THE PROSPECT OF SILVER (AG) NANOPARTICLES AS MIXED NANO CATALYST

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Abstract
Conventional method for the synthesis of biodiesel from vegetable oils entails isolation of oils by extrusion or solvent extraction, degumming, and refining of oil followed by transesterification. This significantly adds to the high cost of biodiesel production from vegetable oils. Herein, we report for the first time, the development of alumina supported silver nano particles as heterogeneous catalysts for in situ generation of biodiesel from castor seeds powder. Prequel to biodiesel production, oil from the seeds of castor was extracted via soxhlet extraction method and analyzed for their physicochemical properties where 65% oil yield was obtained. The obtained silver nano catalyst was prepared by chemical reduction and was supported by loading same on Alumina. The catalyst was characterized by means of X-ray diffraction and X-ray Fluorescence. Result obtained from XRD analysis revealed absorption at 2 θ =45nm whereas XRF analysis revealed the presence of Ag and Al_2O_3 suggesting successful incorporation AgNps onto Alumina. Optimization of various parameters affecting the transesterification process revealed thus; temperature equaling 60^oC, methanol to oil ratio of 6 and reaction time of 45 min. the biodiesel produced was further characterized for its fatty acid methyl ester profile using gas chromatograph coupled with mass spectrophotometer (GC-MS). The results indicate the presence of methyl octadecanoate, methyl hexadecanoate and linoleic acid methyl ester. Biodiesel's fuel properties analysis indicates 5 cSt, 90oC, 0.97, 7.3/100g, 0.012?% and 1.9mgKOH/g for kinematic viscosity, flash point, specific gravity, iodine value, sulphur content and acid value respectively.

Keywords: *in situ* transesterification, silver nanoparticles, vegetable oil.

1. Introduction

It is estimated that the greater amount of energy used in the world and virtually 100% of that used as transportation fuel is driven from fossil fuels (Thiam and Subhash, 2008; Atadashi *et al.*,, 2011). This is as a result of high demand for energy in the industrialized world occasioned by world's increased population. The pollution problem caused by the use of fossil fuel coupled with their finite nature has made the development of alternative renewable energy sources crucial. Biodiesel is a clean energy resource produced from vegetable oils, animal fats and algal oil.

It possesses properties that are almost similar to petrodiesel and can thus be used in diesel engines with little or no modification (Fukuda *et al.,* 2001; Atashi *et al.*, 2010). Furthermore, it is non-toxic, biodegradable and produces much less harmful emissions than conventional fossil-based diesel (Antolin *etal.,* 2002; Issariakul *et al.,* 2008).

However, despite these favorable hallmarks of biodiesel, it faces serious challenges when it comes to the affordability of biodiesel; the cost of biodiesel is higher than that of petroleum based diesel: US $ 1.4-2.4 per US gallon of biodiesel, compared to US $ 1.0-1.5 per US gallon of petroleum diesel (Manhattan and Kansas, 2002). The relatively high cost of biodiesel is mainly due to the high production cost involved (Abbaszaadeh *et al*, 2012).

However, direct biodiesel production by *in situ* homogeneous transesterification was developed in order to reduce the cost and make biodiesel more competitive to petro diesel, (Georgogianni*et al*., 2008; Zakaria and Harvey, 2011; Kartika *et al.,* 2013) eliminating the prior oil extraction step. The technique is fairly fast with up to 95% conversion obtained in 90 minutes (Kartika *et al*., 2013). Furthermore, it has been predicted to be cost effective with total equipment cost reduced by up to 37% compared to the conventional method (Hass *et al*., 2006; Marchelti *et al*., 2008).

Nevertheless, the homogenous catalysis process, which uses acid or strong base catalyst, is further still associated with some problems even in *in situ* transesterification. Such problems include corrosion of reaction vessels, difficulty in removal of the catalyst from the product, generation of large amount of wastes from washing water as well as sensitivity of the process to free fatty acids and water levels in the oil feedstocks (Antolin *etal.,* 2002).

This led to the development of conventional transesterification using heterogeneous catalysts such as basic oxides, rare oxides and supported alkaline earth metal oxides with fairly more tolerance to FFA and water in the oil feedstock. In general, the process is environmentally benign and economical favorable compared to the traditional homogeneous process (Kim *et al.,* 2004). Our published work (Muhammad *et al.,* 2015), using kaolin and CaO/Kaolin as catalysts in conversion of extracted oil to biodiesel show that over 85% conversion could be achieved.

The present study reveals the potential of silver nanoparticles-due to their large surface area, and their mixture on Alumina as heterogeneous catalyst for *n situ* transesterification of castor seeds powder into biodiesel. The catalyst was characterized by XRD, XRF and UV-vis spectroscopy and the obtained biodiesel was evaluated for its fatty acid methyl esther content as well as some fuel properties parameters. The result obtained suggests that the prepared biodiesel possesses fuel properties corresponding to conventional petro diesel and could thus be used as substitute to the latter as alternative transportation fuel.

2. Experimental

2.1 Materials

Castor seeds used as substrate for biodiesel production were collected from Coga farms, Bode Saadu, Kwara State, Nigeria and were identified at Botany Unit of pure and applied science department, Abdu Gusau Polytechnic, Talata Mafara. Kaolin used for the preparation of alumina was obtained from Kankara local government area of Katsina State. Silver nitrate and sodium borohydride were procured from Loba Chemie Mumbai, India. Methanol and n-hexane were obtained from Himedia chemicals Mumbai, India. All chemicals used in this experiment were analytical grade and were used as received from their various suppliers

2.2. Extraction of oils

The extraction of oils was performed by means of soxhlet method with *n*-hexane as extracting solvent wherein, a known quantity of grounded castor seeds powder were transferred into thimble for 10 hrs after which the solvent was removed with rotary evaporator to recover the oil. The weight of oil obtained (x100%) was normalized to the weight of seed extracted to obtain the respective oil yield of the seeds.

2.3. Preparation of Alumina

The preparation of alumina was carried out in accordance with the reported method (Bello, 2018). In a typical experiment, a pre-weighed amount of raw kaolin clay was grounded into powder using mortar and pestle. The grounded sample was allowed to pass through a 40 mesh sieve and the sample was calcined at 500 ^{0}C for 5 hours for the obtainment of alumina. The dried sample was cooled in a desiccators and kept in a plastic pouch till further use.

2.4. Preparation of silver nanoparticles

Silver nanoparticles were prepared by Chemical reduction method using sodium borohydrate as reducing agent. In a typical experiment, an aqueous solution of sodium borohydride was added to an aqueous solution of silver nitrate (0.05M) in drop wise under continuous stirring at room temperature to obtain a precipitate. The brownish color observed after the addition sodium borohydride was taken as evidence for complete reduction of Ag^{+} ions into silver nanopartcles. Subsequently, the aqueous component was sampled and analyze by UV-Vis spectroscopy.

2.5. Preparation of fatty acid methyl ester

Prequel to preparation fatty acid methyl ester via in situ approach, silver nanoparticles and their mixture on Alumina in different ratio selected based on optimization process conducted were prepared. The silver nano particles were loaded on Alumina which was prepared from locally available kaolin. The best silver nano particle mixture on alumina was selected for the *in situ* transesterification of castor seed powder into biodiesel. A single-stage *in situ* heterogeneous transesterification was employed for the production of biodiesel. In a typical experiment, the required quantities of the reagents and catalyst, as reported by Bello, 2018, were transferred into the reactor containing 5g of the pulverized oil seeds. The reaction continued at the design-specified time and temperature conditions under constant stirring speed. Subsequently, the spent catalyst and substrate were separated by centrifugation (4,500 rpm, 10 minutes) and the biodiesel recovered from the supernatant with the aid of separating funnel. The biodiesel yield was evaluated by normalizing the weight of the biodiesel obtained (x100%) to the weight of the oil in 5g of the oil seed. All the trials were performed with the aid of Eyela Personal Organic Synthesizer ChemiStation (Model PPV-4431).

2.6. Instrumental analysis

The silver nanoparticles and its mixture in Alumina developed were characterized for their elemental composition and mineralogy using X-ray fluorescence (XRF) and X-ray diffraction (XRD) spectroscopy respectively. The successful reduction of Ag^+ ions into silver nano particles was assessed by UV-vis spectroscopy. The preparation of fatty acid methylesther was confirmed by means of GC-MS analysis whereas the various fuel properties were determined with the aid of respective instruments.

3. Result and Discussion

3.1 Extraction of oils

Table 3.1 presents the result of oil content of *castors* seeds extracted using hot water and stirring method and solvent extraction method. The high oil yield (65%) obtained is an indication that the seeds are viable source of oil, which could be utilized for the production of biodiesel. The high oil yield obtained via solvent extraction may be due to optimal washing of the lipid content in the samples than in hot water and stirring method. Nonetheless, the oil yield obtained from both method revealed the suitability of both methods for the extraction of oil from plant seeds substrate.

This percentage crude lipid obtained is higher than the one obtained by Muhammad *et al.,* (2012) and is comparable to the value obtained by Gao *et al.* (2008). This high oil yield is attributable to the nature of the substrate and also the extent to which the seeds were grounded.

Table *3.1: Percentage Crude lipid (oil) yield obtained from castor seeds*

Extraction method	Crude lipid yield %
Solvent extraction (soxhlet)	65 ± 0.11
Hot water and stirring	45 ± 0.20

3.2. Physicochemical Properties of the Oil

Table 3.2 presents the results of physicochemical properties of the oil extracted oil from castor seeds. The saponification value was found to be 220.50. (mgKOH). The free fatty acid content (FFA) of the oils was found to be 8 %. The results show that there is high percentage of FFA content in castor seeds oil. As indicated in Table 3.2, the molecular weight, iodine and acid values of the oil sample were found to be 803.7, 6.5 and 20.4 respectively.

Free fatty acids (FFA) content of the raw oil is a parameter that dictate the choice of method for conversion of the oil to Biodiesel and also dictates the selectivity of a suitable catalyst for the transesterification (Deshukh and Shuyar, 2009; and Meher *et a/.,* 2004). A high free fatty acid value of 8% obtained suggests the unsuitability of alkaline catalytic approach as it results to the formation of significant amount of soap which hinders any further conversion. Deshukh and Bhuyar (2009) reported that FFA value of oil greater than 3%, results in inefficient conversion of oil ester in alkaline transesterification. The FFA values of *L. siceraria seeds oil is comparable to 6.2% reported for Karanja oil* (Naik *et al.,* 2007) and higher than those of palm oil (5.3%) and frying oil (5.6%) (Balat and Balat, 2008). The average molecular mass of the extracted crude lipids shows that castor seeds oil has high molecular mass of 787.30 which is associated with lower saponification values.

Table 3.2 Physicochemical properties of the Extracted Oils from the Seeds of Lagenaria siceraria.

Physicochemical parameters	value
Saponification value (mg/KOH)	220.50 ± 0.01
Free fatty Acid %	8.0 ± 0.04
Molecular weight (g/mol)	787.30 ± 0.01
acid value mgKOH/g	20.4 ± 0.10
Iodine value (g/100g)	6.5 ± 0.02

3.3 Fatty acid methyl ester yield

Table 3.3 presents the result of fatty acid methyl ester yield obtained using alumina and alumina supported silver nano particles as catalysts used for in situ transesterificatioin of castor seeds powder into biodiesel. The results show 78% and 95% of biodiesel yield for alumina and alumina supported silver nano particles respectively. The biodiesel yield obtained from Al_2O_3/AgNPs catalyst is higher than the value (71%) reported for waste cooking palm oil by Chin, (2009) and is comparable to the value (94%) reported for soya bean oil by Yan *et al.* (2009). The yield obtained from Al_2O_3 catalyzed FAME (78%) is comparable to the value (75%) reported for canola oil by Zhao (2001). The highest value (95%) obtained using Al_2O_3/AgNPs catalysis may be due to the high surface area of the silver nano particles as compared to the Al_2O_3.

Table 3.3 Percentage biodiesel yields of *castor seeds* using different catalysts

Catalyst type	variables			Biodiesel yield %
	Temperature(^{0}C)	Time (min)	M/O	
Al_2O_3/AgNPs	60	45	6.0	95 ± 0.100
Al_2O_3	60	45	6.0	78 ± 0.115

3.4 Fatty acid methyl esters profile of the biodiesel produced.

Table 3.4 present the percentage composition of fatty acid methyl esters obtained from Biodiesel produced from *castor* seeds oils. The fatty acid methyl esters and their relative percentage are; methyl hexadecanoate (19.38 wt%), methyl octadecanoate (69.53 wt%) and linoleic acid methyl ester (11.09 wt%).

Table 3.4: FAMEs of Biodiesel produced from *L. siceraria* seeds oils

Methyl ester	Molecular Formula
Methyl hexadecanoate	$C_{17}H_{34}O_2$
Methyl octadecanoate	$C_{19}H_{38}O_2$
Linoleic acid methyl ester	$C_{19}H_{34}O_2$

3.5. X-ray diffraction spectroscopy

Figure 1 presents the x-ray diffraction pattern of prepared alumina and alumina supported silver nano particles. It can be observed that XRD diffractogram of Al_2O_3/AgNPs exhibited diffractions at 2 θ value 38.97, 65.33 and 78.44 which may be attributed to (1 1 1), (2 2 0) and (3 1 1) planes of the face-centered cubic silver structure respectively. This is found missing in the diffractogram of Al_2O_3 and is taken as confirmation for the successful preparation of AgNPs

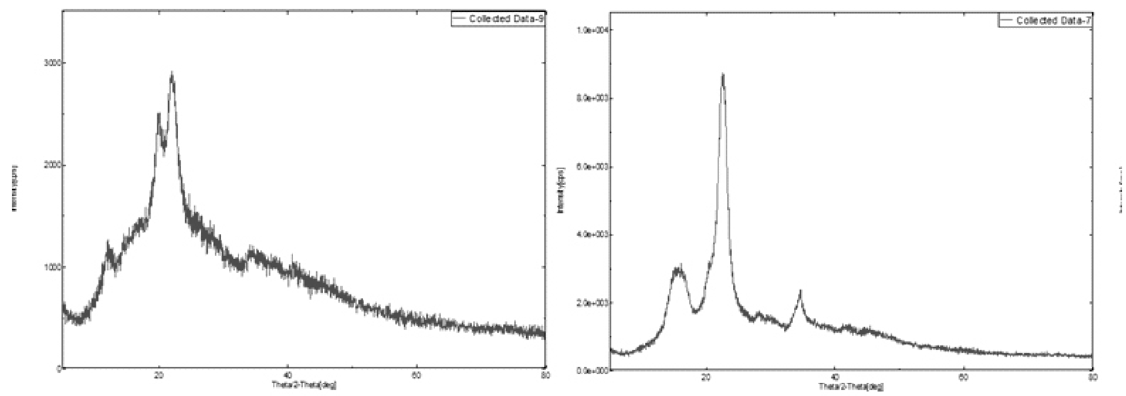

Figure : XRD analysis of (a) alumina and (b) Al_2O_3/AgNPs

3.6. X-ray fluorescence spectroscopy

Table 3.6 present the result of X-ray fluorescence analysis of the Al_2O_3/AgNPs and Al_2O_3 catalysts used in the transesterification of *castor* seeds powder into biodiesel. In addition to the silica, alumina and metallic compounds like Fe_2O_3, K_2O, TiO_2 occurring as minor, the presence of Ag confirm the successful incorporation AgNPs onto Al_2O_3. The respective percentage of the elements present in the catalyst is as depicted in Table 3.5.

sample	Ag	Al_2O_3	Fe_2O_3	K_2O	Mn_2O_3	SiO_2	SO_3
RA	1.15±0.00	39.83±0.09	0.42±0.00	0.30±0.00	0.17±0.00	43.59±0.13	0.01±0.00
TA	1.42±0.00	45.77±0.16	0.44±0.00	0.36±0.00	0.16±0.00	49.80±0.09	0.00±0.00

RK=raw alumina, TA= treated alumina

4. Conclusion

We report herein, an *in situ* transesterification of castor seeds using silver nano particles supported with alumina as heterogeneous catalyst. The parameters affecting biodiesel production were optimized and high yield of up to 95% was obtained. The high yield obtained informed the suitability of castor seeds for production of liquid fuels.

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References

Abbaszaadeh, A., Ghobadian, B., Omidkhah, M. R., &Najafi, G. (2012) Current biodiesel production technologies: A comparative review. *Energy Conversion and Management*, http://dx.doi.org/10.1016/j.enconman.2012.02.027

Agarwal A.K and Das L.M. (2001); Biodiesel development and characterization for use as fuel in compression ignition engines, *Journal of Engineering for Gas Turbines &Power* **123,** 440-447

Antolin, G. Tinaut, F.V., Briceno, Y., Castano, V. Pirez, C. and Ramirez A. I (2002) Calcium oxide as a solid base catalyst for transesterification of soya bean oil,*Bioresour. Technol,* **83**, 111-114.

Atadashi, I.M., Aroua, M.K., and Abdul Aziz, A. (2010) High quality biodiesel and its diesel engine application: A review. Renewable and Sustainable Energy Reviews, **14**: 1999-2008

Atadashi, I.M., Aroua, M.K., and Abdul Aziz, A. (2011) Biodiesel separation and purification: a review. *Renew Energy*, **36**:437–443.

Bello, K. (2018). Development and optimization of novel heterogeneous catalysts for in situ transesterification of vegetable oils into biodiesel, in Erswarmoody, IconSet 2018: AIP conference proceedings. 0200151-0200156.

Bournay, L., Casanave, D., Delfort, B., Hillion, G. &Chodorge, J.A. (2005), New heterogeneous process for biodiesel production: A way to improve the quality and the value of the crude glycerin produced by biodiesel plants, *Catalysis Today,***106**, 190-192.

Cetinkaya, M, Karoasmanaglu, F. (2004) oftrain D. Biodiesel: is it worth Considering? In: Risk and Profit Conference, MohathanKansisi, *Energy Fuels* **18**, 1888 -1895.

Fukuda, H., Kondo, A., and Noda, H. (2001) Biodiesel fuel production by transesterification of oils. *J BiosciBioeng,* **92**:405–416.

Georgogianni, K.G., Kontominas, M.C., Pomenis, P.J., Aolonitis, D., Gergis, V. (2008): Conventional and *in situ*transesterfiication of Sunflower Seed Oil for the Production of Biodiesel. *Fuel Process Technology,* **89**: 503 – 509.

Haas, M.J., Mc-Aloon, A.J., Yee, W. C., Foglia, I. A. (2006): A Process model to Estimate biodiesel Production Cost. *Bioresource Technology*, **97(4):** 671-678).

Issariakul, T., Kulkarni, M. G. Meker, L.C., Dalai, A.K, Backshi, N.N (2008). Heterogeneous Catalyst for Biodiesel Production, *Chemical Engineering J*, **140,** 77-85.

Kartika, I.A., Yani, M., Ariono, D., Evon Ph., Rigal, L. (2013): Biodiesel Production from Jatropha seeds: solve t Extraction and *in situ* transesterification in single step. *Fuel*, **106:** 111-117.

Kim, H. J., Kang, B.S, Kim, M. J., Park, Y. M., Kim D. K., Lee, J. S (2004), **Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst***CatalysisToday,* **93-95**, 315-320.

Marchelti, J.M.., Miguel, V.U., Errazu, A.F. (2008): Techno-economic study of different alternatives for Biodiesel production. *Fuel Processing Technology,* **89 (8):** 740-748.

Montoya, J., Benjumea, P., Pashova, V. (2011): Ethanolysis of Ricin Oil Using the Response Surface Methodology. *Dyna rev. Fac. nac*. Minas [online], **78:** 90 – 97.

Muhammad, A. B., Bello, K., Tambuwal, A. D. & Aliero, A. A. (2015). Assessment and optimization of L. Siceraria seeds oils into biodiesel using CaO on kaolin as heterogeneous catalyst. *International journal of chemical technology,* 7, 1-11.

Thiam, L.C. and Subhash, B. (2008) Catalytic processes towards the production of biofuels in a palm oil and oil palm biomass-based bio-refinery. *BioresourTechnol*, **99**:7911–7922.

Zakaria, R., Havey, A.P. (2012): Direct Production of Biodiesel from Rape Seed by Reactive Extraction/*in situ*tranesterification. *Fuel*, **102:** 53-60.