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# Preparation of Metal Oxide Nano Particle as Heterogeneous Catalyst Transesterification of Vegetable Oils into Fatty Acid Methyl Ester

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***Abstract:*** *The high demand for energy in the industrialized world and the pollution problem caused by the use of fossil fuel coupled with their diminishing supply has made the development of alternative renewable energy sources necessary. Biodiesel is renewable and clean energy resource produced from vegetable oils, animal fats and algal oil. It has properties that are almost similar to petro-diesel and can thus be used in diesel engines with little or no modification. The present study revealed the synthesis of silver nanoparticles due to their large surface area and their mixture on Alumina. The prepared catalyst was employed in the transesterification of vegetable oils particularly, castor oils into biodiesel. The obtained nano-catalyst was characterized by means of spectroscopic techniques. The separate effects of the molar ratio of methanol to oil, reaction temperature, silver nano-catalyst amount and reaction was investigated. Subsequently the biodiesel prepared was characterized for its fuel properties in accordance with ASTM standards.*

***Keywords:*** *Renewable, Metal Oxide, Transesterification & Vegetable Oil*

## 1. Introduction

At the moment 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). The high demand for energy in the industrialized world and the pollution problem caused by the use of fossil fuel coupled with their diminishing supply has made the development of alternative renewable energy sources necessary. Biodiesel is renewable and clean energy resource produced from vegetable oils, animal fats and algal oil. It has properties that are almost similar to petrodiesel and can thus be used in diesel engines with 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 attributes of biodiesel, the economic aspect of its production is still a major barrier; 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).

Moreover, 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 high 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 this work, silver nanoparticles due to their large surface area and their mixture on Alumina were employed as catalyst for transesterification of vegetable oils to biodiesel. The catalyst and the biodiesel prepared were characterized using spectroscopic techniques. Study on the effect of transesterification parameters on biodiesel yield was conducted.

## 2. Methods

### 2.1. Sampling

Castor seeds oils, being the most common oils used in biodiesel production, were used throughout the investigation. The oil-seeds collected were taken to the Biology Unit of the Science Laboratory Department, Umaru Ali Shinkafi Polytechnic, Sokoto for identification. The oil seeds were allowed to dried and grinded in to powdered for oil extraction.

The kaolin clay was collected from Kankara, Katsina State and was used in the preparation of alumina. The sample was allowed to dried at 110˚C and stored in glass bottles until required.

### 2.2. Extractions

Oil was extracted from the grounded seeds using Soxhlet method with *n*-hexane for 10 h and 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 in order to obtain the respective oil yield of the seeds.

### 2.3. Sample Preparation

#### 2.3.1. Preparation of Alumina

The Kaolin sample were grounded into powder using mortar and pestle, and then sieved. The powdered Kaolin are allowed to dried at 110 $^0$C for 5 hours, cooled in a desiccator and kept in glass bottles until required.

#### 2.3.2. Preparation of silver nanoparticles

Silver nanoparticles was 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 dropwise under continuous stirring at room temperature,a precipitate was obtained. The reduction of $Ag^+$ ions by sodium borohydride was monitored by sampling the aqueous component and analyze by UV-Vis spectroscopy. Furthermore, the morphology was analyzed by Field Emission Scanning Electron Microscopy.

### 2.4. Characterizations of the catalysts

The silver nanoparticles and its mixture in Alumina developed were fully characterized. Elemental composition of the catalysts was also determined using X-ray fluorescence (XRF) and the mineralogy of the catalysts was determined using X-ray diffraction (XRD) while morphology were examined using Scanning electron microscopy (SEM). furthermore, particle size of the catalysts was determined using particle size analyzer.

### 2.5. Biodiesel Analysis

Each of the biodiesel fraction/run produced were analyze with GC-MS. However, in order to make sure that the biodiesel produced meet the ASTM standard, the produced biodiesel was taken for fuel properties analysis. The analyses conducted are: pour point, cloud point, flash point, aniline point, viscosity, acid value, distillation temperature, specific gravity etc.

## 3. Result and discussion

### 3.1. Oil yield

The extraction method was performed by means of soxhlet method with *n*-hexane as extracting solvent wherein, a known quantity of grounded castor seeds powder was transferred into thimble for 10 h 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.

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 (75%) 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) | 75 ± 0.11 |
| Hot water and stirring | 56 ± 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 223.50. (mgKOH). The free fatty acid content (FFA) of the oils was found to be 7 %. 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 19.4 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) | 223.50 ± 0.01 |
| Free fatty Acid % | 7.0 ± 0.04 |
| Molecular weight (g/mol) | 787.30 ± 0.01 |
| acid value mgKOH/g | 19.4 ± 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 showed 65% and 90% 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 (91%) reported for soya bean oil by Yan *et al.* (2009). The yield obtained from $Al_2O_3$ catalyzed FAME (65%) is comparable to the value (66%) reported for canola oil by Zhao (2001). The highest value (90%) 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 | 90 ± 0.100 |
| $Al_2O_3$ | 60 | 45 | 6.0 | 65 ± 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 (21.38 wt%), methyl octadecanoate (72.53 wt%) and linoleic acid methyl ester (12.07 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 fluorescence spectroscopy**

Table 3.5 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.

Table 3.5. Percentage compositions of compounds present in the catalysts

| 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 alumin

**4. Conclusion**

In this study, the synthesis of silver nanoparticles and its use as catalyst in the esterification of castor oil into fatty acid methylester was investigated. The catalyst was prepared using reduction method and was loaded onto alumina as a support. Prior to being used in the preparation of biodiesel, the obtained nano-catalyst was characterized by means of spectroscopic techniques. The separate effects of the molar ratio of methanol to oil, reaction temperature, silver nano-catalyst amount and reaction was investigated. Subsequently the biodiesel prepared was characterized for its fuel properties in accordance with ASTM standards. The high biodiesel yield obtained indicates the viability of silver nano-catalyst in the preparation of fatty acid methyl ester.

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