The Potential of Potassium Loaded Gamma Alumina from Kaolin as a Solid Base Catalyst for Biodiesel Production

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Abstract

The investigation on enhancing the activity of single promoted catalyst, K_2O/γ-alumina, for transesterification reactions has been carried out. The K_2O was first precipitated from KNO_3, the gamma alumina was impregnated with potassium ions and subsequently CaO sorption was carried out. Calcination time was observed while the temperature was closely monitored by a locally fabricated 3liter capacity reactor coupled with a reflux and a thermometer. BET and X-ray diffraction were used to characterize the catalyst. The transesterification reaction proceeded between waste oil and methanol on the prepared catalyst. After optimization of a 6hours reflux process, 40% KNO_3 was required at 50^oC. However at 590^oC of a 6hours heating of the alumina, the methanol: waste oil ratio of 25:1 was observed at the molar scale. The catalyst can be classified as a double promoted catalyst. The double promoted catalyst show a brilliant potential compared to results reported on single promoted catalysts.

Keywords: Transesterification, Biodiesel, Gamma-alumina, Kaolin, Potassium

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1. Introduction

Single promoted catalyst has been employed and reported in all transesterification reactions involving oils. Mono–alkyl esters have been produced bytransesterification of triglyceride using mono-alkyl alcohols popularly called methanolysis process.In fact,biodiesel fuels havebeen produced with reactions normally carried out with homogenized base and acid catalysts where hydrochloric acids and sulfonic acid are used. The drawback to these oil production routes is that the reaction time is as long as two days and a higher methanol tooil rangeis involved (40–140:1mol%)[1-3]. The base catalysts used are sodium alky oxides, such as $NaOCH_3$, sodium hydroxide, potassium hydroxide, and their carbonates.

The quest for alternative sources of energy has generated a lot of interest in recent years, due to limitation of conventional fossil fuel and the increasing price of oil in the international market as well as concern over greenhouse gas emission. Biodiesel is a biodegradable and renewable form of energy, consisting of mono alkyl esters of fatty acids derived from sources such as animal fats and vegetable oil [4]. Vegetable oil was first used as fuel for a diesel engine invented by Rudolph Diesel in 1911 and it was concluded that diesel engine can be fed with vegetable oil [5]. Recently, of its many advantages such as high flash point, high cetane number, low viscosity, high lubricity, biodegradability, environmentally friendly due to less carbon monoxide emissions, as well as fewer emission profiles compared to conventional fossil fuels, there has been renewed interest on vegetable oils and animal fats as bio diesel [6]. They can also be used in conventional compression-ignition engines without the need for engine modifications [7]. Furthermore, the fuel can reduce the particulate emissions from engine either by using it in pure form or by blending it [8, 9]. Some of the vegetable oils studied by researchers as a precursors for biodiesel production includes; canola [10], palm [11], jatropha [12], palm kernel [13], sunflower [14], and coconut [15]. However, the high cost of vegetable oils compared to that of fossil based diesel fuel is the main concern

for bio diesel production. This has caused some countries to prefer some non-edible oils such as jatropha or waste cooking oils due to their low prices.

The major problem in a in a conventional homogeneous manner is the removal of the base catalyst after reaction,   since saponification and stable emulsion formation resulting from aqueous quenching, thereby making separation methyl esters difficult and the catalyst and the products are clean and separated by a large amount of water. Therefore, environmentally friendly heterogeneous catalyst is expected to replace conventional homogeneous catalyst in the near future, mainly because of environmental constraints and simplifications in the existing processes. Transesterification of vegetable oils with methanol has been catalyzed by many different heterogeneous catalyst developed in the laboratory [14-18]. For example, conversion of 78% at 513 K and >95% at 533 K for transesterification of vegetable oils with methanol was achieved by Suppes et al. [15] using calcium carbonate rock as a catalyst. Besides, the alcoholysisof rape seed oil in the presence of Cs-exchanged NaXfaujasites and commercial hydrotalcite (KW2200) catalyst [2]. The cesium-exchanged NaXfaujasites gave a conversion of 70% at a high methanol to oil ratio of 275 and 22hours of reaction time, while hydrotalcite was used to obtain 34% conversion. The two studies above required temperatures in excess of 473 K to obtain a good conversion within the time scales of the experiments. Of recent, a solid super base of $Na/NaOH/\gamma\text{-}Al_2O_3$ was prepared by Kim et al [18], which have almost the same catalytic activity under the optimized reaction conditions as that of the conventional homogeneous catalyst. The rate of reaction in most experiments using homogeneous catalyst usually proceeds in at a very slow rate. The reaction mixture constitutes a three-phase system, oil/methanol/catalyst because of the presence of heterogeneous catalysts, which for diffusion reasons inhibits the reaction. However, the synthesis methodsfor the development of an environmentally benign process and the reduction of production cost can be improved by heterogeneous catalyst.

This work is a major attempt to eliminate some of the drawbacks stated above and obtain a catalyst based void of acid removal, aimed towards achieving an economical and none corrosive and not requiring washing of impurities from the prepared fuel oil thus improving production route.

2. Methodology

2.1 Development of gamma alumina

The raw Kankara kaolin was sourced from Kankara in Kastina state. Beneficiation involved the removal soluble impurities. Calcination was done at $800^{\circ}C$ to yield metakaolin. Sulphuric acid wad sued to leach out the alumina. Ammonium sulphate crystals were used to crystalize the alum out. The ammonium alum formed was calcined at a range of $800^{\circ}C$ to $1500^{\circ}C$ and the gamma alumina was characterized with the XRF machine to ascertain the presence of alumina.

2.2Catalyst Preparation.

Gamma alumina was extracted from the kaolin sourced from Kankara field and the used vegetable oil was sourced from Mr Biggs in Minna Niger state, Nigeria. Methanol 99%, Nitrate acid analytical grade, CaO 99%, Sulphuric acid 98% and Oleic acid 99% were used.

$(K_2O/Ca_2O/\gamma\text{-}alumina)$ catalyst isa double promoted alumina–supported catalystprepared by the impregnationand precipitation.50 grams of $\gamma\text{-}Al_2O_3$was mixed with 70 ml ofdistilled water, Potassium nitrate was addedand the amount of K_2O loading (w% to $\gamma\text{-}Al_2O_3$) was varied as a factorial, the mixture was magnetically stirred for 5 hours under room temperature. Potassium nitrate was synthesized by reacting as a stoichiometricallyPotassium oxide with nitrate acid. The formed suspension was impregnated by 50 ml of 25% CaO solution (40 % weightto alumina). The solution was dried in an oven at $100^{\circ}C$. The slurry was solid catalyst, the solid was grinded and calcinatedat $800^{\circ}C$. The catalystwas dried in a

desiccator containing silica gel in order to avoid water and CO_2 going into companions with the prepared catalyst.The catalyst was characterized with the Brunauer-Emmet-Telle (BET)to determine pore diameter, pore volume and specific surface area. X-Ray Powder Diffraction (XRD) was used to identify distinctive peaks to define double promoted catalyst.

2.3Transesterification Reaction

Transesterification reaction was made to proceed inside a fabricated reactor coupled with relux condenser and a thermometer using waste vegetable oil and methanol with a molar ratio of 1:50 was filledwith 5% amount of catalyst with respect to weightof oil. The mixture was refluxed at $60^{o}C$and 5 hours of reaction time under stirring at a constant speed of magnetic stirrer inside the reactor. The catalyst was filtered off the solution. A separating funnel was used to separate into three layers, top layer was methanol, the middle wasfatty acid methyl ester and the bottom layer was glycerine.

3. Results

Table 1 shows the catalyst properties using the Brunauer-Emmet-Telle(BET) techniques.The reduction in the values of the surface area and pore volume with K_2O addition and CaO compared to the initial surface area of 99-110 m^2/g was evidently due to the site occupied by potassium and CaO loading. Kaolin extract, ɣ-Al_2O_3, was loaded with K_2O and CaO, was an indication that the pore has been occupied with the calcium oxides. The similar result was reported by Nyoman et al.2012. Since alkalinity is important for transesterification reaction, the crystal structure of CaO and K_2O seem to be form by the reaction Ca-acetate and K_2NO_3 with ɣ-Al_2O_3. The mean pore size and pore volume of $55A^o$and 0.342 cm^2/g respectively were adequate for transesterification reaction to proceed at limited reaction time of 3 hrs. Finely adsorption of KCa and K_2O were ascertained by the surface area dropping sharplyfrom 99 m^2/g to 4.311m^2/g. KCa and K_2O can therefore be clearly considered as are active components for catalysing transesterification reaction [19]. The 95% biodiesel production was achieved because of the excellent active component available for the transesterification reaction.

Table 1: Catalyst Properties Using the Brunauer-Emmet-Telle(BET) techniques

Catalyst Properties	K_2O/ɣ-Al_2O_3	K_2O/ Ca_2O/ ɣ-Al_2O_3 with 40% addition of K_2O
Mean pore size (A^o)	35.311	40.211
Pore volume(cm^2/g)	0.201	0.112
Specific surface area(m^2/g)	92.00	66.001

3.1Effect of loading K_2O

In Figure 1, the active site of CaO and K_2O was agglomerated by the covering of the basic site, which lowers the surface area and reduced over 40%V, loading amount of K_2O, the excessive addition of K_2O making biodiesel yield significant at about 50% K_2O addition of activity of the catalyst. The sorption process of KNO_3/Al_2O_3 in literature show clear agreements with this percentage.An optimum addition can be taken to lie between 40%-50%K_2O addition.This optimum value was used to obtain the duration temperature of calcination shown in Figure 2 and Figure 3. Which are impressive for an optimum production route for the double promoter catalyst.
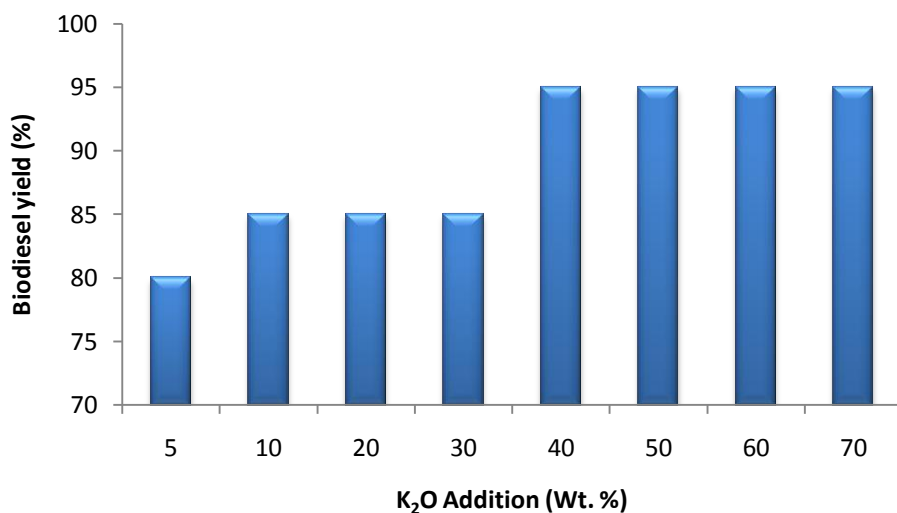
Figure 1: Yield of Biodiesel (%) versus addition of K_2O addition (wt.%) duringtransesterification reaction
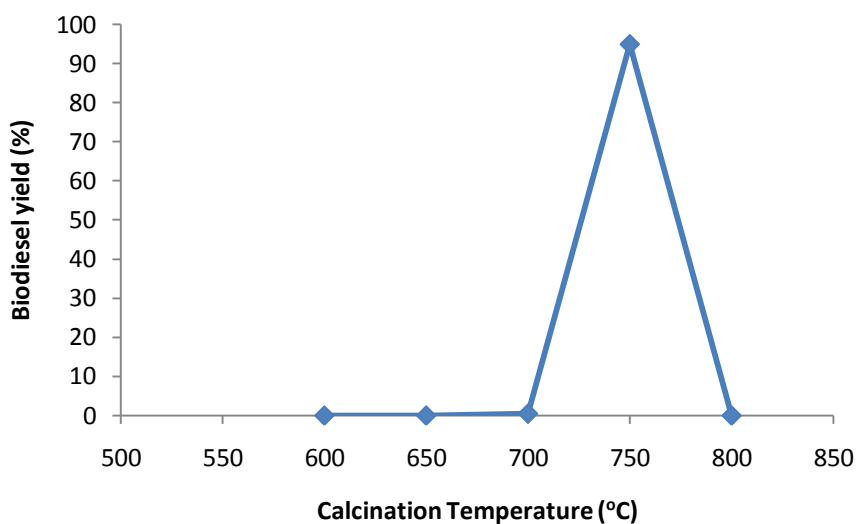

Figure 2:Yield of Biodiesel (%) versus Temperature during transesterification reaction
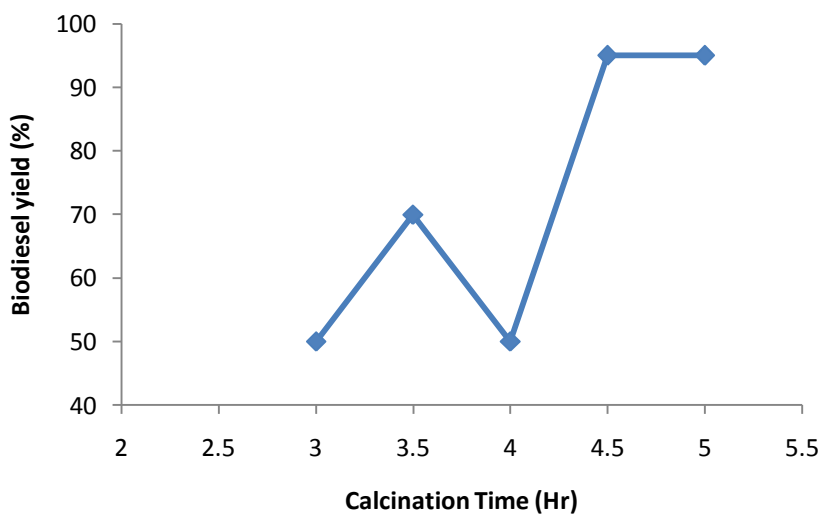

Figure 3:Yield of Biodiesel (%) versus Calcination time during transesterification reaction

3.2 XRD oriented slide Diffraction of the Catalyst

XRD shown in Figure 4 shows that the characteristic peaks of KNO_3 of 2u equals 200, 250, 293, 330 and 350 and K_2O of2u equals 320 and 500 was observed, indicatesa satisfactory dispersionof KNO_3 on the alumina. As the amount of addition $KNO_3$was above 15 wt. % loading, the characteristic XRD peaks ofKNO_3 appeared on the XRD patterns peaks intensities increasesas the amount of loaded KNO_3, increases indicates that anuncovered phase of the phase of $KNO_3$was available for occupying. A spontaneous dispersion capacity of KNO_3 onalumina was between 20 and 30 wt.%. The monolayer seen in the XRD shows the undetectablephase of KNO_3 and K_2O which clearly dispersed on alumina. The sites loaded with potassiumnitrate at greater than the spontaneous dispersion onalumina beyond it capacity, on the composite only the residual bulk phase of $KNO_3$is left unoccupied. Accordingly, sinceKNO_3 hasinteraction with the alumina surface, only a portion of KNO_3decomposed during activation indicated very reliable characteristics peaks.
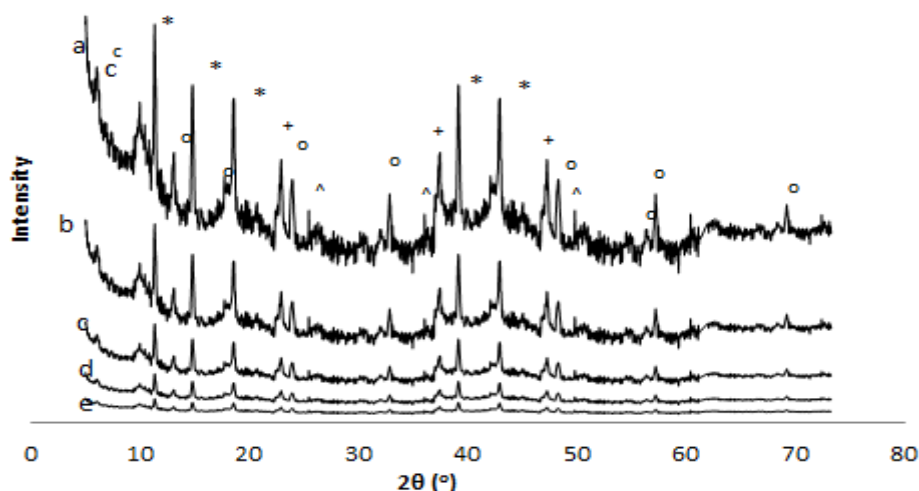

Figure 4: XRD patterns for samples: (a)20% KNO_3/Al_2O_3calcined at 700°C, (b) 30% KNO_3/Al_2O_3calcined at 800°C, (c) 20% KNO_3/Al_2O_3calcined at 700°C,(d) 15% KNO_3/Al_2O_3calcined at 700°C.

4. Conclusions

Potassium loaded alumina shows a stronger solid based double promoted catalyst used for transesterification reactions. At high degree of 700°C calcinationof gamma alumina, an optimum production route was defined by a 5hr reaction time and a 50% wtaddition.A high basicity bettercatalytic activity was obtained for transesterification reactions. Better conversion was reached at 95% biodiesel yield. Compared with similar reactions are corresponding basic properties and activities, the base catalysts show a reliable relationship. The products of the used KNO_3, precipitating K_2O species in the composite, were the active basic sites.

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References

1. K.J. Harrington, C. D'Arcy-Evans, Ind. Eng. Chem. Prod. Res. Dev. 24(1985) 314.
2. K.J. Harrington, C. D'Acry-Evans, J. Am. Oil Chem. Soc. 62 (1985) 1009.
3. S. Siler-Marinkovic, A. Tomasevic, Fuel 77 (1998) 1389
4. C.-Y. Lin, H.-A. Lin, L.-B. Hung, Fuel structure and properties of biodiesel produced by peroxidation process, Fuel 85 (2006) 1743–1749.
5. A.C. Pinto, L.L.N. Guarieiro, M.J.C. Rezende, N.M. Ribeiro, E.A. Torres,W.A. Lopes, P.A. de Pereira, J.B. de Andrade, Biodiesel: an overview, Journal of the Brazilian Chemical Society 16 (2005) 1313–1330.

6. M.P. Dorado, E. Ballesteros, J.M. Arnal, J. Gómez, F.J. López, Exhaust emissions from a diesel engine fueled with transesterifiedwaste olive oil, Fuel 82 (2003) 1311–1315.

7. M.A. Dubé, A.Y. Tremblay, J. Liu, Biodiesel production using a membrane reactor, Bioresource Technology 98 (2007) 639–647.

8. J.P. Szybist, J. Song, M. Alam, A.L. Boehman, Biodiesel combustion, emissions and emission control, Fuel Processing Technology 88 (2007) 679–691.

9. A. Mohammed, A. A. Adeniyi, A. B. Hassan, O. O. Adeyeye. Performance and Emission Characteristics of Heptane and Toluene Blends at Constant Injection Operation on a CI Engine. International Journal of Engineering Science and Technology, Vol. 4 (4) (2012):1835-1841.

10. A.K. Dalai, M.G. Kulkarni, L.C. Meher, Biodiesel productions from vegetable oils using heterogeneous catalysts and their applications as lubricity additives, IEEE EIC Climate Change Technology Conference EICCCC art 057358, 2006.

11. S. Baroutian, M.K. Aroua, A.A.A. Raman, N.M.N. Sulaiman, Density of palm oil-based methyl ester, Journal of Chemical and Engineering Data 53 (2008) 877–880.

12. A.K. Tiwari, A. Kumar, H. Raheman, Biodiesel production from jatropha oil (Jatrophacurcas) with high free fatty acids: an optimized process, Biomass and Bioenergy 31 (2007) 569–575.

13. H. Li, W. Xie, Transesterification of soybean oil to biodiesel with Zn/I2 catalyst, Catalysis Letters 107 (2006) 25–30.

14. G.J. Suppes, M.A. Dasari, E.J. Doskocil, P.J. Mankidy, M.J. Goff, Appl. Catal. A: Gen. 257 (2004) 213.

15. G.J. Suppes, K. Bockwinkel, S. Lucas, J.B. Mason, J.A. Heppert, J. Am. Carbon balance implications of coconut. Oil Chem. Soc. 78 (2001) 139.

16. E. Leclercq, A. Finiels, C. Moreau, J. Am. Oil Chem. Soc. 78 (2001) 1161.

17. C.R. Beynese, H. Hinnekens, J. Martene, US Patent 5,508,457 (1996).

18. H.J. Kim, B.S. Kang, M.J. Kim, Y.M. Park, D.K. Kim, J.S. Lee, K.Y. Lee, Catal. Today 93–95 (2004) 315.

19. Indonesia ((2012) 2012 3rd International Conference on Biology, Environment and Chemistry IPCBEE vol.46 (2012) © IACSIT Press, SingaporeDOI: 10.7763/IPCBEE. 2012. V46. 25.