PRODUCTION OF BIODIESEL FROM NON-EDIBLE SEED USING IMPREGNATED CATALYST OF CALCIUM OXIDE AND ZINC OXIDE

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ABSTRACT

The major part of all energy consumed worldwide comes from fossil sources. However, these sources are limited, and will be exhausted by the near future. Biodiesel (Methyl ester of fatty acids), an alternative diesel fuel, Is made from renewable biological sources such as vegetable oils and animal fats. This study deals with the transesterification of Prosopis Africana seed oil with heterogeneous catalyst using CaO loaded with ZnO as solid base catalyst. Four different parameters were optimize namely: methanol to oil ratio (5:1), Temperature (50 ^{0}C), catalyst concentration (2.2 wt%) and reaction time (60 min) to have high yield of biodiesel with 95% conversion rate. The fuel properties of the produced biodiesel were compare with ASTM and EU standards and they are all in conformity with the standards.

Keywords: Impregnation, Calcination, *Prosopis africana*, Heterogeneous catalyst, Calcium oxide, Zinc oxide

INTRODUCTION

Prior to the advent of biodiesel, petroleum fuels have remained almost entirely unchallenged since the motor vehicle was invented. However, their reserves are not uniformly distributed and their increased use contributes to a variety of local and regional air pollution problems and potential climatic change (Anigo *et al.*, 2013).

Biodiesel is most commonly made by transesterification process of the oil through the use of a catalyst and an alcohol, typically methanol. The chemical reaction that occurs through this process breaks down the oil molecules and replaces the glycerin portion of the molecule with an alcohol molecule. The glycerin separates to the bottom and is drained off resulting in biodiesel. The biodiesel is then typically washed, to remove any extra impurities and is then used as a fuel in a diesel engine without making any modifications to the engine. The use of enzymes (lipases) is timely as we embrace the practice of green production technologies (Green chemistry) which ensures sustainable use of resources, energy and maintenance of a clean environment (Walker, 2016).

The main advantages of using biodiesel fuels as 100 % mono alkyl esters of vegetable oil and animal fat or biodiesel blends (up to 20 % blend to the diesel fuel) are producing less smoke and particulates and having higher cetane numbers (Kimilu *et al.*, 2013). In addition, the production of biodiesel should be encouraged especially in developing countries because of the following considerations; Biodiesel is produced from sustainable/renewable biological sources; Ecofriendly and oxygenated fuel.

Biodiesel is an energy efficient, alternative fuel which can fulfill energy security needs without trading the engine's operational performance (Van Gerpen, 2015). This is because it can be applied to compression-ignition diesel engines with very little or without modifications. It therefore provides possible solution to the dual crises of fossil fuel exhaustion and environmental degradation. In terms of engine emissions, it has been indicated that exhausted gas from biodiesel combustion does not contains SO_2 and relatively small amount of CO, unburned hydrocarbons when compared to the combustion products of conventional diesel fuel (Watkins *et al.*, 2014). In addition its lubricant property can extend the engine's life. Other benefits of the biodiesel are high cetane number, high flash point, and acceptable cold filter plugging point (CFPP) (Dorado *et al.*, 2014).

EXPERIMENTAL PROCEDURE

Collection of Sample

A non-conventional feed stock of *P. africana* seed was selected for this study, as this plant is native to Bida, and there is a need to exploit the benefit of this plant as substitute feed stock for biodiesel production.

Pretreatment of *P. africana* Seeds

Seeds were first unshelled and made clean of any other impurity and sundry for seven days. The dried seeds were pulverized into uniform powdered, sieved, weighed, bottle, labeled and stored in plastic container (air-tight) to air contamination.

Extraction of *P. africana* oil

100 g of ground seeds were taken in a soxhlet apparatus on a water bath. Extraction was done in petroleum ether for 3 h and repeated twice to obtain enough quantity of oil sample. Extracted oil was made free of the solvent under vacuum in rotary evaporator (Heidolph HB digital, Laboratory 4001 efficient). The percentage oil yield was calculated using the formula:

$$\text{Oil content} = \frac{\text{weight of oil extracted}}{\text{weight of seed}} \text{x} \frac{100}{1}$$

Physicochemical Properties of *P. africana* Oil

All the test done for physicochemical chemical properties of *P. africana* were according (AOAC, 2006). The tests performed were iodine value, pH, free fatty acid, saponification value, peroxide value, acid value, odour, specific gravity, ash content, moisture content and colour. The test was tabulated in Table below.

Table A: Physicochemical Properties of *P. africana* oil

Properties	*P. africana*
Yield (%)	35
pH	4.2
Colour	Bright yellow
Density (g/cm^3)	0.85
Refractive index	2.2
Specific gravity	1.5
Saponification value (mgKOH/g)	120
Acid value (mgKOH/g)	3.3

Values are mean ± SD of duplicate determinations

Catalyst Preparation

Calcium oxide was loaded onto zinc oxide at the following amounts of 20, 25, 30, 35, 40, 45 and 50 wt % by an impregnation from aqcous solution, following by drying at 100 ^{0}C for 14 h. Prior to each reaction, the catalyst were calcined at desired temperatures (400 ^{0}C) in air for 5 h.

Transesterification procedure

The oil extracted from *P. africana* seed was transesterified using transesterification reaction. 200 g of the *P. africana* oil seeds was heated to 60 ^{0}C with 100 cm^3 of methanol followed by addition of 5 w% of CaO loaded on ZnO. The reaction was carried out under reflux at a stirring speed of 250 – 350 rpm. The mixture was stirred at all-time throughout the transesterification process.

An electronic temperature controller was used to vary the reaction temperature in the range of 50 – 70 ^{0}C, reaction time 30 – 65 min. After the reaction time was over, the catalyst is filtered out and the product was poured into a separation funnel and was left overnight for separation of methyl ester and triglyceride to occur. After separation the lower layer which is triglyceride (glycerol) is drawn out of separating funnel and the methyl ester was the product obtained which is biodiesel.

RESULTS AND DISCUSSION

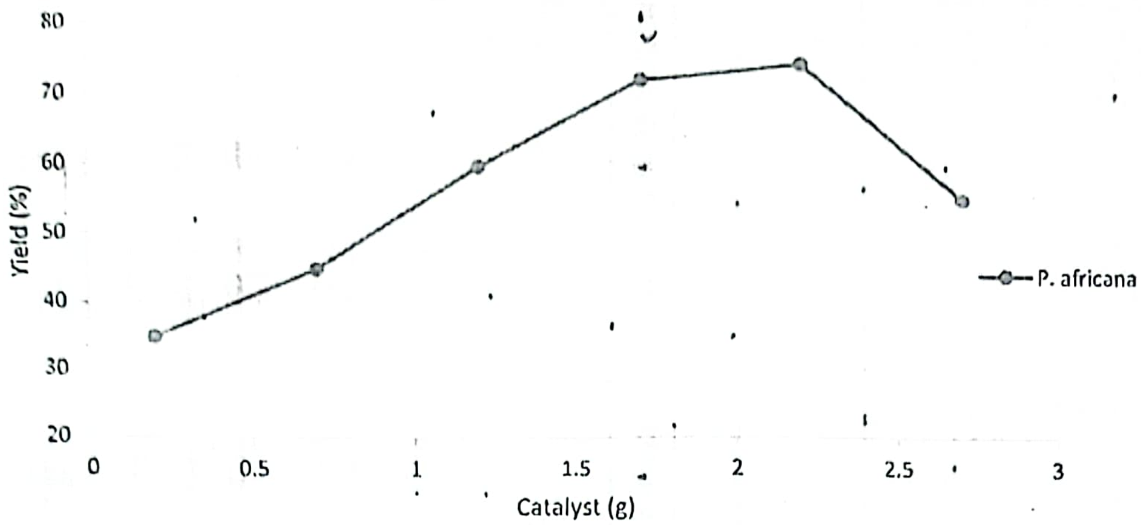

Fig. 1: Effect of catalyst concentration on the biodiesel yield. Reaction condition: temperature 50 ^{0}C, reaction time 60 min, mole ration (5:1).

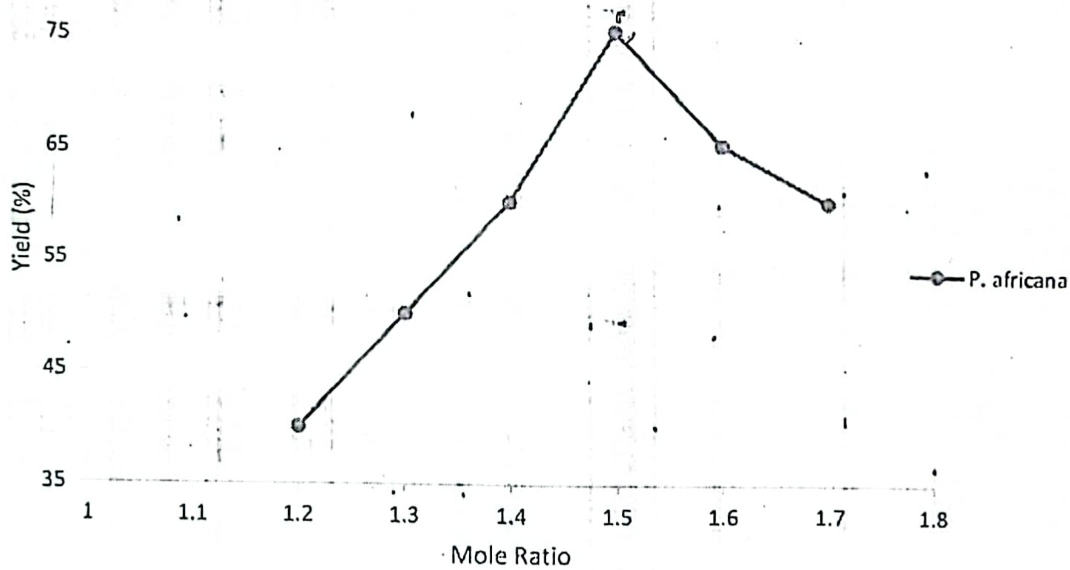

Fig. 2: Effect of methanol to oil mole ratio on the biodiesel yield. Reaction condition: catalyst concentration 2.2 wt%, reaction time 60 min, reaction temperature 50^{0}C.

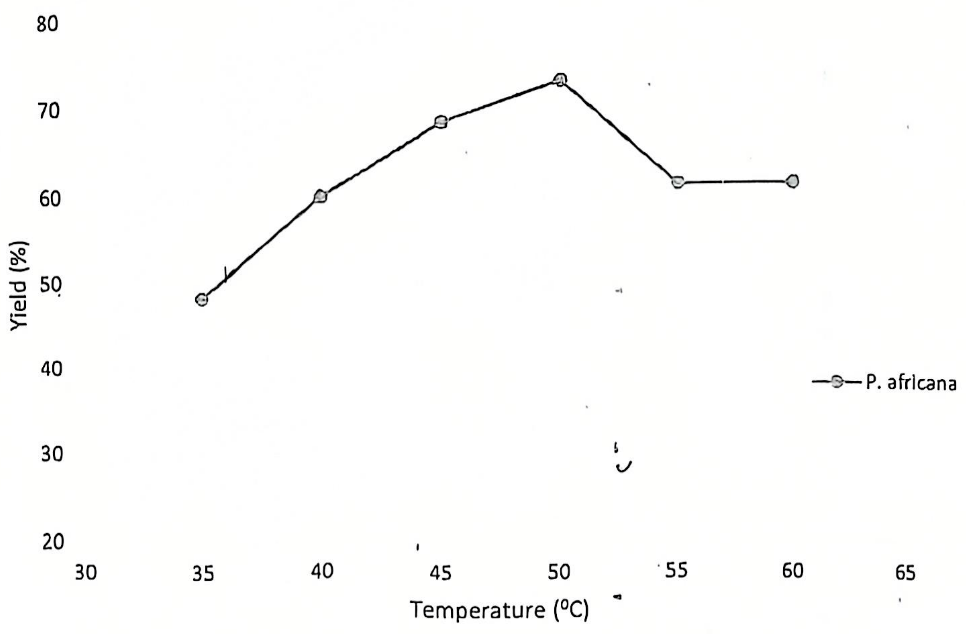

Fig. 3: Effect of reaction temperature on the biodiesel yield. Reaction condition: catalyst concentration 2.2 wt%, reaction time 60 min, mole ratio (5:1).

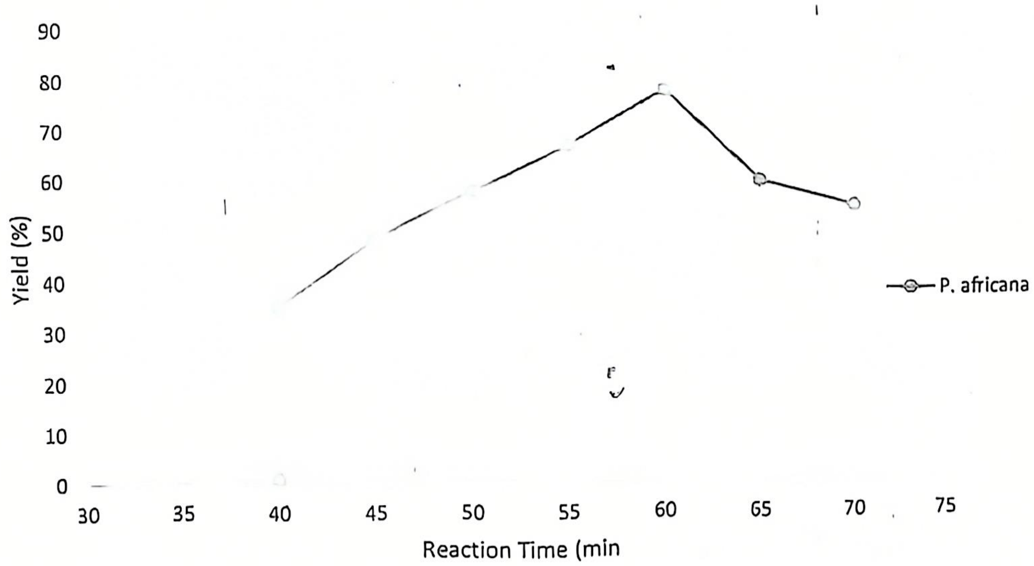

Fig. 4: Effect of reaction temperature on the biodiesel yield. Reaction condition: catalyst concentration 2.2 wt%, reaction time 60 min, mole ratio (5:1):

Table B: Fuel properties of produced biodiesel

Properties	*P. Africana*	*ASTM*
Density	0.83	0.75 – 0.84
Pour point	6.5	5 – 10
Cloud point (^{0}C)	-9.3	-12 - -13
Flash Point (^{0}C)	130	100 – 170
Cetane no.	38.3	48 – 64

DISCUSSION OF RESULT

Heterogeneous catalyst of impregnated CaO/ZnO prepared was calcined and tested for the production of biodiesel. In the presence of calcination at 500 ^{0}C, the catalyst were active and exhibited a higher catalytic activity. As a result, the catalyst activity is generated by loading the calcium oxide with zinc oxide followed by the calcination of the samples.

Effect of loading amount of CaO on the conversion of the *P. africana* seed oil at the loading amount range from 15 – 40 wt%. When the loading amount of CaO was increased to 25 wt%, the conversion increased and the highest conversion of 88.4% was achieved. However, when the loaded CaO was over 25 wt%, the conversion was decreased. This result could be attributed to the effect of CaO on ZnO support weakens the combination of Ca^+ and ions of O^{-2} due to the interaction of CaO and the surface of the support, which is beneficial for the decomposition of CaO. At low loading of CaO, the active base sites are more dispersed on the zinc oxide surface and strong adsorption of reactant may occur at unreactive surface sites.

The extracted oil colour is brown yellow from *P. africana*. This colour is acceptable for biodiesel production according to Codex, (2011). Singh and Singh, (2017) reported brown colour for Jatropha oil for the product of biodiesel, Sanjay (2013) reported brown yellow colour for neem oil for the production of biodiesel which are all accepted by Codex Standard for biodiesel production.

The study shows that 3.3 mg/g was obtained for *P. africana*, and this value is low compare to that of breadfruit seed oil that is 7.38 mgKOH/g but higher than that of butter oil which is 1.79 mgKOH/g (Asuquo *et al.*, 2012) but are lesser than those of cashew nut (10.7 mgKOH/g) (Akintayo, 2014), avocado seed oil 16.8 mgKOH/g. The low acid value suggest that the oil may be good for paint making (Akpan *et al.*, 2011). The lower the acid value of oil, the few fatty acid it contains which makes it less exposed to the phenomenon rancidity (Roger *et al.*, 2010).

The physicochemical properties and the percentage oil yield of the extracted oil were determined. After the extraction it was found that the seed contains 37.0% (*P. africana*) of oil, which was slightly higher compared to *A. africana* (35.5%) reported by (Ajala and Adeleke, 2014). The variation in the oil yield could be attributed to the extracting solvent, difference in variety of plant, cultivation climate. In this study *n*-hexane was used using soxhlet extractor. The results of the physicochemical properties of *P. africana* oil seed is presented in Table A.

Four process parameters affecting transesterification reaction namely methanol to oil ratio, temperature, catalyst and reaction time were determine for optimal biodiesel production. Figure 4.1 presented the effect of methanol to oil molar ratio. Optimum biodiesel was observed at methanol to oil ratio of 5:1 and yield of 75.3%. An increase in mole ratio beyond the optimum mole ratio of 5:1 had a negative effect on the yield. The yield decreased above this optimum point. Alamu *et al.*, (2018) showed that the most suitable molar ratio was found to be within the range of 5:1 to 10:1, in the production of biodiesel using egg shell ash (CaO) as heterogeneous catalyst.

Figure 1 shows the catalyst concentration increases from 0.2 – 2.7 wt%, a progressive increase in percentage conversion in the reaction was achieved and thereafter experienced a decrease in yield above this concentration (2.2 wt% of CaO). It was obvious that increased in catalyst concentration beyond 2.2 wt% of CaO result to decrease in biodiesel yield (Birla *et al.*, 2012).

Temperature plays an important role during biodiesel production; this is because the rate of reaction strongly influenced by the reaction temperature. Figure 3' shows the result of temperature variation from (35 – 60 ^{0}C) at a catalyst concentration of 2.2 wt%. As the temperature increases from (35 - 60 ^{0}C) the conversion yields of biodiesel also increases considerably. Further increase in temperature result in decrease in the yield of biodiesel. In this study, optimum temperature for the production of biodiesel took place at 50 ^{0}C. Patil and Deng (2016), reported that alkaline-transesterification at temperature above 60 ^{0}C cause excessive methanol loss due to evaporation as significantly reduce overall biodiesel yield.

Some of the important fuel properties of the biodiesel produced from *P. africana* seed oils are compared with the biodiesel standard (ASTM 6751) and are presented in Table B. Flash point is the minimum temperature at which a fuel must be heated for it to ignite air-vapour mixture. The flash point for this work is 130 ^{0}C. This result shows appreciable consistency with both

ASTM, EN standard for biodiesel and works of other researchers. The high value obtained in this study clearly signifies that the biodiesel produced in basically free from methanol; this is because even small quantity of methanol can reduce the flash point reasonably and also negatively affects diesel engine parts such as fuel pumps, seals and elastomers.

The cloud and pour point are criterion used for low temperature performance of a fuel. This work report 5.2 ^{0}C. This properties help to show the behavior of the biodiesel under a specified climate setting. This shows the biodiesel produced from *P. africana* can be used in cold climate region.

Cetane number is a measure of ignition quality of diesel fuel. The higher the cetane number, the easier the fuel will ignite when it is injected into the engine the better the fuel. Beside the reduction of viscosity resulting from transesterification of vegetable oil, one of the most evident changes that result from process is the significant inceases in the cetane number of the fuel produced. This work indicates that the cetane number is 38.2. The value obtained is in agreement with both ASTM and EN standard. This implies the *Jatropha curcas* biodiesel produced to have high ignition quality (Ochigo and Paiko, 2011).

CONCLUSION AND RECOMMENDATION

The catalytic activity of the impregnated and calcined catalyst of CaO/ZnO prepared shows that the CaO /ZnO samples present catalytic activity, as expected, due to the presence of strong basic sites on which methanolysis reaction could occur. However, after calcination at 600°C these catalysts were active and exhibited a higher catalytic activity. As a result, the catalyst activity is generated by loading the calcium oxide with zinc oxide followed by calcination of the samples. On account of the high activity of the catalysts in the transesterification reactions, the influence of catalyst preparation conditions on the conversion of *P. africana* oil was studied to find a higher activity catalyst. Four different parameters were optimize namely: methanol to oil ratio (5:1), Temperature (50 ^{0}C), catalyst concentration (2.2 wt%) and reaction time (60 min) to have high yield of biodiesel with 95% conversion rate. The fuel properties of the produced biodiesel were compare with ASTM and EU standards and they are all in conformity with the standards. In order to diversify the economy, biodiesel should be encourage and the feedstock should be domesticated for easy production of biodiesel.

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