The Effects of Process Parameters on Biodiesel Production from Jansa Seed Oil using Lithium-Doped CaO and MgO as Catalysts

[1]Nwachukwu E. I., [2]Ugwu H.U., and [3]Amaechi U.G.
[1]Department of Mechanical Engineering, Abia State Polytechnic, Aba
[2]Department of Mechanical Engineering, Michael Okpara University of Agriculture, Umudike
[3]Department of Mechanical Engineering, Abia State Polytechnic, Aba
ekwueme.nwachukwu@abiastatepolytechnic.edu.ng| ugwu.hyginus@mouau.edu.ng| uba.amaechi@abiastatepolytechnic.edu.ng

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ORIGINAL RESEARCH

Abstract—This study presents process parameters analysis on biodiesel production from jansa seed oil using transesterification process. Following the quest to achieve improved economic viability and clean production process for biodiesel, lithium ion from lithium carbonate was applied to improve the catalytic properties of calcium oxide and magnesium oxide for biodiesel production. Oil produced from jansa seed was characterized to determine its suitability for biodiesel production. Based on the characterization, an appreciable oil weight or yield of 38.09% was produced. Also, 0.493mgKOH/kg free fatty acid (FFA) content, 205.923 gKOH/kg saponification value and 99.95% ester value which specified its great tendency to be converted into methyl ester (biodiesel) were obtained. Li-CaO and Li-MgO catalysts were prepared in diverse concentrations for use in biodiesel production. Li-CaO-1.50 and Li-MgO-1.50 gave the optimal yield of 76 and 83% volume of biodiesel. The Free fatty acid (FFA) value recorded for the jansa seed oil was 0.493 mgKOH/kg with a corresponding acid value of 0.986 mgKOH/kg which was expected for a good bio-oil sample for biodiesel production. The catalyst were varied for biodiesel production and among the catalysts, the variants (CaO and MgO) doped with 1.5 wt% lithium gave the best biodiesel yield of 76.0 and 83.00 % by volume respectively. These were applied to study the effects of other process parameters (reaction time, reaction temperature, agitation speed, and methanol to oil molal ratio) and other optimal yield of biodiesel were obtained at 2hrs reaction time, 60^0 reaction temperature, 400rpm agitation speed and alchohol/sample mole ratio of 10:1. Overall, the results were found to meet standard properties for biodiesel. At such, Li-CaO, Li-MgO, other similar materials should be adopted as catalyst for the production of biodiesel to bridge the energy gaps.

Keywords— Biodiesel, catalyst, characterization, jansa seed, process conditions.

1 INTRODUCTION

The environmental benefits of biodiesel fuel has made it more attractive in recent times. Its primary advantages deal with it being one of the renewable fuels currently available and it is also non-toxic and biodegradable. It can also be used directly in most diesel engines without requiring extensive engine modifications. Biodiesel according to Arzamendi *et al*.(2008) is an alternative to petroleum-based fuels. It has found a very wild application as energy source to drive passenger cars, sport utility vehicles, light trucks, buses, ships, trains, off-road heavy equipment, and mining equipment, as well as for home heating fuel, power generation, and as a mixing agent in two-stroke engines. Thus, in long term prospect, biodiesel usage will radically cover all types of consumer demand in ground transportation, aviation, and maritime fuel markets (Arzamendi *et al.,* 2008).

Van (2005) defined biodiesel as a renewable, biodegradable, environmentally benign, energy efficient, substitution fuel which can fulfill energy security needs without sacrificing engine's operational performance. From the above definition, it can be deduced that biodiesel is a resource that satisfies both vehicular and industrial energy need (fuel for engines without causing damage to them) as well as being environmentally compatible (renewable and biodegradable). The use of vegetable oil as a direct form of fuel has its challenges following some of the unfavourable physical properties. Lee *et al*. (2015) identified the undesirable physical properties of straight vegetable oils that made them non excellent choices for biodiesel production. They include; high viscosity which leads to poor fuel atomization, inefficient mixing of oil with air leading to high smoke emission, coking and trumpet formation (carbon deposit) on the injectors which results to clogged orifices, low volatility as a result of high flash point, lubrication oil dilution, thickening or gelling of lubricating oil, high carbon deposits, oil ring sticking, scuffing of the engine liner, injection nozzle failure and high cloud and pour points. The seeds of *Cussonia bateri* used in this research work are commonly called Jansa seeds in Cameroun, in West Africa, and *Ugbaokwe* (Igbo), *Takandagiwa* (Hausa), *Bumarlahi* (Fulani) and *Shigo* (Yoruba) languages in Nigeria. The tree is common in Northern Nigeria (Nwokonkwo *et al*., 2016). The work is aimed at studying the effects of process parameters in biodiesel production from jansa seed using modified catalyst.

*Corresponding Author

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2.0 Materials and Methods

2.1 Materials

Materials used for this work include glass wares and other consumables; Conical flask, beaker, Soxhlet extraction apparatus, measuring cylinder, pycometer, three-neck round bottom flask, reflux condenser, separating funnel, viscometer, analytical grade reagents; methanol, ethanol, sodium hydroxide, calcium oxide, magnesium oxide, lithium carbonate, sodium thiosulphate, chloroform, acetic acid, potassium hydroxide, sulphuric acid, hydrochloric acid, phenolphthalein and starch. and electronic equipment such as weighing balance, laboratory hot plate, heating mantle, table top refractometer, muffle furnace and hot air oven.

2.2 Methods

Methods adopted for this work are sequential pattern of events which include sample collection and preparation, oil extraction and characterization, catalyst preparation, biodiesel production from jansa seed oil using the modified catalysts, analysis of the jansa seed oil and the optimal biodiesel yield, preparation of the biodiesel blends of optimal yield and characterization.

2.2.1 Sample collection and preparation

Raw jansa seed was purchased from retail shop at Umuahia main market. The seed was selected to remove impurities and washed in distilled water to remove dust. They were allowed to dry in open air. The dried seeds were milled in industrial ball mill to permit proper oil extraction. The milled samples were stored in air tight container until when used for oil extraction.

2.2.2 Oil extraction (Soxhlet method)

Oil extraction was done in a 500 g capacity Soxhlet apparatus. The whole system consists of a heating mantle, round bottom flask, the thimble and condenser fitted with water circulation tube. Hundred grams (100g) of prepared sample was weighed into a semi permeable sample holder and introduced into the thimble. Afterwards, 300 ml n-hexane was measured into the round bottom flask, containing the n-hexane and placed on the heating mantle. The thimble holding the sample was fitted into the flask and the condenser connected with the water tubes fitted to the thimble. Water was allowed to circulate in the condenser in the opposite direction of vapour such that volatile vapour is cooled by water. The cooled n-hexane vapour condensed and returned to the thimble which housed the sample in the semi permeable membrane. Condensed n-hexane gradually and continuously leached the oil in the sample until little or no oil was left in the jansa seed oil. The system was allowed to cool and the oil and the n-hexane mixture in the flask separated by distillation. The oil was further dried in water bath at 90^0C for 2 hours, cooled and stored in air tight container. Thus, the oil yield was calculated using the equation (1).

$$Oil\ yield\ (\%) = \frac{Weight\ of\ oil}{Sample\ weight}\ (100) \qquad (1)$$

2.2.3 Oil characterization

The obtained oil was characterized for moisture, density, refractive index, kinematic viscosity, free fatty acid, peroxide value, saponification, molecular weight and ester value.

a) **Moisture content**

Moisture content was determined by dry oven method described in Carneiro *et al*.(2018). It is a procedure that quantifies the amount of moisture present in the oil.

$$\%\text{moisture} = \left(\frac{\text{Weight loss}}{\text{sample weight}}\right) = \frac{(a+b)-c}{a} \times 100\% \qquad (2)$$

b) **Density**

The density was determined using the method of Yau *et al*. (2020). An empty beaker was weighed and the weight recorded, while 50ml of the sample was introduced into a 50ml density (specific gravity) bottle. The weight of the density bottle and the sample was taken. Sample weight was obtained by subtracting the weight of the empty density bottle from the weight of the sample and the density bottle.

$$\text{Density},\varrho = \frac{\text{Sample weight, } w_s}{\text{Sample volume. } v_s} = \frac{(W_{sgb}+W_s)-W_{sgb}}{V_s} \qquad (3)$$

Where; W_{sgb}= weight of sg bottle, W_S = sample weight, Vs= sample volume.

c) **Refractive index**

Refractive index was determined using a digital table top refractometer (HI96800) manufactured by Hanna Instruments, Romania adopting the AOAC (2000) method described in Yau *et al*.(2020).

d) **Kinematic viscosity**

Measurement of kinematic viscosity was done using a glass u-tube viscometer manufactured by Poulten Selfe and Lee Ltd (PSL ASTM-IP 350).

e) **Free fatty acid**

Free fatty acid (FFA) or acid value was determined according to the method specified in ASTM (2004).

$$\text{FFA}=\frac{Tv \times N_{KOH} \times 56.1}{W_s}(\text{mgKOH/g}) \qquad (4)$$

Where N_{KOH}= normality or concentration of KOH = 0.5N; Tv = titre value and

5.61 = M_{wKOH} divided by 10.

f) **Peroxide value**

Peroxide value (PV) was determined according to the method of Boerlage and Broeze (1990). The PV is the measure of the peroxides contained in the oil, and determines the rancidity of a sample containing fat or oil subject to oxidation.

$$\text{Peroxide value (PV)} = \frac{(100)(V_1-V_2)(N)}{W_S} \qquad (5)$$

Where; 100 = milliequivalent conversion factor, N = normality of titrant = 0.02N

of sodium thiosulphate ($Na_2S_2O_3$) solution, V_1 = titre value of sample and V_2 =

titre value of blank.

g) **Saponification value**

Saponification value (SV) was determined according to the method of Boerlage and Broeze (1990) reported in FSSAI (2015) and Yau *et al.* (2020). This is

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the quantity (mg) of KOH required to neutralize the fatty acids resulting from the complete hydrolysis of 1g of the sample.

$$\text{Saponification value} = \frac{(V_2 - V_1)(N_{HCL})(56.1)}{W_S} \quad (6)$$

Where; N_{HCL} = normality of HCL acid = 0.5N, 56.1g/mol = molecular weight (molar mass) of KOH (M_WKOH) and $V_2 - V_1$ = titre value, Tv.

h) **Molecular weight**

Molecular weight of the bio-oil was determined according to the method of Zhu *et al* (2006), given as:

$$\text{Molecular weight} = \frac{56.1\ X\ 1000\ X\ 3}{(SV - AV)} \quad (7)$$

Where; AV= Acid value (mKOH/M_{oil}, mg/g) and; SV = saponification value (mKOH/M_{oil}, mg/g).

(i) Ester value

The ester value (EV) of the sample was determined according to the method of Edmilson *et al.* (2014) expressed in equation (8).

$$\text{Ester value (EV)} = \frac{100\ X\ (IS - IA)}{IS} \quad (8)$$

Where; IS and IA represents index of saponification and index of FFA respectively.

2.2.4 Catalyst preparation

Nano crystalline matrix alkali metal ion impregnated CaO catalyst was prepared by cold wet impregnation method as described by Watkins *et al*. (2004). Compared to the homogeneous catalyst, heterogeneous catalysts, which usually appear in solid form, act at different phases in the reaction mixture of liquids (Borges and Diaz,2012). No additional pretreatment is required for the reduction of the FFA content while using heterogeneous catalysts (Leung *et al*.,2010). Moreover, this can simply catalyze the biodiesel production from high acid oil. The series of alkali (lithium ion) metal impregnated calcium and magnesium oxides in varied concentrations (0.5, 1.0, 1.5, 2.0, and 2.5 wt.%) were obtained such that a total of 10 catalysts were applied for the biodiesel production.

2.2.5 Effects of process parameters on the biodiesel production

Standard procedures as utilized in Colombo *et al.* (2017) using MgO and in Di Serio *et al.* (2005) using CaO as catalyst for biodiesel production were adopted in this present work. They investigated the same vegetable oil developed from jansa seed and obtained similar physiochemical properties as those in this present work by studying the effects of process parameters variation (catalyst concentration, reaction time, reaction temperature, agitation speed and methanol to oil molal ratio) on jansa seed oil for biodiesel production. The reaction system consisted of a 500ml three-neck round bottom flask, reflux condenser with water circulation fitted onto the mid neck of the three-neck flask. A mercury-in-glass thermometer fitted through a plastic bong was inserted into the flask. The whole set-up was placed on a magnetic heating mantle which provided the required heating and magnetic field to rotate a capsular nub placed inside the flask that supplied the stirring effect. A constant volume of 50 ml of the jansa seed oil was used per production. Effects of catalyst concentration, reaction time, temperature, methanol / sample molal ratio and agitation speed were varied sequentially in the following order;

a. **Catalyst concentration**

Keeping all other parameters constant (time at 3hours, temperature at 55 ^{0}C, molal ratio at 10:1 and agitation speed at 300 rpm), the catalysts concentration were varied at 0.5, 1, 1.5, 2 and 2.5% respectively.

b. **Reaction time**

Process time for the production of the biodiesel was varied at different intervals; 1, 2, 3, 4 and 5h For each production, the other process conditions were kept constant (optimal catalyst concentration from (a), temperature at 55 ^{0}C, molal ratio at 10:1 and agitation speed at 300 rpm).

c. **Reaction temperature**

Reaction temperature was varied at 30, 40, 50, 60, and 70 ^{0}C. Catalyst concentration and reaction time remained constant at the optimal conditions obtained in (a) and (b) respectively, while the molal ratio and the agitation speed remained constant at 10:1 and 300 rpm for the reaction period respectively.

d. **Methanol / sample molal ratio**

While all other parameters were kept constant following their optimal conditions (catalyst concentration (a), reaction time (b), reaction temperature (c)), the methanol / sample molal ratio was varied at 4:1, 6:1, 8:1, 10:1 and 12:1 respectively, while the agitation speed remained also constant at 300rpm for the reaction period.

e. **Agitation speed**

The effect of agitation speed on the biodiesel production was studied at different agitation speeds (100, 200, 300, 400, and 500 rpm). All other parameters: Catalyst concentration, reaction time, temperature and methanol/ sample molal radio were held constant at the respective optimal conditions obtained.

3.0 Results and Discussion

3.1 Characterization of the jansa seed bio-oil

From the table, the oil weight or yield produced by the jansa seed (*Cussonia bateri*) was 38.09 %. This oil yield was appreciable when compared to those from other high yielding samples used for biodiesel production as reported in Umar *et al*., (2018) that got a total oil yield of 37.80 % by weight from calabash seed.The Free fatty acid (FFA) value recorded for this *Cussonia bateri* seed was 0.493 mgKOH/kg with a corresponding acid value of 0.986 mgKOH/kg. This value was lower than 5.92 mgKOH/kg recorded by Olaefe *et al.* (2012) which was expected for a good bio-oil sample for biodiesel production.

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Table 1 presents the characterization test results (Physicochemical properties) of the jansa seed bio-oil investigated.

Table 1. Physicochemical properties of the jansa bio-oil

Sample	Oil Yield (%wt)	Density (g/cm^3)	Kenimatic Viscosity @ 40^{0}c (mm^{2}s^{-1})	Refractive index @ 29^{0}c	Moisture Content (%)	Acid value (mgKOH/kg)	Free fatty acid (mgKOH/kg)	Saponification (mgKOH/kg)	Peroxide value (meq/kg)	Molecular weight (g/mol)	Este valu (%)
Oil	38.09	0.919	135.324	1.5001	0.86	0.986	0.493	205.923	1.18	821.23	99.9

3.2 Variation of biodiesel yield with catalyst

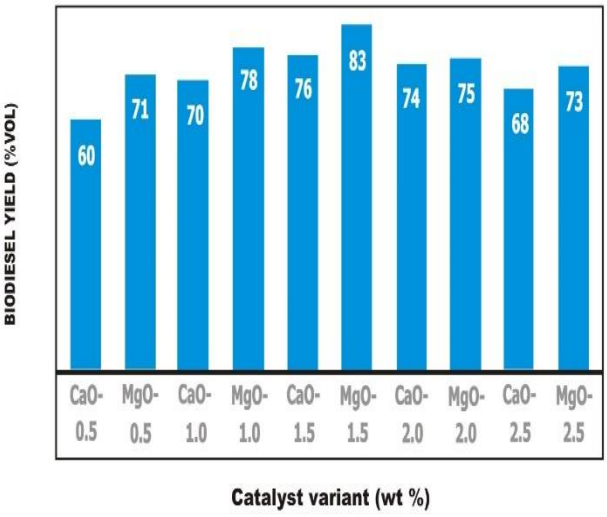


Fig.1: Variation of biodiesel yield with catalyst variants for the initial biodiesel.

From fig. 1, among the catalysts, the variants (CaO and MgO) doped with 1.5 wt% lithium gave the best biodiesel yield of 76.0 and 83.00 % by volume respectively. Consequently, these two variants were thus taken as optimal values for analyzing other effects of the process conditions on the biodiesel yield.

Fig. 2: Effect of catalyst conc. on biodiesel yield

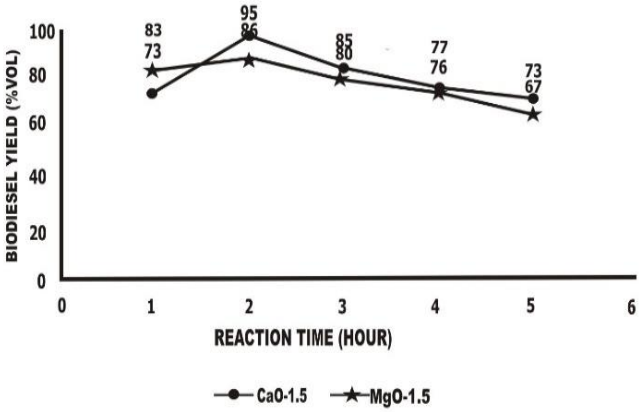
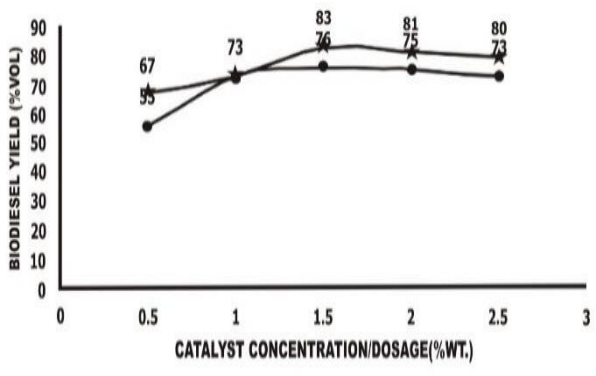


Fig. 3: Effect of reaction time on biodiesel yield

3.2 Effects of catalyst concentration variation on the biodiesel yield



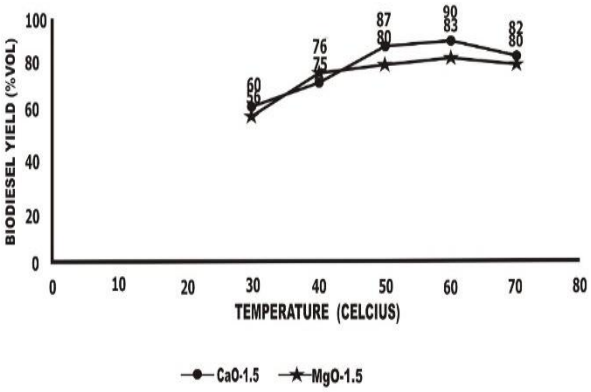


Fig. 4: Effect of temperature on biodiesel yield

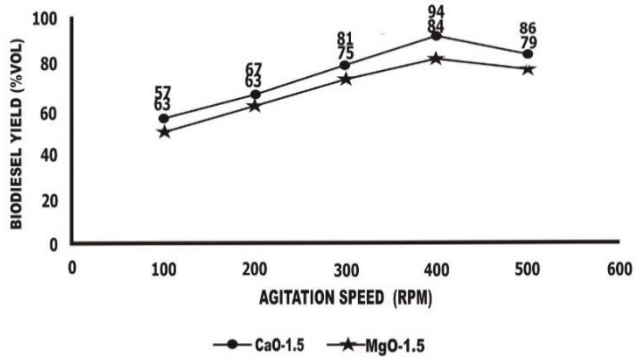


Fig.5: Effect of agitation speed on biodiesel yield

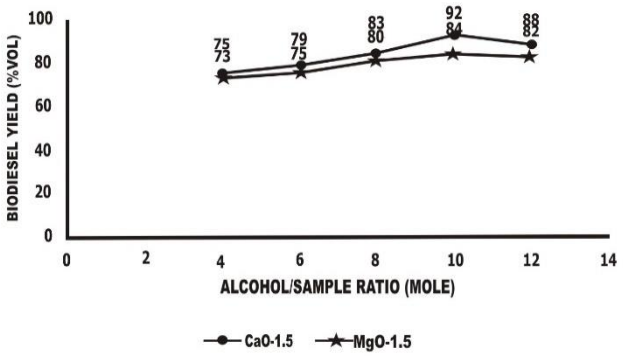


Fig. 6: Effect of alcohol/sample ratio on biodiesel yield

Fig.2 showed an appreciable increase in biodiesel yield as catalyst concentration increased. This was due to more active sites (pore spaces) for reaction at Li-CaO-1.5 and Li-MgO-1.5 with the best yield at those points. MgO at 1.5 % wt. gave the highest yield of 83.00 %, while the highest yield of CaO at 1.5 % wt. catalyst dosage was 76.00 % by volume. Fig.3 showed that an increase in reaction temperature for the limits under study (30, 40, 50, 60 and 70 ^{0}C) increased the quantity of biodiesel. For the catalysts (CaO and MgO) at the optimal value (1.5 % wt.), the highest biodiesel yields of 90.00 and 83.00% vol. were respectively obtained at the reaction temperature of 60^{o}C. The agitation speed variation presented in Fig. 4 for the two metallic oxides at optimal points showed a simultaneous increase in biodiesel yield as agitation speed increases. Agitation speed of 400 rpm from the result gave the highest biodiesel yields of 94 and 84% vol. respectively for the catalysts. However, higher agitation speed at 500 rpm may have caused catalyst dissolution into the media, thus lowering the conversion effect. Methanol (alcohol) and sample (bio-oil) variation in molal ratio as presented in Fig.5 had little effect on biodiesel yield as little difference in yield were observed for various ratio. From the result, the molal ratio of 10:1 at the optimal value of 1.5% wt. gave the highest biodiesel yields of 92.00 and 84.00% vol. respectively for the CaO and MgO doped catalysts.

From the overall study on the effects of the process conditions, it is evident that lithium-doped CaO (Li-CaO-1.5) gave the best biodiesel yields by volume for process parameters considered, except its catalyst concentration which favored the MgO-doped sample.

4.0 Conclusion and recommendations

4.1 Conclusion

This study involved the production of biodiesel from seed oil of *Cussonia bateri* (jansa) through transesterification using varied forms of lithium-ion-doped CaO and MgO. Focus was made to understand the catalytic performance of the two catalyst forms to understand the most effective form as a pilot project for industrial replication. Catalyst yield in volume and characteristic properties were used as yardstick. It was observed that the variants Li-CaO-1.5% and Li-MgO-1.5% were the most effective among CaO and MgO species. Among these two, the Li-CaO-1.5% variant was most effective at 1.5% concentration by weight.

4.2 Recommendations

From the study, it was recommended that;

i. Li-doped CaO and MgO, and other similar materials be adopted for the production of biodiesel to bridge the energy gaps.
ii. More research to advance the utilization of catalysed materials for biodiesel production be performed.

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