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USE OF COAL FLY ASH AS A CATALYST IN THE PRODUCTION OF BIODIESEL

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Abstract

South Africa is largely dependent on the combustion of coal for electricity production; Eskom's coal-fired power stations consume approximately 109 million tons of coal per annum, producing around 25 million tons of ash, to supply the bulk (93%) of South Africa's electricity. The management of this fly ash has been a concern with various approaches for its beneficial use being investigated. This work presents the results of transesterification reaction using sunflower oil as feedstock with methanol and class F fly ash catalyst derived from a coal fly ash dump in South Africa to produce methyl esters (biodiesel). The fly ash based catalyst was prepared using the wet impregnation procedure with different loadings of potassium. This was characterized by powder X-ray diffraction (XRD), FTIR spectroscopy. The XRD patterns obtained indicated that the structure of the support gradually deformed with an increase in the loading and the extent of decomposition of KNO_3 varied with the amount of loading. The influence of various reactions parameters such as loading amount of active components, methanol: oil ratio, reaction time, temperature and catalyst deactivation was investigated. The fly ash based catalyst loaded with 5% wt KNO_3 at a reaction temperature of 160ºC exhibited maximum oil conversion (86.13%). The biodiesel synthesized was tested and important fuel properties of the methyl esters (Biodiesel) compared well with ASTM biodiesel standard.

Key words: Fly ash; Heterogeneous catalyst; Sunflower oil; Transesterification; Methyl ester.

1. Introduction

The recent energy crisis, largely driven by factors of economic growth and social integration, has lead to the construction of new coal power plants in South Africa. Despite the mounting interest surrounding the renewable sector, coal-fired power stations still account for a large percentage of South Africa's electricity generating capacity. Specifically, South Africa generates 93 % of its electricity from coal combustion. Eskom's coal-fired power stations consume approximately 109 million tons of coal per annum, producing around 25 million tons of ash, to supply the bulk of South Africa's electricity [1]. Almost 90% of the ash produced in the generation process is called fly ash or pulverised fuel ash (a waste by-product of burning coal to generate electricity). This is because, the coal is pulverised into a very fine dust (rather like cake flour) before being fed into the boilers to ensure efficient combustion. It is estimated that around 300 billion tonnes per year of fly ash is produced worldwide and the amount is expected to increase in future due to the pressing need for generation of sufficient energy [2]. The disposal and management of the huge quantities of fly ash generated has been a concern to the policy advisers, industrial and the scientific communities. Specifically, South Africa's coal is high in ash content, and as such, the use of fly ash is an environmentally important issue. Most of these approaches are either geared to utilize the ash beneficially in order to reduce the cost of disposal, or to minimize their environmental impact [3]. The utilization of fly ash as a suitable feedstock for use as heterogeneous catalyst for the transesterification would allow beneficiation of fly ash in an environmentally friendly way which would make the process more economically viable.

Biofuels are derived from renewable sources such as naturally occurring fats and oils, which may be obtained from variety of plants and animals. Since, diesel-fuel figures as an essential function in the industrial economy, biodiesel-synthesis has constituted the essence of current research in the field of biofuels. Biodiesel, a green fuel, is comprised of mono-alkyl esters of long chain fatty acids which are derived from fatty acid glycerides, and are major components of an oil or fat. Transesterification is the key and foremost important process to convert vegetable oil or animal fat into a diesel-like fuel [4, 5]. This is illustrated in Figure 1.

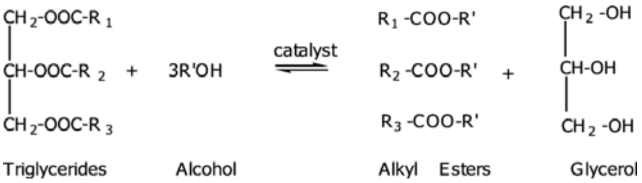

Fig. 1 Transesterification of triglyceride with alkyl alcohol

In transesterification, triglycerides in vegetable oil react with alcohol to form a mixture of glycerol and fatty acid alkyl esters. Transesterification of oil/fat can be catalyzed by alkali [6], acid or enzyme [7]. Among, alkali and acid-catalyzed transesterification; reaction is much slower with acid catalysts [8]. Moreover, the corrosive acid-catalyzed transesterification needs extreme temperature and pressure conditions. Although, the catalytic activity of a base is higher than that of an acid, use of homogeneous base catalyst is non-practical because of the various issues such as catalyst removal after the reaction, substantial low ester yield and difficulty in product separation. These problems have provided an impetus for the search of stable and more environmental friendly solid base catalysts. While searching for promising solid base catalysts, several attempts have been made using basic zeolites, alkali and alkali earth oxides, alkali and alkali earth carbonates, supported guanidine and basic hydrotalcites. [9]. Moreover, various supported catalysts were examined for their activity with use of supports like zinc oxide [10, 11], NaX zeolite [12] and mesoporous silica [13]. The promise of cheaper process still exists because there is a constant need of developing an improved cost-effective and eco-friendly process for manufacturing of biodiesel that could potentially lead to easier refining of the produced biodiesel and glycerol, recycling of the catalysts and hence, lower production costs [14]. Fly ash, an inorganic residues arising from coal combustion processes consists essentially of SiO_2 and Al_2O_3 and being an environmental pollutant, constant generation of fly ash in huge quantities is a matter of concern. In view of its important economical and environmental implications, the disposal and utilization of fly ash represents a significant challenge. Although, fly ash is mainly used as building materials and in other civil engineering works (cement and dry wall board manufacturing), there is still a proportion which is being disposed off in ponds or landfills. These products use refined fly ash which has been cleaned of contaminants. Development of environmentally safe applications for the utilization of coal fly ash is very important. Consequently, attempt was made to develop an efficient, inexpensive and environmental friendly fly ash-based heterogeneous catalyst for the esterification and/or transesterification reactions, for example for the production of biodiesel.

In view of above, solid fly ash-based base catalysts were prepared and their catalytic performance in transesterification of sunflower oil was studied. In this study, fly ash loaded with KNO_3 was assessed for the transesterification of sunflower oil with methanol to methyl esters. Potassium was the metal of choice because previous studies carried out by Ramos et al identified a problem of leaching when sodium was impregnated unto zeolite supports [15]. Another aim of this study is to ensure a long term stability rendering economical benefits to the biodiesel production process.

2. Experimental

2.1 Materials

Pulverized fly ashes that were collected from the ash collection systems at Arnot Thermal Power station in the Mpumalanga District of South Africa was used as a support. The elemental chemical composition of the fly ash (on dry basis) was SiO_2 50.91%, Al_2O_3 30.91%, Na_2O 0.10%, CaO 6.2%, Fe_2O_3 3.46%, MgO 1.48%, TiO_2 1.65%, MnO 0.02%, K_2O 0.60%, P_2O_5 0.56%. Before its use, material was ground to a fine powder. The average SiO_2/Al_2O_3 ratio of Arnot fly ash was found to be 1.65. The major elemental chemistry of the Arnot fly ash is consistent with $SiO_2+Al_2O_3+Fe_2O_3 \geq 70\%$ meaning that it is "class F" fly ash (ATSM method C 618). This is a typical composition of fly ash from combustion of bituminous coal from South Africa [16]. The alkali salt KNO_3 (99% purity from Merck Chemicals, South Africa) was used in as-received form to prepare its stock solution (aq. 5% wt/wt). Apart from fly ash from a pulverized coal power plant, another primary source of fly ash is from a municipal waste incineration plant.

2.2 Catalyst preparation

The catalysts were prepared using established method of wet impregnation. Appropriate quantities of aq. stock solution of KNO_3 salts were loaded separately onto different portions of fly ash. After drying, they were calcined at desired temperature for 5 h in air. Typically, to freshly dried 10 g of fly ash, 10.2 ml of aq. stock solution of KNO_3 was added slowly with constant manual stirring. Stirring was continued till homogeneous mixture was obtained. The removal of water was accomplished by using rotary evaporator. Then the powder was calcined at 500ºC for 5 h. This fly ash-based catalyst with 5, 10, 15 and 20 wt. % KNO_3 loading was labeled as catalysts A, B, C, and D respectively. These were then characterized to determine the effect of the KNO_3 loading on the structure and its catalytic effect. This method is similar to the one reported in a recent article [17].

2.3 Catalyst characterization

Catalysts prepared were characterized to measure the properties such as pore size, surface area, structure, number and strength of basic sites to thus understand the performance of the catalyst.

2.3.1 X-ray powder diffraction (XRD)

The quantification of mineral and amorphous phases in Arnot fly ash was determined after the addition of 20 % Si (Aldrich 99 % pure) for determination of amorphous content and milling in a McCrone micronizing mill, the fly ash sample was prepared for XRD analysis using a back loading preparation method. It was analysed with a PANalytical X'Pert Pro powder diffractometer with X'Celerator detector and variable divergence- and receiving slits with Fe filtered Co-Kα radiation. The phases were identified using X'Pert Highscore plus software. The relative phase amounts (weight %) was estimated using the Rietveld method (Autoquan Program). While the phase/s identification by XRD, were obtained using a Phillips X-ray diffractometer with Cu-K® radiation over a 2θ range of 4ºC to 60ºC with a step size of 0.02º at a scanning speed of 5º /min. The phase identification was performed by searching and matching obtained spectra with the powder diffraction file data base with the help of JCPDS (Joint committee of powder diffraction standards) files for inorganic compounds.

2.3.2 BET surface area

The surface area and pore size determination was conducted by the application of gravimetric nitrogen Brunauer-Emmett-Teller (N2-BET) surface analysis technique. The samples to be analysed was out gassed at 110ºC on the Flow Prep 060 using helium gas. Micromeritics Tristar instrument was used with nitrogen as the analysis gas based on a 5 point with 30 adsorption and 30 desorption points.

2.3.3 Fourier transformed infrared (FTIR) spectroscopy

Fourier Transform Infrared spectroscopy **(**FT-IR) was used to provide information about molecular structure. FT-IR requires virtually no sample preparation. The scanning range was from 400 to 46000cm$^-$1.

2.3.4 Scanning electron microscope (SEM

The morphology of the fly ash and the fly ash based catalyst were examined using a Hitachi X-650 scanning Electron Microanalyser equipped with a CDU- lead detector at 25kV equipped with energy dispersive spectroscopy (EDS). Samples were mounted on aluminum pegs and coated with a thin film of gold to make them conductive.

2.4 Transesterification reaction

Sunflower oil was obtained from a local supplier in Cape Town (situated in the Western Province of South Africa) and use without any further refinement. Its acid value was 0.05mgKOH/g with a viscosity value of 29.4mPas. Fatty acid composition of the sunflower oil used is highlighted in Table 1.

Table 1 Fatty acid composition of sunflower oil

Fatty Acid	Content (%)	Fatty Acid	Content (%)
Palmitic (16:0)	6.08	Linoleic (18:2)	71.73
Stearic (18:0)	3.26	Linolenic (18:3)	0.56
Oleic (18:1)	16.93		

All the reactions were run at atmospheric pressure, and the influence of several variables in its conversion was studied using the following ranges: temperature (100-200°C), reaction time (5-24hrs), various amounts of catalyst (5-20wt %) and a methanol/oil molar ratio between 6 and 15 were taken in a two neck round-bottom glass batch reactor placed in an oil bath under reflux with a stirring speed of 700rpm. No inert atmosphere was used and all reactions occurred in contact with air at ambient pressure. The reaction mixture was heated up to 180ºC with continuous stirring until the completion of the reaction. After completion of the methanolysis reaction, mixture was centrifuged. The solid catalyst was recovered and the residual methanol was separated via rotary evaporation.

The glycerol was separated and recovered after petroleum ether treatment, samples were withdrawn from the separated mixture with a glass capillary and diluted with hexane to perform thin layer chromatographic (TLC) studies. The completion of the reaction and primary characterization of the product was analysed by silica gel TLC technique to check the conversion of the triglyceride into methyl esters according to the method described by Damyanova [18]. The TLC was chosen because it is a rapid analytical method that gives quite accurate indication of oil and methyl esters content in mixture. Silica gel TLC plates (20x20cm-Sigma Alrich) were used and various samples were analysed on each plate shown in Figure 2. A mixture of using hexane/ethyl acetate/acetic acid (80:20:2 v/v/v) was used as the mobile phase and silica gel as the stationary phase. Detection was obtained by spraying the plate with 10% ethanolic phosphomolybdic acid solution and heating the plates for 10minutes at 180ºC in an air circulating oven. Biodiesel shows a higher mobility than vegetable oil with the selected solvent system and complete conversion of vegetable oil to biodiesel was supported by the disappearance of the vegetable oil spot on the TLC plate.

2.5 Viscosity measurements

The basic parameter reflecting the extent of the reaction could also be the viscosity, since it is directly related with the fatty acid methyl ester (FAME) content of the product and is one of the specifications to comply with in manufacturing a biodiesel (it is as an indicator to measure the effectiveness and completeness of the ester conversion process). Generally, the product with less viscosity is the one with higher total methyl ester content. For all the light phase products obtained, an empirical correlation between the viscosity and the methyl ester content can be attained. This type of relationship has been reported in the literature [19], thus allowing the total concentration of methyl ester to be obtained from only the viscosity measurement; then the difference in viscosity between the sunflower oil triglyceride and the alkyl ester derivative can be used to monitor biodiesel production in all the experiments and therefore catalyst activity. The dynamic viscosity of the original oils and the produced biodiesel was determined using Anton Parr Physica MCR 501 Rheometer operating on a rolling ball principle. One replicate for each sample was done as the instrumentation gave consistent results. The oil conversion value was obtained from the results which was calculated using the equation

$$\text{Oil Con} = (\text{Viscosity of triglyceride} - \text{Viscosity of methyl ester}) * 100 / \text{Viscosity of triglyceride} \quad [1]$$

3. Results and discussion

3.1 Catalyst characterization

3.1.1 XRD

The Powder XRD patterns and the mineral composition of the Arnot fly ash and that of the fly-ash based catalyst (5% KNO_3-flyash) are presented in depicted in Figures 3 and 4. The XRD patterns of the other fly ash catalysts loaded with different percentages of KNO_3 designated as B, C and D are not included in the spectra. The XRD pattern of the Arnot fly ash exhibited the characteristic peaks of crystalline phase's viz. ἀ-Quartz, Hematite, Magnetite and Mullite. From the XRD pattern of Arnot fly ash presented in Figure 3, it was found that the predominant phases were quartz (SiO_2) with major peak at 26.9 degrees 2θ and less intense peaks also identified, mullite ($3Al_2O_3.SiO_2$), major peaks at 26.4 degrees 2θ (i.e as a shoulder on the quartz peak), magnetite, and hematite. The presence of amorphous phases are identified as a broad diffraction 'hump' in the region between 18 to 32 degrees 2θ [20-22] (b) shows that the quantity of the phases identified were in the following order; Amorphous (58.22 %) > Mullite (24.84 %) > Quartz (13.66 %) > Magnetite (2.75 %) > Hematite (0.53 %).

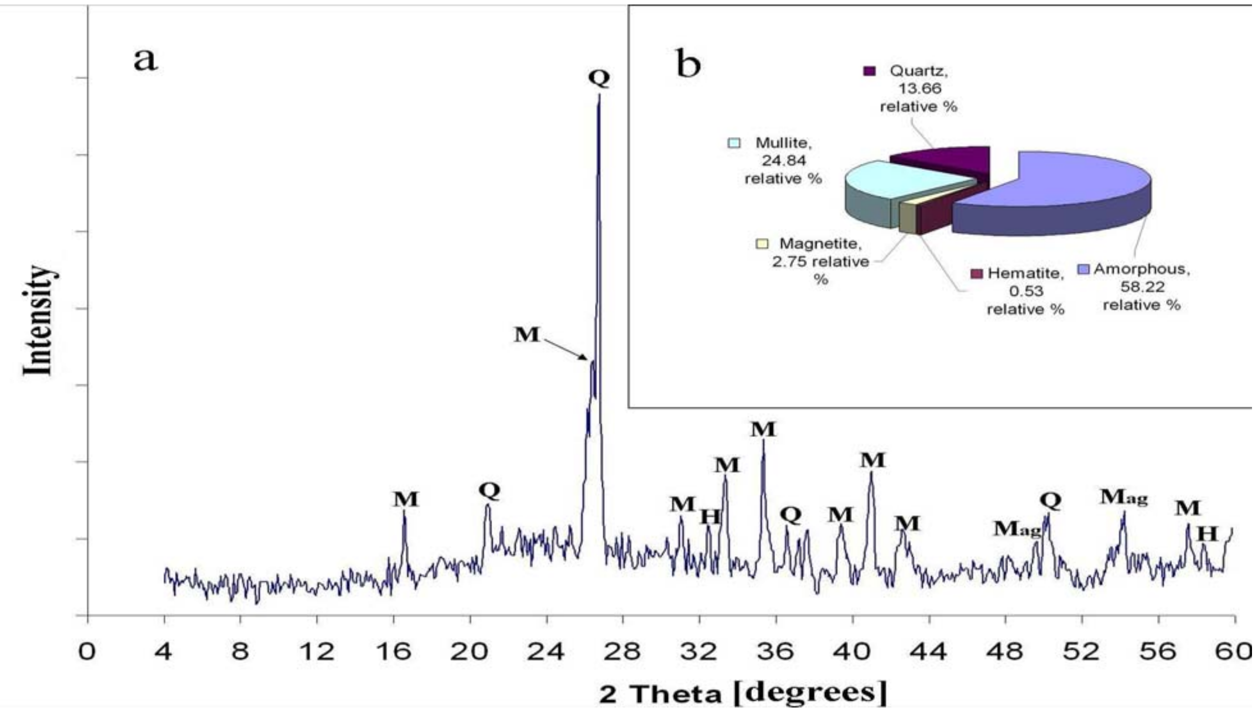

Fig 3 XRD of Arnot: (Q = Quartz, M = Mullite, H = Hematite, Mag = Magnetite).

(a) Qualitative analysis (b) Quantitative analysis

The fly ash based catalyst exhibited the characteristic peaks of crystalline phase's viz. ἀ-Quartz, Hematite, Magnetite and Mullite and showed the presence of characteristic peaks of KNO_3 as well as of K_2O at (23.7º and 29.5º) and (31.08º) respectively. This suggests that a good dispersion of KNO_3 occurs up to 5% (wt/wt) loading under the activation condition used in this study agreeing with reports in literature [17]. Occlusion of potassium metal clusters enhances the basicity of the fly ash by increasing the negative charge of the framework oxygen atoms. The supported species typically introduced through wet impregnation of a solution containing the solvated precursor into the pores and calcination decomposes the occluded compounds thus creating the supported alkali metal oxides [23].

3.1.2 BET surface area and pore size

The results of BET analysis for the samples are shown in Table 2. The raw Arnot fly ash and the various loadings of potassium impregnated fly ash were subjected for the evaluation of specific surface area and the measurements was repeated and results reproducible. The BET surface areas for the Arnot fly-ash and the potassium impregnated fly ash catalysts are comparable as observed.

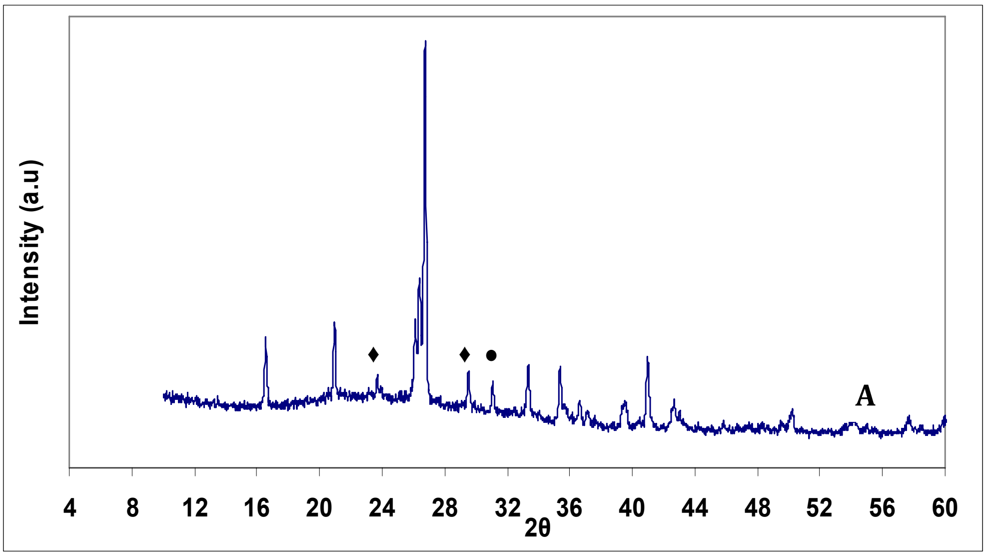

Fig . 4 XRD patterns of potassium impregnated fly ash catalyst with characteristic peaks due to KNO_3 ● and K_2O♦.

Table 2 BET surface area

Catalyst	Surface area m^2/g
Arnot fly ash	0.52±0,001
5% KNO_3wt/wt	0.55±0,001
10% KNO_3wt/wt	0.78±0,001
15% KNO_3wt/wt	0.53±0,001
20% KNO_3wt/wt	0.45±0,001

There was no alteration in the surface area when the fly ash used as a support was modified by the wet impregnation followed by calcination at 500ºC. The N_2 adsorption and desorption isotherms obtained showed that no mesopores were formed and that the micropore volume of the samples decreased with the loading. The micropore volume of the fly ash decreased monotonously with the potassium oxide loading even for high loadings. The decrease of surface area and micropore volume with increasing potassium loading could be assigned to a decrease of the available void volume. From the nitrogen adsorption-desorption isotherms, presented in Figure 5, the type III isotherm convex to the axis indicates that the P/P_o attractive adsorbate-adsorbent interactions are relatively weak and the lower adsorption volume on the potassium impregnated fly ash indicates a low surface area. The N_2 adsorption and desorption isotherms obtained also showed that mesopores were formed and that the micropore volume of the samples decreased with the agglomeration process.

3.1.3 FTIR

The spectrum for Arnot fly ash (Figure 6) shows the three wide bands characteristic of aluminosilicates: the band at 460 cm^-1 was associated with T–O bending vibrations [*] the bands appearing at around 704, 780 and 800 cm^-1 were associated with T–O (T = Al, Si) symmetric stretching vibrations that correspond to quartz present in the original fly ash; the band appearing at 1053 cm^-1 was associated with T–O (T = Al, Si) asymmetric stretching vibrations. An adsorption peak observed at 1380-1400 cm^-1 with the potassium impregnated fly ash catalyst shows the presence of weak aliphatic bonds associated with N-O bond identifying the presence of occluded nitrates within its pores Similar observations were made by Choi et al [24] and Piantone et al. [25]. These observations are also in agreement with reports from literature [26].

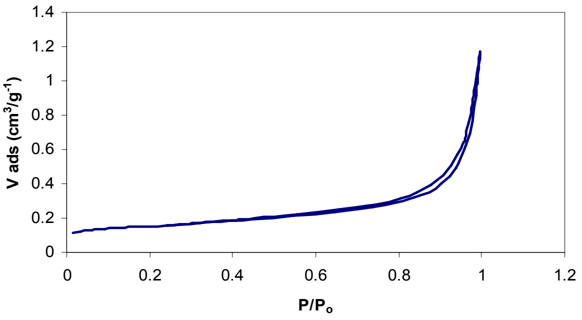

Fig. 5 N_2 adsorption-desorption isotherms of the potassium impregnated fly ash fly

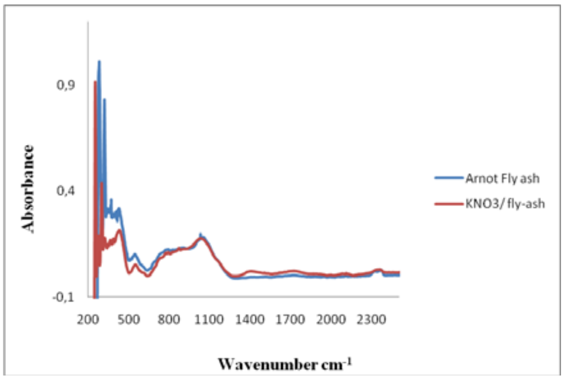

Fig. 6. FT-IR spectra of Arnot fly ash and the potassium impregnated fly ash catalyst

3.1.4 SEM

The SEM image of the surface of the Arnot fly ash particle was observed to be smooth and spherical because the glass phase covers the particle [27] .The morphology of fly ash grains is determined by the heating and cooling regimes in the pulverised coal boiler. Micro spheres, typically between 30 and 100 µm in diameter, can be described as hollow cenosphere or non crystalline glass beads [28]. The images of the potassium impregnated fly ash where spherical particles aggregates higher than 10µm were observed. It was also observed that the loading of potassium on the fly ash did not show any disruption in the structural morphology of the fly ash used as support. This is illustrated in Figure 7.

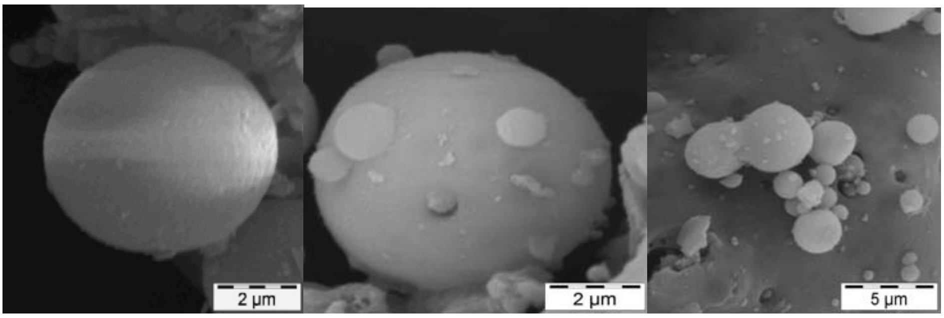

Fig. 7. SEM images of the (a) Arnot fly ash (b) and (c) potassium impregnated fly ash catalyst

3.2 Influence of process parameters

In order to fully understand the catalytic activity of the loaded catalyst and with the aim of maximizing the conversion of the sunflower oil to methyl esters (biodiesel), an optimization of the transesterification reaction with regards to some process parameters were carried out, they include % catalyst loading (wt/wt), methanol to oil molar ratio, reaction time, temperature and reusability of catalyst.

3.2.1 Effect of catalyst loading

The effect of the amount of catalyst used in the conversion of the triglyceride to methyl esters was studied as the % loading of catalyst with respect to oil was varied from 5 to 20% wt /wt keeping all other reaction parameters identical. As shown in Figure 8, it was observed that the oil conversion increased with an increase in catalyst loading. The highest conversion of 87.45% was obtained at a catalyst loading of 20% wt/wt which was comparative with the conversion value of 86.56% at 15%wt/wt. From the view-point of the reaction kinetics, a larger amount of catalyst leads to a higher yield of methyl esters in a shorter reaction time, however here we can say that this is sufficient from the viewpoint of economics. As a consequence, the optimal amount of catalyst used in this pilot was 15wt % loading as it was sufficient in catalyzing the reaction despite the challenge posed by the three phase reaction system where initial mass transfer control is inhibited due to heterogeneous kinetics. This is because of the fact that the solid catalyzed process is an immiscible liquid/liquid/solid 3-phase system (corresponding to oil, methanol and catalyst) that is highly mass transfer limited [29].

3.2.2 Effect of reaction time

In order to study the influence of the reaction time on the oil conversion using the KNO_3/fly-ash catalyst, a set of experiments were carried out at 2, 5, 8, 12 and 24 hours. The results are shown in Figure 9. It can be observed that the oil conversion was not greatly affected by an increase in the reaction time. This implied that, the reaction equilibrium had been reached after 5hrs when the reaction temperature was 160ºC. A study by Kotwal et al [17] showed that reaction times higher than 8 hrs had a negative impact on the oil conversion.

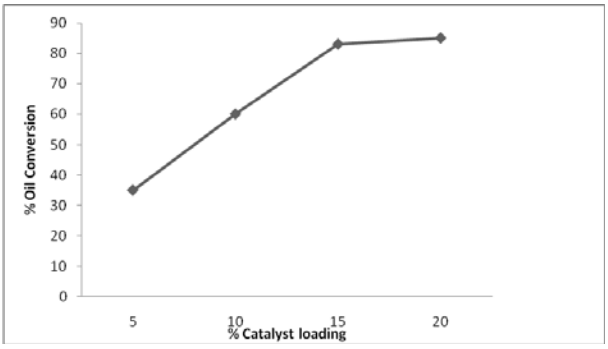

Fig. 8. Influence of catalyst loading on oil conversion under the reaction conditions of 160ºC, reaction time of 5hrs and a methanol: oil ratio of 15:1

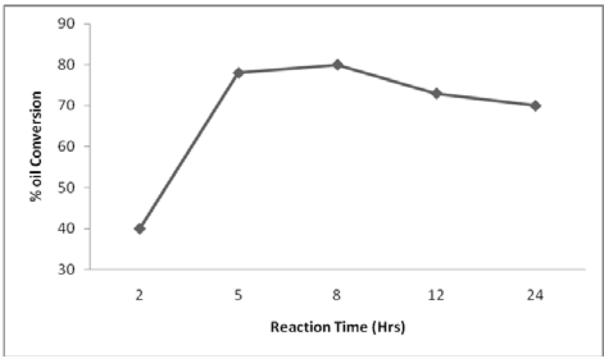

Fig. 9. Influence of reaction time on oil conversion under reaction conditions of 160ºC, 15% catalyst loading and a methanol: oil ratio of 15:1 and

3.2.3 Effect of reaction temperature

Transesterification can occur at different temperatures depending on the oil used and temperature is a crucial parameter as it influences the reaction rate and yield of the methyl esters and in order to determine the effect of reaction temperature on the oil conversion, experiments were conducted at 100, 120, 160, and 200°C. The results are shown in Figure 10 and from the activity profile, it was observed that as reaction temperature increased, there was a corresponding increase in the conversion of the triglycerides to methyl esters, showing peaks at temperatures ≥ 160°C. The highest conversion was 89.34% at a reaction temperature of 200°C which compares to the conversion value of 87.12% at the reaction temperature of 160°C.

Artkla et al. [30] carried out the transesterification of palm oil with methanol at 60, 120 and 150ºC in the presence of K2O loaded on MCM-41 synthesized from rice husk. The performance depended on the K2O loading and temperature with the highest conversion observed on 8% K_2O/RH-MCM-41 at 100 °C. However reports by Ramos et al. [15] showed that a methyl ester content of 95.1 wt% was obtained at 60ºC by transesterification of sunflower oil over zeolites as catalyst using different metal loading.

3.2.4 Effect of molar ratio of methanol:oil

One of the most important factors that affect the yield of ester is the molar ratio of alcohol to triglyceride [31]. It is of important for screening catalyst performance. Although the stoichiometric molar ratio of methanol to triglyceride for transesterification is 3:1 (Figure 1), higher molar ratios are used to enhance the solubility and to increase the contact between the triglyceride and alcohol molecules. Specifically, it has also been proven that that the use of excess alcohol is a good option in improving the rate of the transesterification reaction where heterogeneous catalysts are considered [32]. The effect of the molar ratio was of methanol to oil on the conversion of the methyl ester was examined by varying the amount of methanol with a fixed amount of sunflower oil (20g) in the reactions at 160°C. The initial amounts of methanol were set and amounts corresponding to the methanol: oil molar ratios of 6:1, 9:1, 12:1, 15:1 were used. The result is illustrated in Figure 11.

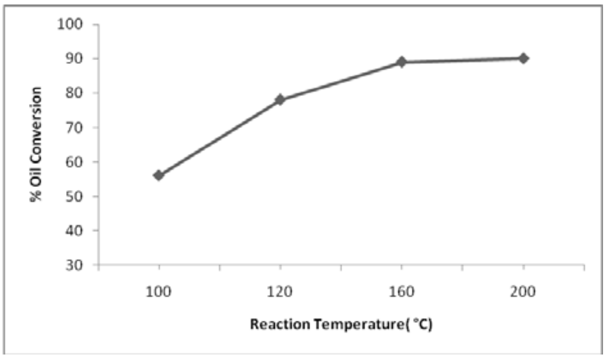

Fig. 10. Influence of reaction temperature on oil conversion under reaction time of 5hrs, a catalyst loading of 15%wt/wt and a methanol: oil ratio of 15:1.

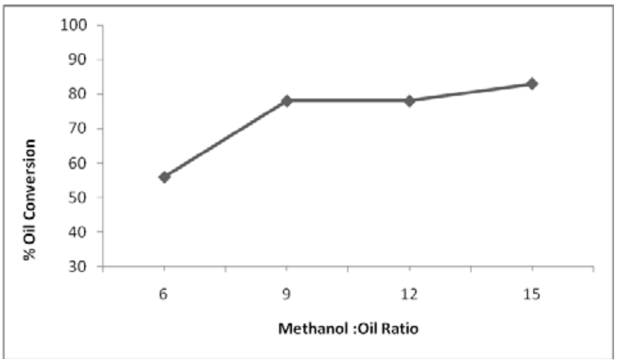

Fig.11. Influence of methanol: oil ratio on oil conversion under reaction temperature of 160°C reaction time of 5hrs and a catalyst loading of 15%wt/wt.

From the Figure, it can be seen that the highest methyl ester conversion of 86.1% was observed at a methanol: oil molar ratio of 15:1. It can be also be observed from the activity profile that as the molar ratio increased from 6:1 to 15:1, the conversion was found to increase from 56.23 to 86.1%. Further addition of methanol into the reaction phase did not show any significant increase in the conversion. Moreover, a limitation to the use of a greater amount of methanol needed to propel the forward reaction is that an occurrence of flooding of the active sites by the methanol molecules rather than triglyceride molecules which might hinder the completion of the triglyceride conversion to methyl esters as conversion at methanol oil ratios higher than 15 appeared to decline [33]. Also, feeding too much alcohol adversely affects the transesterification process by rendering the product separation difficult as glycerol; co-product specie of methyl ester is highly soluble in methanol, which reverses the transesterification progress according to Le Chatelier's principle [34] . Another important variable affecting the yield of methyl ester is the type of alcohol to triglyceride. In general, short chain alcohols such as methanol, ethanol, propanol, and butanol can be used in the transesterification reaction to obtain high methyl ester yields. This was not considered in this study.

3.3 Catalyst stability and reusability test

In order to assess the stability of the fly ash based catalyst, the re-use of the prepared catalyst was investigated in the production of biodiesel from sunflower oil to its methyl ester via the transesterification reaction. Initially, the reaction was conducted at 500 rpm at 180º C. Then, the reaction was repeated three times under the same reaction conditions described previously above. After each cycle of use in the production of biodiesel, the catalyst was recovered by filtration before re-use. The relative activity of the catalyst employed for the first batch was defined as 100%. Figure 12 describes the de-activity profile of the catalytic runs where 1, 2 and 3 denotes the number of runs where the oil conversion values of 85, 47.34 and 23.56 % were observed respectively. A decline in oil conversion was observed after each run can be attributed to the leaching of active species into the product in the course of the reaction.

3.4 Characterization of the biodiesel

Some properties of biodiesel specified in the standard ASTM D6751 [35] were analysed and listed in Table 3. Viscosity data of pure fatty esters can be used for predicting the viscosity of the mixture of fatty esters comprising biodiesel. Dynamic [36] and kinematic [37] viscosity data (which are related by density as a factor) of some individual fatty compounds are available in the literature as mentioned previously. The sunflower oil (triglyceride) exhibited an initial high viscosity value of 29.0 mPas before transesterification and after transesterification the dynamic viscosity of biodiesel produced with the KNO_3/fly-ash catalyst sample was in the range of the standard ASTM D6751 for biodiesel.

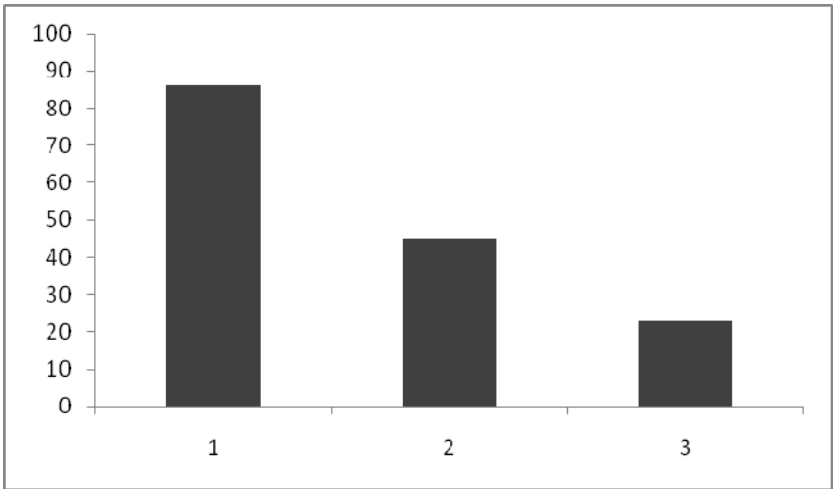

Fig. 12. Column graph showing the de-activity profile of the catalyst.

Table 3. Values for the American Society for Testing and Materials (ASTM D6751) Standards of Maximum Allowed Quantities in Biodiesel.

Property	Biodiesel	Biodiesel(in this work)
Viscosity at 40°C, mPa.	3.40-4.10	4.08
Viscosity at 40°C, mm^2/s	1.9-6.0	
Specific gravity, g/ml	0.88	0.88
Flash point, , CC, °C	100-170	150
Cloud point, °C	-3 to 12	9.8
Pour point, °C	-15 to 16	12

Conclusion

A study of heterogeneous acid catalysts for biodiesel production based on methanol transesterification is presented in this article. The use of fly ash loaded with KNO_3 has been found suitable for the conversion of sunflower oil to methyl esters and glycerol. The fly ash based catalyst loaded with 5% wt KNO_3 at a reaction temperature of 160ºC exhibits maximum oil conversion (86.13%). The oil conversion increases with increased catalyst loading. The highest conversion of oil was obtained at a catalyst loading of 20%wt/wt. Influence of process parameters such as reaction time, reaction temperature and molar ratio of methanol to oil were also carried out. The oil conversion was not greatly affected by an increase in the reaction time. However, reaction time between 5 to 8 hours will lead to better oil conversion. The highest conversion was observed at a temperature of 200°C. The activity profile shows that increase in the methanol to oil ratio from 6:1 to 15:1 resulted in increased conversion from 52.23% to 86.1%. A decline in the oil conversion was observed when the recovered catalyst was recycled for use. Heterogeneous catalysts are the key to new developments in the production of biodiesel. Their combined application in continuous process and easy separation could lead to substantial decrease in the cost of biodiesel production.

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