

## Transesterification for the preparation of Biodiesel from Crude Oil of Milk Bush

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**Abstract:** In this research study, biodiesel was produced via transesterification process from the crude oil of milk bush (*thevetia peruviana*) with methanol as alcohol. Two molar ratio 1:6 and 1:10 of oil to methanol was used to determine the conversion rate at two different temperature 45 and 60°C. Sodium hydroxide was used as catalyst at. The experiment was carried out at atmospheric pressure. The reaction was carried out in a batch-type reaction vessel. The results obtained shows that a maximum conversion of 94% of oil to methyl ester was achieved at 60°C with molar ratio 1:10 of oil to methanol. The biodiesel produced agrees with ASTM and German standards.

**Key words:** Base catalyst, biodiesel, Milkbush, non-edible oil, transesterification

### INTRODUCTION

Biodiesel is one of the many alternative fuel options that can help in reducing petroleum oil dependence. It is renewable and biodegradable with less harmful emissions than petroleum based diesel. It is derived from vegetable oil or animal fats via a transesterification reaction,

The most commonly used oils for the production of biodiesel are soyabean, sunflower, palm, rapeseed, cotton seed and jatropha. Most of these oils are edible except *Jatropha* (Ma and Hanna, 1999). Before petroleum fuels were in widespread use in tropical countries, there was considerable interest in the use of both vegetable and animal oils as fuel (Akor *et al.*, 1983). Milkbush oil is readily available, popular, and non-edible. However, as for other oils there are limitations in the use of this non-edible oil as fuel. Its high viscosity and poor combustion characteristics can cause poor atomization, fuel injector blockage, and excessive engine deposit and engine oil contamination. With the esterification of oil we can get better fuel properties (Boocock, 1996), rather than using Straight Vegetable Oil (SVO) as a fuel.

In Nigeria, the ever increasing demand of edible oils for food which prevents their use in biodiesel production makes us to look for alternative oil that is not edible, readily available with better fuel properties which can be used fuel (Olatunji, 2010). However, non-edible oils are affordable for biodiesel production. Biodiesel is synthesized from oils and fats by either an acid or a base. The transesterification reaction of triglycerides is known to be a three step process. The kinetic studies of

transesterification of soyabean sunflower, palm and rapeseed have been reported, (Darnoko and Cheryan, 2000). More recently, research on alcoholysis of oil has focused on the use of heterogeneous catalysts. Zeolites and metal catalysts have also been used for the transesterification of soyabean oil (Suppes, 2004). Although, base catalyzed transesterification of oils is widely accepted method of biodiesel preparation, chemical properties and purity of oil warrants complete optimization of the reaction conditions (Canakei and Gerpen, 1999). Therefore the objectives of this study to prove the detail process of base catalyzed transesterification of crude milk bush oil with methanol. The fuel properties of milk bush oil methyl esters (biodiesel) in comparison with the accepted biodiesel standards that shows that esterification of oil does improve its properties making it similar to diesel.

### MATERIALS AND METHODS

Fresh milk bush (*Theretia Peruviana*) fruits were obtained from Federal Government College, SNAPS compound, Port Harcourt, Nigeria on 15<sup>th</sup> January, 2010. The fruits were transported to the process centre and manually separated to remove all foreign matter and immature seeds. The clean seeds were then held at room temperature for three days to soften the mesocarp for easy removal of the kernel. The kernels from the fruits were crushed to obtain a paste which was exhaustively extracted by soxhlet method with petroleum ether (60-80°C) to obtain the oil. The seed of the plant contains

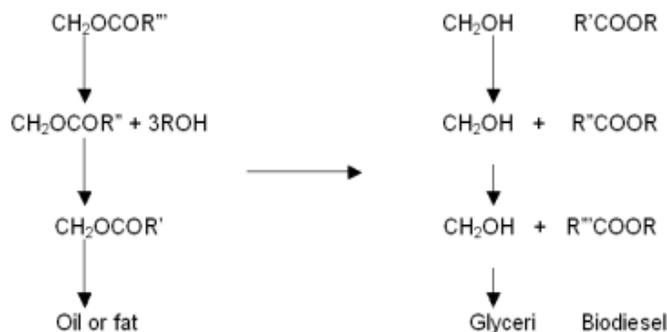


Fig. 1: The biodiesel reaction

about 60% oil, which hydrolyses to give about 48.9% oleic acid, 20.39% palmitic acid, 19.27% linoleic acid, 7.56% stearic acid, 1.66% Arachidic acid, 0.19% palmitoleic acid and 0.08% myristic acid (Olatunji, 2010). The defatted seed cake is about 30% protein but rich in toxins.

The production process for biodiesel are well known. Different ways to reduce viscosity include dilution, microemulsification, pyrolysis, catalytic cracking and transesterification (Schwab *et al.*, 1987; Otera, 2003). Because of the simple process and glycerol obtained as byproduct which has a commercial value, transesterification is preferred over others.

There are three basic ways to biodiesel productions from oils and fats this includes: base catalyzed transesterification of the oil, direct acid catalyzed transesterification of the oil and conversion of the oil to its fatty acids and then to biodiesel (Canakei and Gerpen, 1999). Most of the biodiesel produced today is done with the base catalyzed reaction because it carried out at low temperature and pressure, it yields high conversion (88%) with minimal side reactions and reaction time, it is a direct conversion to biodiesel with no intermediate compounds and no exotic materials of construction are needed.

The chemical reaction for base catalyzed biodiesel production is shown in Fig. 1. One hundred (100) L of fat or oil (such soyabean or milkbush oil) are reacted with about 20 L of a short chain alcohol in the presence of a catalyst to produce 20 L of glycerin and 100 L of biodiesel. The short chain alcohol, signified by ROH (usually methanol, but sometimes ethanol) is charged in excess to assist in quick conversion. The catalyst is usually sodium or potassium hydroxide that has already been mixed with the methanol (known as sodium methoxide). R', R'' and R''' indicate the fatty acid chains associated with the oil or fat which are largely palmitic, stearic, oleic and linoleic acids for naturally occurring oils and fats.

**Transesterification of crude oil of milk bush:** A lye was prepared using NaOH, 1 g of lye of NaOH was dissolved in 1 L of distilled water to make 0.1% lye. 1 g of oil was also dissolved into 10 mL of Isopropyl. The 1 g of oil that was dissolved was put in a beaker and warmed gently in hot water for 4 min. Some of the quantity of the oil evaporated due to heating. The oil was then warmed until it was dissolved and turned clear.

Two drops of phenolphthaleine was added to the cleared oil (0.1% lye). After titration, the titre value from 0.00 reached 0.5, thereby turning the 0.1% lye into pink and was allowed to stayed for 15 sec. The titre value of 0.50 was added to 3.5 g of NaOH to sum it up to 4.0 g of NaOH. The sum of the lye that was gotten from the burette reading was used to measure 4.0 g of undissolved NaOH and then was added to 1 L of milk bush oil. This process was used to neutralize the Free Fatty Acid (FFA) in the 1 L of milk bush oil. 200 mls of methanol was measured into a container and the undissolved 4.0 g of NaOH was added to it and cocked. It was swirled (in a blender) until the lye was totally dissolved.

The methoxide was poured into the oil container and mixed for 30 min. Two different temperatures were used, 45 and 55°C. These temperatures were maintained and the process continued for 1 h. As soon as the process was completed, the mixture was allowed to cool before pouring it into the separation filler. The oil was left in the separation filler to separate the oil from the glycerol. The glycerol was removed from the oil after 48 h. The collected milk bush methylester may vary between 700 to 950 mL while the amount of glycerin collected varies from 150 to 250 mL based on the methanol ratio with respect to milk bush oil (Fig. 2).

## RESULTS AND DISCUSSION

**Effect of molar ratio of oil: Methanol and temperature on transesterification of milk bush oil:** In transesterification reaction, three moles of (3 mol) alcohol



Fig. 2: Preparation of milk bush oil and biodiesel

requires one mole of triglyceride to yield three moles (3 mol) of fattyesters and one mole of glycerol (Agarwal and Das, 2001). To estimate the molar ratio, the molecular weight of crude oil of milk bush is taken as 903.8 and the density is 0.942 kg/k (Olatunji, 2010). With two different molar ratios of milk bush oil to methanol (1:6 and 1:10) at 45°C during transesterification of milk bush oil was studied (Fig. 3 and 4).

At a molar ratio of 1:6 a maximum conversion 80% was observed whereas at 1:10 molar ratio the conversion

was 85% with an initial lag time. The initial lag phase is usually attributed to transport effects required to transfer the methanol into the oil phase. At a molar ratio of 1:10 (Oil: Methanol), increasing the reaction temperature from 45 to 55°C resulted in a significant increase in conversion from 85 to 94% (Fig. 5 and 6).

It is important to note that crude milk bush oil was used in this study for biodiesel preparation. The degree of refinement of the vegetable oil affects the yield of ester formation (Freedman *et al.*, 1984; Darnoko and

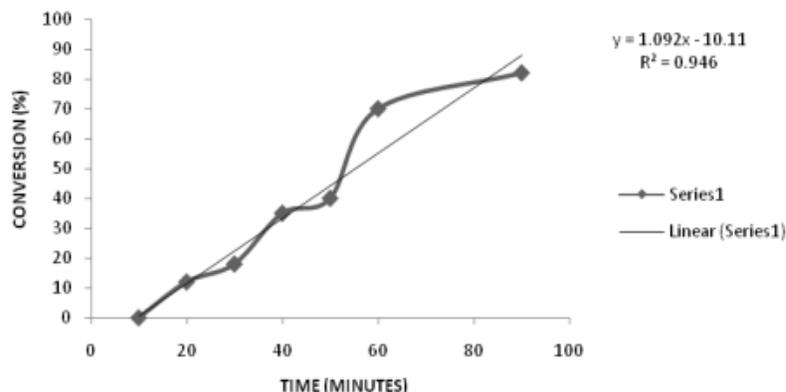


Fig. 3: Conversion of Milkbush oil fatty acid methylesters at molar ratio of 1:6 at 45°C

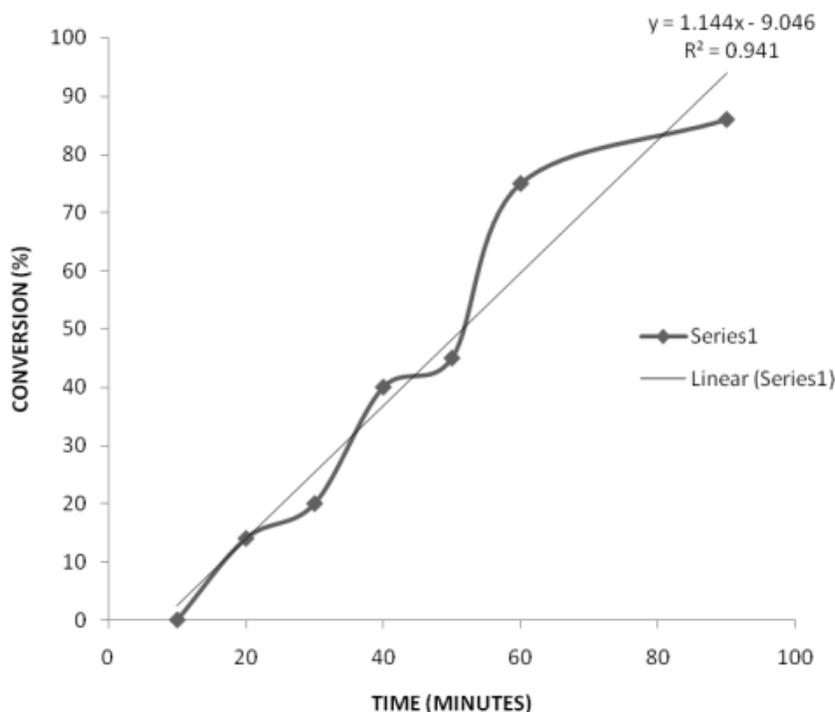


Fig. 4: Conversion of Milkbush oil fatty acid methylesters at molar ratio of 1:10 at 45°C

Cheryan, 2000; Ghadge and Raheman, 2005). The conversion can only be expected to improve when refined milk bush oil is used using alkaline catalyst (0.5% of NaOH or methoxide) at 55°C and a molar ratio of 1:6 (Oil: Methanol) with fully refined oils resulted in complete conversion to methyl esters in 1 h but at a moderate temperature (32°C) these oils were transesterified with 1wt % KOH at 60°C and a molar ratio of 1:6 (Oil: Methanol), using a continuous stirred tank reactor to give a yield of 58.8% of methylester at a reactor residence time of 40 min which increased to 97.3% at a residence time of 60 min (Darnoko and Cheryan, 2000).

Biodiesel from rape seed oil was prepared in supercritical methanol at a molar ratio of 1:42 (Oil: Methanol) in the absence of catalyst where the temperature was as high as 240°C. The conversion was 95% after 240 sec (Kusdiana and Saka, 2001). Fatty acid methylesters from jatropha oil were prepared (92% yield) in a two step process with an oil to methanol molar ratio of 1:4.5 at 30°C and reaction time of 10 h. The optimized conditions for transesterification of heated refined sunflower oil and used frying oils were reported recently (Siler-Marinkovic and Tomasevic, 2003; Antolin, 2002). The methanolysis of different used frying oils were

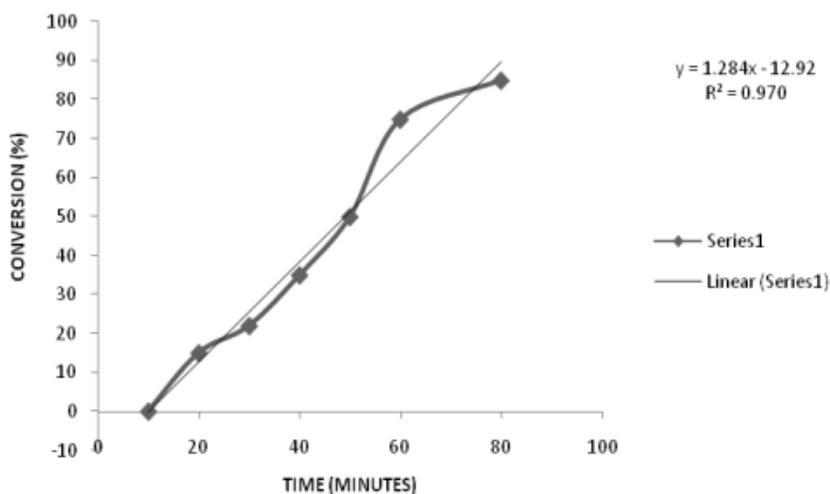


Fig.5: Conversion of Milkbush oil to fatty acid methylester at temperature 45°C at 1:10 (Oil:Methanol molar ratio)

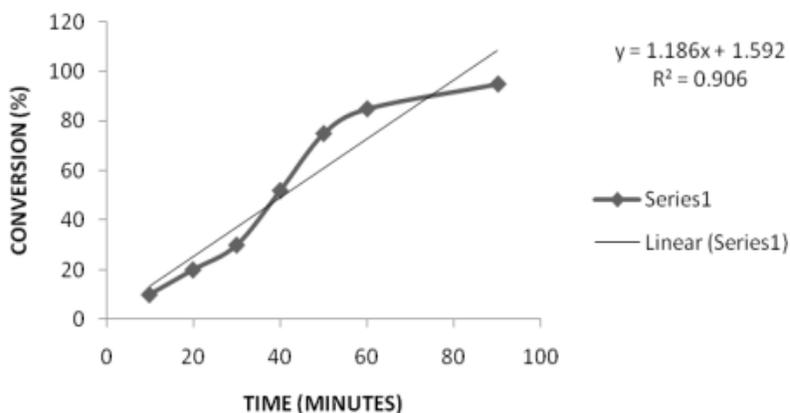


Fig.5: Conversion of Milkbush oil to fatty acid methylester at temperature 60°C at 1:10 (Oil:Methanol) molar ratio

Table 1: Fuel properties according to Milk bush FAME, ASTM and German biodiesel Standard.

| Parameters                 | Milk bush FAME | ASTM Standard 100% Biodiesel | German biodiesel Stand DIN V51606 |
|----------------------------|----------------|------------------------------|-----------------------------------|
| Viscosity (Cst)            | 4.82(40°C)     | 1.9 to 6.0                   | 3.5 to 5.0 (40°C)                 |
| Acid value (mg KOH/g)      | 0.62           | 0.80 max.                    | 0.5                               |
| Flash pointn (°C)          | 160            | 130 min.                     | 100 min                           |
| Cetane number              | 57             | 48-65                        | >51                               |
| Density gL/cm <sup>3</sup> | 0.885*         | 0.875-0.89                   | 0.82-0.86@15°C                    |

performed at 25°C with 0.5-1.5% (KOH or NaOH) with a molar ratio of oil to methanol as 1:4.5, 1:6 and 1:9 and 1% KOH, 25°C, 1:6 molar ratio was found to be optimum.

**Fuel properties of fatty acid Methylsters in comparison with Milkbush oil and diesel:** The two important properties of methylsters processed from milk bush oil which are viscosity and flash point were found to be 4.82Cst (40°C) and 160°C (Table 1), respectively Milk bush oil has a high viscosity of 74.14Cst (30°C) which drops down dramatically on transesterification to 4.82 Cst

(40°C). Both these properties meet the specifications of ASTM and German biodiesel standards.

### CONCLUSION

Crude milk bush oil was transesterified using NaOH as catalyst and methanol to produce biodiesel. The conversion was 94% at 55°C with 1:10 molar ratio (oil: methanol) for NaOH (1 wt %) catalyzed transesterification. The fuel properties especially viscosity (4.82 Cst at 40°C) and flash point (160°C) of the

transesterified product (biodiesel) compare well with accepted biodiesel standards.

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#### AUTHOR'S CONTRIBUTION

Asst. Prof. A.J. Akor is the Chairman of my Ph.D. Supervisory team; Prof. M.F.N. Abowei is a co-supervisor; Dr. Mrs. C.O. Akintayo assisted in the extraction of milkbush oil.