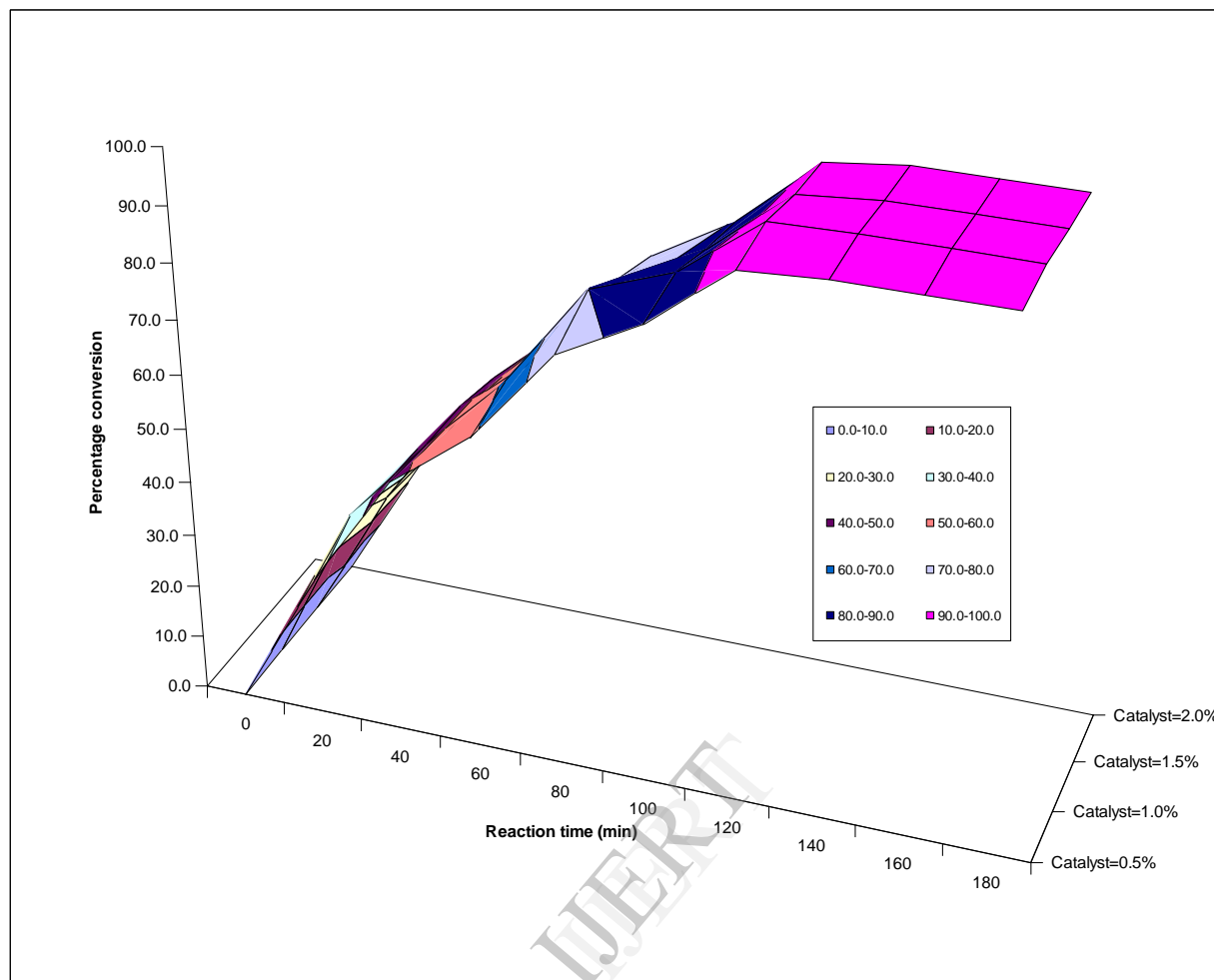
The reaction was treated as a homogeneous liquid-phase reaction that does not proceed in the absence of a catalyst. Therefore, reaction conditions were selected in order to maintain liquid phase: Routinely, an agitation speed of 464rpm was used in all the experimental runs, as recommended by Zheng [19] and Bambase [1] to overcome mass transfer limitations, much more methanol than that given by the stoichiometric 1:1 mole ratio of methanol to oil was employed to drive the reaction to completion, i.e. excess methanol used to overcome equilibrium limitations and the oil was preheated to 55 °C to obtain higher conversion of the FFA.



**Figure 1:** Effect of Different Amounts of Methanol to Oil Ratio

The reaction was found to proceed up to 96% conversion levels at appreciable rate beyond which the rate of progress of the reaction was substantially slower [17]. The variation of the conversion of FFA for seven different methanol-to-oil molar ratios at a sulfuric acid concentration of 1% is shown in Figure 1. The conversion increased with increasing the quantity of methanol up to molar ratio of 7:1 after which it reduces. This can be attributed to the fact that water being formed during the esterification reaction gets dissolved in the

excess methanol till it can no longer accommodate it. The reaction progressed rapidly during the first 120 min showing about 96% conversion of FFA for methanol to oil molar ratio of 7:1 and over 92% for the remaining methanol to oil molar ratios. After 120 min, there was no significant improvement in the FFA conversion for all of methanol to oil molar ratio used. This might be due to the effect of water produced during the esterification of FFA, which prevented further reaction [9][18][17]. In almost all the experimental runs, the reaction approached equilibrium after 120 min, prolonging the reaction time did not efficiently increase conversion of FFA.

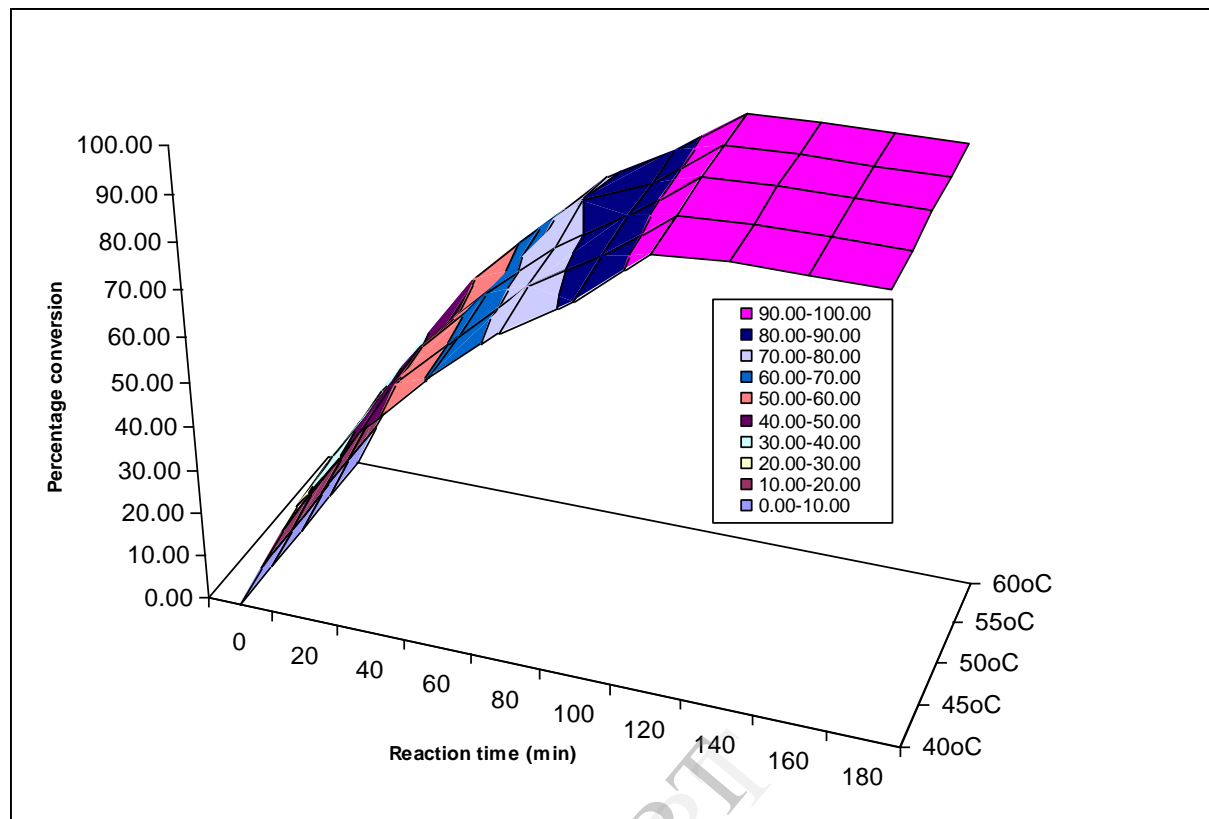


**Figure 2:** Effect of Different Catalyst Concentration.

An optimum condition in the preceding experimental runs of 7:1 methanol to oil molar ratio was used to study the effect of different catalyst concentrations (0.5, 1.5 and 2%). The result obtained is presented in Figure 2. These results revealed a conversion of 95%, 94% and 93% for catalyst concentrations of 0.5% 1.5% and 2% respectively, after 120 min reaction time, in contract to 96% for 1% catalyst concentration, after which no significant increased in the FFA conversion, was noticed. The highest conversion of 96.7% was achieved in 140min, using catalyst concentration of 1%.

Since the reaction temperature was also expected to affect the conversion of FFA, an optimum condition in the preceding experimental runs of 7:1 methanol to oil molar ratio and 1% catalyst

concentration by weight was used to study the effect different reaction temperatures on FFA conversion. Figure 5 shows the variation of the FFA conversion with the reaction temperature. From this figure, it can be seen that the rate of reaction was greatly influenced by both the reaction temperature and reaction time.



**Figure 5:** Effect of different Reaction Temperature on the esterification of crude cottonseed oil

The results showed that when the temperature was increased, the final conversion increases as well. This result corroborates those obtained by previous reported [6][3]. As expected, raising the temperature increased the esterification rate. The highest rate was obtained at 60°C, which is close to the boiling point of methanol at atmospheric pressure. A higher temperature obviously increased the rate further, but required using a pressure above atmospheric level or a more sophisticated experimental set-up such as that employed by Kocsisova [10]. In addition, a higher temperature will provide a higher possibility of methanol losing and produced darker product [6].

#### 4. Conclusion

The non-conventional treatment of low-cost raw materials, which generally contain high amount of free fatty acids (FFAs) in association with the triglyceride, is a valuable alternative that would reduce the cost of biodiesel production and make its retail

prices more competitive than petroleum-derived diesel fuel. In order to reduce the FFA content of crude cottonseed oil, esterification reaction should be carried out using sulfuric acid catalyst concentration of 1%, using methanol to oil ratio of 1:7 at atmospheric pressure and a reaction temperature of 55°C. The product was found to contain approximately the same amount of triglyceride which is an indication that there were no side reactions during the process. The FFA which was partly converted to methyl ester was reduced from about 5.2% to 0.9%.

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