CHARACTERIZATIONS OF REFINERY SLUDGE, CHAR AND ASH

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ABSTRACT

Fly ash and sludge ash are waste products of the gasification process. Using these ashes as a catalyst material can minimise waste disposal at landfill sites. Fly ash and sludge ash can be used as a catalyst for gasification as they are abundant in catalytic materials such as silica, alumina, ferric oxide, calcium oxide and a host of other catalytic materials.This article explains the characteristics of sludge fuel, fly ash, sludge ash and charcoal (gasification by products). Characterizations of inorganic materials found in the sample of sludge, char, fly ash and sludge ash catalysts were described by FESEM-EDX. The particle size of calcined and non-calcined fly ash and sludge ash catalysts has been calculated using the TEM technique. The sample of calcined fly ash consists of almost uniform small crystals with a particle size ranging from 11. 5 to 25.3 nm while, the average particle size of the calcined sludge ash varied from 19.9 to 33.2 nm. The phase composition of the fly ash and sludge ash catalysts was determined by XRD and O-Si-O by FTIR. Sludge ash consists of crystalline quartz, mullite, hematite and cristobalite, while mullite and quartz are the two main phases of the crystalline elements of fly ash.

Key words: Refinery Sludge, sludge ash, fly ash , Char.

INTRODUCTION

Catalytic gasification has been used as an attractive route for the processing of syngas, and the presence of condensable organic compounds or tar in the product gas is undoubtedly troublesome (Lee et al., 1999). The persistent build-up of tar in the gases produced makes the gas unsuitable for particular applications and induces blockages and corrosion in downstream systems, thereby decreasing overall gasification performance (Udomsirichakorn 2014). Fuel and catalyst are also applied directly to the gasifier, which works under the predetermined conditions of the gasifier, to generate product gas along with liquid tar and solid fly ash (Spiro 1982).

Fly ash is the finely divided mineral waste arising from the burning of coal in power plants for the generation of power. Fly ash consists primarily of inorganic materials composed of silicon dioxide (SiO_2), aluminium oxide (Al_2O_3), calcium oxide (CaO) and iron oxide (Fe_2O_3). Fly ash contains trace amounts of the following heavy metals: nickel, vanadium, cadmium, barium, chromium, copper, molybdenum, zinc and lead; (Ismail et al., 2007, Amir 2016).

Fly ash has many potential uses, such as raw material, for the extraction of metals, as a soil improvement agent in agriculture, for the processing of glass and ceramics, for the development of mesoporous materials, for the synthesis of geopolymers, for use as catalysts and catalysts, as an adsorbent for gas and wastewater systems (Blissett et al.,2012). The use of this waste fly-ash substance as a heterogeneous catalyst has gained a great deal of attention today, (Omotola et al., 2010, Sarmah et al., 2013). It can also be used to produce activated carbon products that have been used as efficient CO_2 sorbents and by impregnating carbons with chemicals that have a high tolerance for carbon dioxide capture (Arenillas et al., 2005). Coal fly ash was used in the manufacture of zeolites to synthesise X-type zeolite through alkali fusion accompanied by hydrothermal treatment (Ojha et al., 2004). It has recently been used in the photo-Fenton method as a heterogeneous catalyst to remove amoxicillin (Franco 2019).

Sludge ash is a mineral residue that occurs from the gasification of the refining sludge which is transferred by the exhaust gas from the combustion chamber (R.Ahmed 2013). Its use as an industrial by-product has gained a great deal of interest over the last two decades as more efficient alternatives to waste issues have been pursued.

Added oil sludge ash, Al_2O_3, Fe_2O_3 And CaO minimised the carbon residue and the movement of S, N and O from the oil sludge to the oil product. The increase in oil consistency was due to the catalytic effects of Al_2O_3, Fe_2O_3 and CaO composition in oil sludge ash (Shuo et al., 2016). The purpose of this analysis is to classify coal ash, refinery suldge ash and charcoal using a variety of sophisticated techniques. The main goal of this research is to present and illustrate the possible turn of these unused compouds into a more useful product.

EXPERIMENT SETUP

Elemental analysis and surface morphology of sludge, char, fly ash and sludge ash were determined using (LECO CHNS-932, VTF-900 CHNS analyzer) and (Zeiss Supra 55 VP FESEM-EDX equipment) respectively. The catalytic efficiency of the catalyst is highly determined by its catalytic properties. The crystalline phases of calcined and non-calcined fly ash and sludge ash have also been described by TEM and X-ray diffraction powder XRD (Bruker A&S D8 Advanced Diffractometer instrument). FTIR has been used to describe the functional group of catalysts, while the chemical compositions of calcined and non-calcined fly ash and sludge ash catalysts have been determined by percentage (BRUKER, S8 TIGER, WD XRF Spectrometer).

RESULTS & DISCUSSION

ELEMENTALS ANALYSIS

The elemental analysis of refinery sludge char and ash and coal fly ash were measured by LECO CHNS-932, VTF-900 CHNS analyzer reveals the mass fraction on a dry basis of individual elements present in a material such as carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) over a total sample weight. Table 1 lists the contents of elements in fly ash, sludge ash, char and refinery sludge. The percentage of carbon of fly ash and sludge ash samples were about 1.21% and 4.19%, respectively. Nitrogen and sulfur content in fly ash were about 0.22% and 0.03%, respectively.

Table 1: The elemental analysis of refinery sludge, char, sludge ash and coal fly ash.

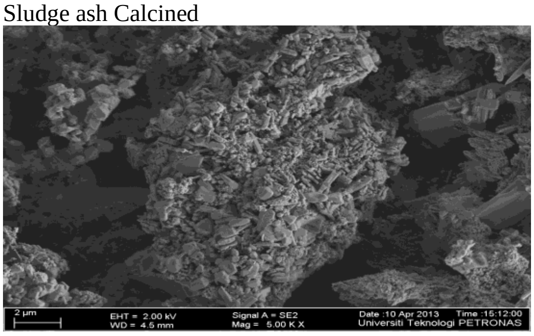
Elements	Fly Ash	Sludge Ash	Char	R.Sludge
C	1.21	4.188	32.04	55.8
H	0.09	0.377	1.803	7.3
N	0.22	0.344	3.473	5.7
S	0.03	0.882	1.804	2.7

The amount of nitrogen and sulphur in the fly was smaller than that of the sludge ash sample. Although the sludge content has a higher concentration of nitrogen and sulphur than the sludge ash and the charcoal specimen. This means the release of nitrogen and sulphur as SO_x and NO_x during the gasification process.

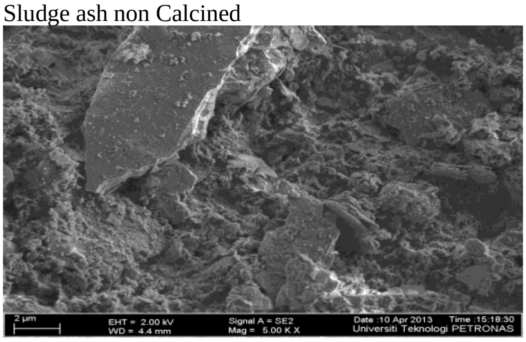
FESEM- EDX ANALYSIS

FESEM-EDX technique is considered to be one of the most common techniques for imaging the surface region of the sample. FESEM analysis was conducted on Zeiss Supra 55 VP equipment for sludge, char, calcined and non-calcined fly ash and sludge ash catalysts. This method also involves the Energy Dispersive X-ray Analysis (EDX) system, which incorporates quantitative element analysis and element localization of the samples being analysed. . Morphological differences in sludge ash and fly ash existed during calcination as seen in Figure 1. Calcination of sludge ash and coal fly ash at 800 ^{o}C was observed to remove excess carbon in ash and increase the concentration of inorganic elements. CHNS alaysis conferimed that fly ash and suldge ash has 1.21 % and 4.19 % of unburned carbon respectively.

Sludge ash Calcined



Sludge ash non Calcined



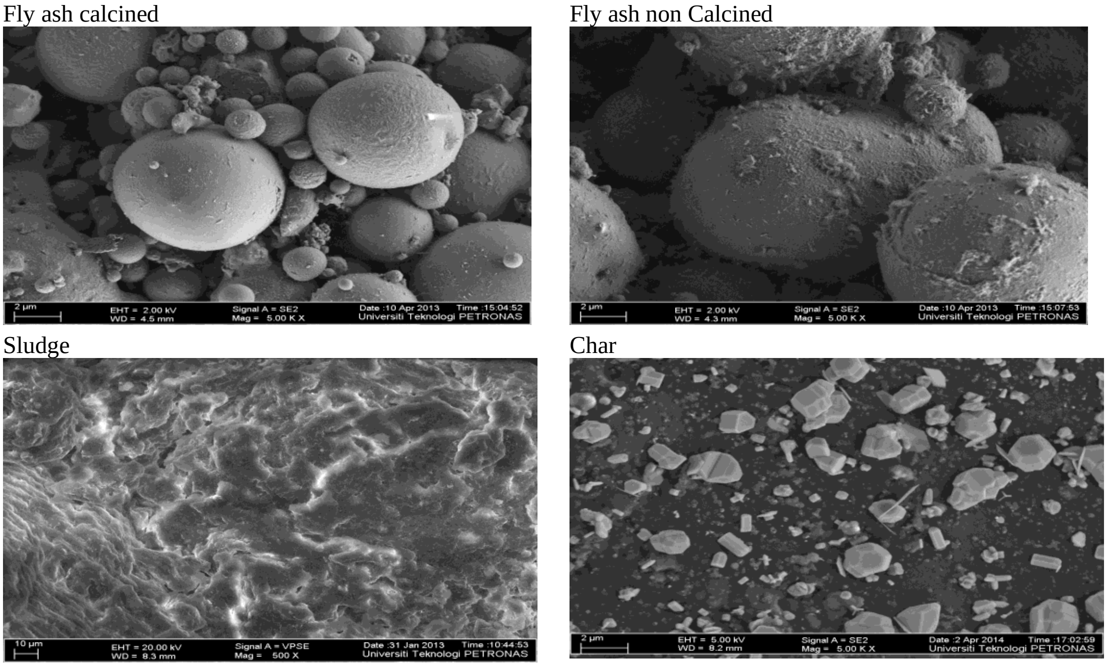
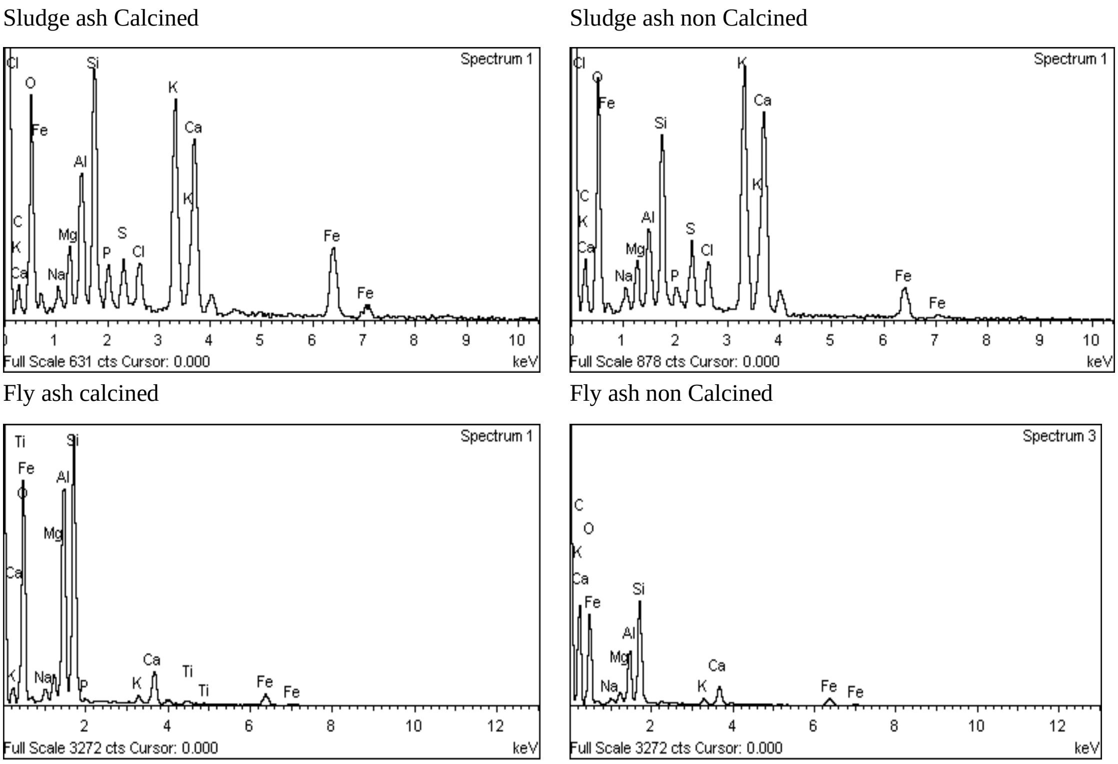


Figure 1. Field emission Scanning electron micrographs FESEM of sludge, char, coal fly ash and refinery sludge ash.

FESEM micrograph of the fly ash catalyst under the electron microscope scan reveals that the fly ash morphology was made of small spherical particles, which results in accordance with (Çelik 2008). The refinery sludge and sludge ash until calcinations display an amorphous surface, while the samples of the char are mostly small crystals.

Elemental mapping of sludge, char, calcined and non-calcined fly ash and sludge ash catalysts is used by energy dispersive X-ray technique (EDX) to assess the distribution of the elements as seen in Figure 2. It can be seen that the concentration of K, Ca, Si, Mg, Al and Fe elements in the sludge sample and the sludge ash is greater than that of the coal fly ash and the char sample.



Sludge Char

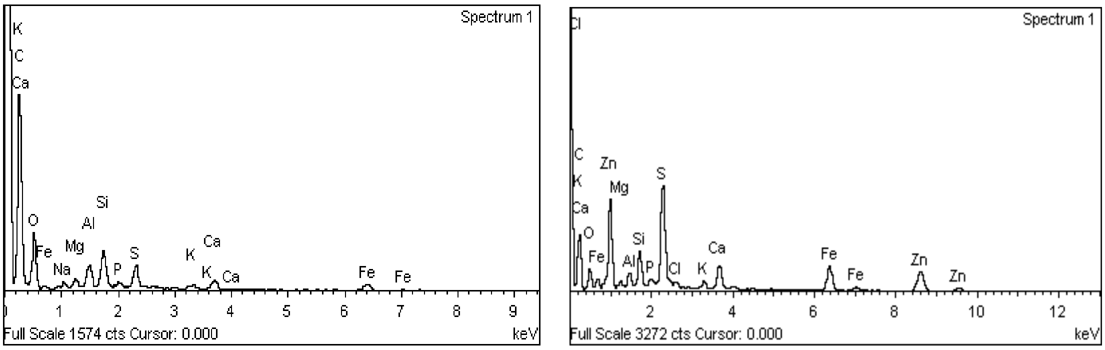


Figure 2. Energy dispersive X-ray of sludge, char, calcined and non-calcined coal fly ash and refinery sludge ash.

The energy dispersive X-ray technique was used to analyse the chemical composition of the materials referred to above, as seen in Table 2. The carbon content of the plant sludge obtained by EDX is 4.93 greater than that of the ultimate analysis (Table1). The overestimation of the carbon content may be attributable to the loss of nitrogen and hydrogen in EDX detection. However, the sulphur provided by EXD is 0.92 lower than that of the ultimate analysis. The elemental compositions of the char revealed an insignificant difference in the Wt percent of the carbon and sulphur detected by EDX and in the ultimate analysis.

The fly ash and sludge ash catalysts showed high percentages of heavy and alkali metal such as Al, Mg, Fe, Ca, K ...etc. The involvement of alkali metal in fly ash and sludge ash catalysts improves the method of gasification (Amir 2016). It has been stated that carbonates and oxides of alkali and alkaline earth metals are among the most active catalysts for the gasification of carbonaceous materials (coal carbon) in steam and carbon dioxide. Alkali metal catalysts are also immediately applied to biomass through dry mixing or wet impregnation. When applied in this manner, the catalyst is difficult to extract, and this is not necessarily cost-effective for the gasification process. Catalytically active alkali oxides may have derived from the oxidation of halides during carbon gasification, possibly due to a form of reaction (Sutton 2001).

$$2MX + C + \frac{3}{2}O_2 = M_2O + CO_2 + X_2$$

Table 2. Elemental compositions of sludge, char, calcined and non-calcined fly ash and sludge ash by EDX analysis

Element	Weight%					
	sludge	char	Sludge ash Calcined	Sludge ash non Calcined	Fly ash calcined	Fly ash non Calcined
C	60.73	38.31	-	13.71	-	-
O	28.30	14.42	40.14	47.47	54.60	54.66
k	0.51	0.86	10.48	8.46	1.07	0.91
Mg	0.40	0.71	2.14	1.73		0.78
Al	1.11	1.35	3.74	2.31	16.99	17.11
Si	2.68	3.48	6.92	5.15	23.22	22.61
P	0.46	0.70	1.44	0.65	-	-
S	1.78	1.37	1.63	2.11	-	-
Ca	1.65	3.11	9.46	7.51	1.3	1.25
Fe	2.38	8.22	8.62	3.91	2.05	2.10

X-RAY FLUORESCENCE SPECTROMETRY SCANNING (XRF)

XRF is a detailed study of the atomic structure of the solid with the application of incident x-ray radiation to eject electrons from the inner atoms. The chemical composition of the calcined fly ash and sludge ash was determined by x-ray fluorescence (BRUKER, S8 TIGER, WD XRF Spectrometer).

The coal fly class C comprises primarily of small particles of inorganic minerals, as seen in Table 3 the bulk chemical compositions comprising a number of metal oxides in the order of SiO_2 > Al_2O_3 > MgO > Fe_2O_3> CaO > K_2O > P_2O_5 > TiO_2 . Sludge ash compounds comprising a number of metal oxides in the order of CaO > Fe_2O_3> K_2O >SiO_2 > Al_2O_3 > P_2O_5 > MgO > SO_3>TiO_2.

Table 3. Compositions of oxides of calcined and non calcined coal fly ash and refinery sludge ash

	Concentration %			
Formula	Fly ash calcined%	Fly ash non Calcined %	Sludge ash Calcined %	Sludge ash non Calcined %
SiO_2	40.00	38.80	12.90	10.90
Al_2O_3	18.90	19.20	4.78	5.93
Fe_2O_3	11.69	12.57	25.00	24.80
CaO	11.73	10.95	25.70	22.20
MgO	13.00	12.99	2.19	1.66
K_2O	2.04	1.92	13.80	18.60
P_2O_5	1.65	1.82	4.40	3.77
TiO_2	0.46	0.53	0.51	0.56
SrO	0.38	0.37	0.14	0.11
SO_3	0.25	0.22	4.46	4.97
BaO	0.14	0.17	0.38	0.35

Generally, coal fly ash from subbituminous and lignite coals are characterized by higher CaO, MgO, and SO_3 and lower SiO_2 and Al_2O_3 relative to the higher quality fuels such as bituminous and anthracite coals. Bituminous and lignite fly ash contain less than 10% CaO in total often consist mainly of aluminosilicate glass and usually do not contain any crystalline compounds of calcium. CFAs that contain more than 15% total CaO are composed of calcium aluminosilicate glass (Blissett 2012, Amir 2016).

A interesting finding was that calcined sludge ash and fly ash have a comparatively higher proportion of CaO than non-calcined ash. The percentage increase from 22.2 to 25 % and from 10.9 to 11.7 % for sludge ash and fly ash respectively. This was due to the release of excess carbon from calcium carbonate as carbon dioxide by calcination, thereby rising the percentage of CaO. It can also be observed that the fly ash mainly consist of SiO_2 of about 40% while CaO was detected as the major oxide in sludge ash. The percentage of furious oxide in the sludge ash is 13.31 % higher than the fly ash. The high percentage of Fe_2O_3 in the sludge ash catalyst was found to promote a water-gas shift reaction and improve the conversion of tar into gas products. As stated in (Shen 2013), that a modified dolomite (mixed with natural dolomite and Fe_2O_3 powders) showed high catalytic activity.

Higher potassium oxide was found to be one of the major cause of agglomeration of fuel in the gasifier bed due to a drop in its melting point. Potassium, react easily with silica sand, which is a typical bed material and is often used as a bed material in this gasification phase by breaking the Si–O–Si bond and forming silicates. Adding such bed ingredients, such as magnesium, iron, calcium and aluminium in the form of MgO, Fe_2O_3, CaO and Al_2O_3 to the K_2O–SiO_2 Suppress the propensity of agglomeration by the creation of high temperature compounds. Sludge ash contains high levels of CaO and Fe_2O_3, they are effective in reducing agglomeration. Such types of pretreatment, such as leaching and fractionation or use of bed additive products, such as MgO, CaO, Fe_2O_3, dolomite, and limestone can effectively reduce the bed agglomeration potential. Because of their mineral chemistry, which is particularly rich in CaO, silica and alumina, and their catalytic nature,(Mohammed 2012, Lahijani 2011).

FTIR IDENTIFICATION TECHNIQUE

FTIR was used to study the structure of adsorbed molecules on the surface of fly ash and sludge ash catalysts under controlled atmospheric conditions as seen in Figure 3.

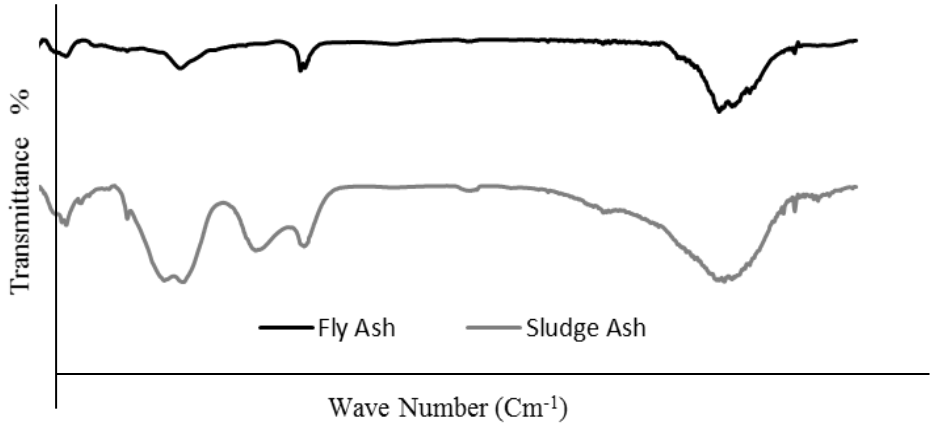


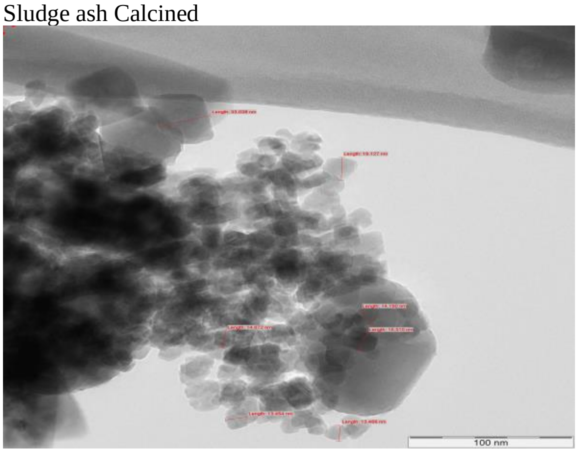
Figure 3. FTIR analysis for fly ash and sludge ash catalysts.

From figure 3, the presence of the Si-O-Si quartz groups in the fly ash sample was validated. The FT-IR spectra of the fly ash are occupied by a broad band around 1056 cm^{-1} owing to Si-O stretching vibration. The IR spectrum of the fly ash and sludge ash respectively at 3388 cm^{-1} and 3400 cm^{-1} these broad peaks for O- H functional groups, −Si-OH and absorbed water molecules on the surface (Sarmah 2013, Yaumi 2013, Amir 2016). The band around 1610 cm^{-1} and 1613 cm^{-1} in the spectra of fly ash and sludge ash samples respectively, which are attributed to pending mode (δ_{O-H}) of water molecules. The peaks at 564 cm^{-1} (Al, Mg, Fe–O stretching band) of the fly ash . For the sludge ash sample the strong and broad band at 1047 cm^{-1} due to Si-O-Si groups, The peaks at 585 cm^{-1} (Al, Mg, Fe–O stretching band) of the sludge ash has a similar pattern than that in the fly ash. The broad band 1381 cm^{-1} in IR spectrum of sludge ash represent the presence on substituted Al atom in tetrahedral forms of silica frame work, (Ojha 2004,Jain 2013).

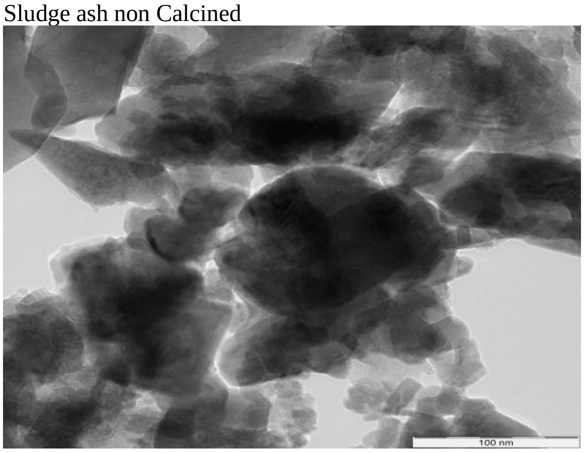
TRANSMISSION ELECTRON MICROSCOPY (TEM)

TEM facilitates the determination of the microstructure of the electron transparent samples by sending a concentrated parallel electron beam to a fluorescent screen with a resolution currently greater than 0.2 nm. The TEM review was performed in this research to observe the discrepancy between calcined and non-calcined samples (fly ash and sludge ash). Calcinations were performed by incineration of sludge and fly ash using a furnace at 800 ºC for 24 hours. Calcinations are meant to calculate the sum of unburned carbon or LOI. The ignition loss (LOI), which is a measure of the amount of unburned carbon remaining in the sample, is one of the most significant chemical properties, especially as an indicator of suitability. loss of ignition was found to be about 1.57% and 4.12% for coal fly ash and sludge ash respectively, (Bartholomew 2006).

Sludge ash Calcined



Sludge ash non Calcined



Fly ash calcined Fly ash non Calcined

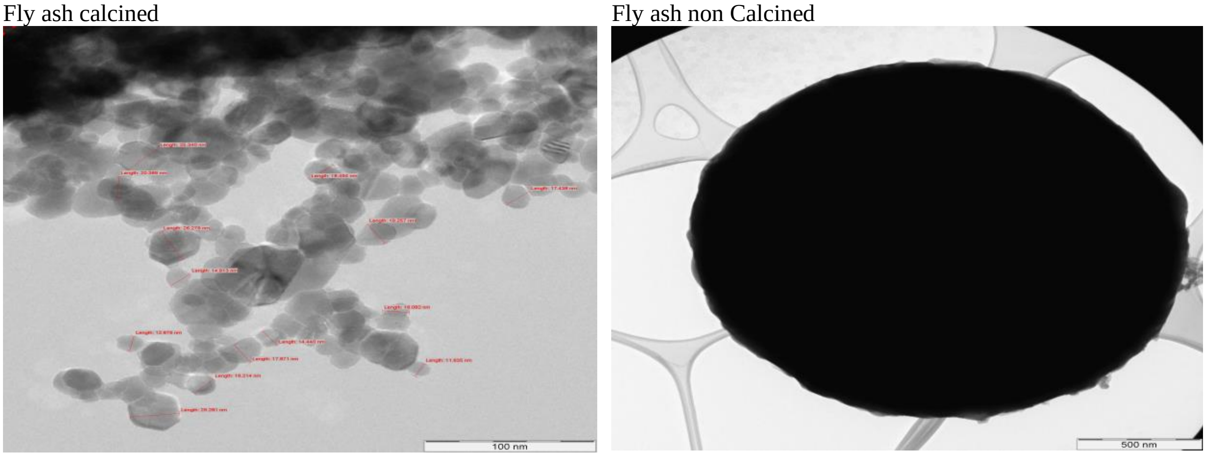


Figure 4. TEM image of Calcined and non-Calcined fly ash and sludge ash catalysts.

TEM has been shown to be a very effective method for characterising nano-crystal materials and measuring the particle size of nanoparticle catalysts. TEM technique was used in this analysis to measure the particle size of calcined and non-calcined fly ash and sludge ash catalysts. Figure 4 reveals that the fly ash sample before calcination (raw fly ash) displayed a smooth spherical particle. After calcinations, the fly ash sample consists almost of uniform small crystals with particles varying in size from 11.5 to 25.3 nm. Although the average particle size of the calcined sludge ash varied from 19.9 to 33.2 nm. In addition, the type of phase present in sludge and fly ash catalysts has been studied using XRD technology, (Jain 2013).

X-RAY DIFFRACTION (XRD)

XRD was used to determine the bulk crystal structure and the chemical phase composition of the fly ash and sludge ash by diffraction of the x-ray beam as a function of the angle of the incident beam. The composition of the two catalysts was determined using the Bruker A&S D8 Advance Diffractometer (XRD) as seen in Figures 5 and 6. The XRD analysis of the refinery sludge ash showed the presence of crystalline quartz (28.92° and 44.46°), mullite (40.78° and 31.62°), hemetite (35.74°) and cristobelite (26.42°) at 2θ value. While for the fly ash sample, many peaks at 16.65°, 26.68°, 35.26°, 41.08° and 60.78° were detected corresponding to quartz. mullite detected at 14.76°, 31.20° and 46.82°. This indicates that mullite and quartz are the two main phases of the crystalline components of the fly ash, the cristobelite in the fly ash sample detected at (21.96°). These results in agreement with (Ismail 2007, Omotola et al., 2010, Lwee 2016, Maciej 2016).

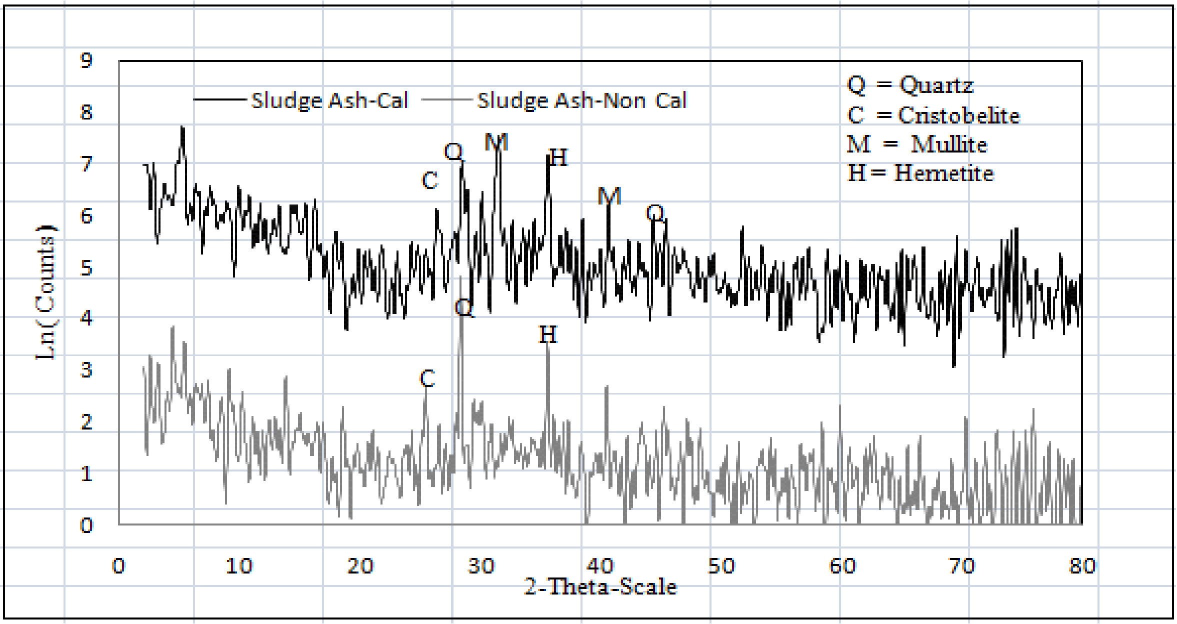


Figure 5. X-Ray diffraction pattern of Calcined and non-Calcined refinery sludge ash

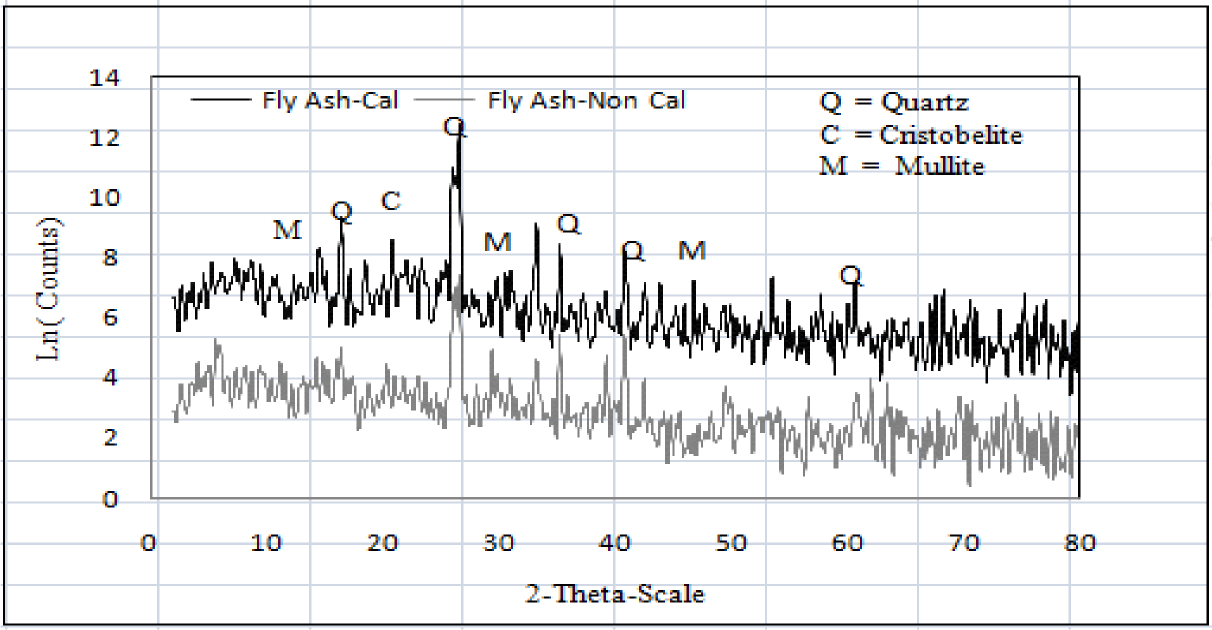


Figure 6. X-Ray diffraction pattern of Calcined and non-Calcined Coal fly ash

CONCLUSION

Inorganic materials in the sludge sample, char, fly ash and sludge ash catalysts have been identified by FESEM-EDX. The phase compositions of the fly ash and sludge ash catalyst were determined by XRF and O-Si-O by FTIR. The coal fly was found to comprise primarily of small particles of inorganic minerals, the bulk of the chemical compositions comprising a number of metal oxides in the order of SiO_2 > Al_2O_3 > MgO > Fe_2O_3> CaO > K_2O > P_2O_5 > TiO_2 . While its formulations of sludge ash include a number of metal oxides in the order of CaO > Fe_2O_3> K_2O >SiO_2 > Al_2O_3 > P_2O_5 > MgO > SO_3>TiO_2. Fly ash sample consist almost of a uniform small crystal with particles size ranged from 11.5 - 25.3 nm, while the sludge ash showed an average particle size ranged from 19.9 - 33.2 nm. The presence of Fe_2O_3, Al_2O_3, CaO and MgO in good percentage shows its potential to catalyze the gasification process. Utilization of Coal Fly ash and by-product Sludge ash catalysts can improve the products gas yield, producer gas heating value and gasification effeciency. The role of alkali metal in catalysts of fly ash and sludge ash strengthens the gasification process. Carbonates and oxides of alkali and alkaline earth metals have been described as one of the most active catalysts for gasification of carbonaceous materials in steam and carbon dioxide. Fly ash and sludge ash can then be used as catalysts to destroy tar and improve gas quality and gasification efficiency.

REFERENCES

Lee S.-W., S.-B. Kim, K.-W. Lee, and C.-S. Choi, (1999) “Catalytic Gasification of Rice Straw at Low Temperature,” Environ. Eng. Res, 4, 293–300.

Sutton, D., Kelleher, B. & Ross, J.R.H., (2001). Review of literature on catalysts for biomass gasification. Fuel Processing Technology, 73, pp.155–173.

Ojha, K., N. C. Pradhan, and A. N. Samanta, (2004) “Zeolite from fly ash : synthesis and characterization,” 27 , pp. 555–564.

Arenillas, K. M. Smith, T. C. Drage, and C. E. Snape, (2005) “CO_2 capture using some fly ash-derived carbon materials,” Fuel, 84, 2204–2210.

Bartholomew C. H., R.J.F., (2006). Fundamentals of Industrial Catalytic Processes Seconed ed., USA: John Wiley &Sons.

Ismail K. N., K. Hussin, and M. S. Idris, (2007) “physical , chemical & mineralogical properties of fly ash,” , 4, 47–51.

Radzi, F., Mohd, B. I. N., Isa, M. H., Kutty, R. M., & Malakahmad, A. (2008). solidification stabilization of waste activated sludge from petroleum refinery.

Çelik, Ö., Damcı, E. & Pi, S., (2008). Characterization of fly ash and it effects on the compressive strength properties of Portland cement. , 15, pp.433–440.

Omotola .B , Leslie .P , Nicholas .M , Bamikole , Farouk. A (2010) "Use of coal fly ash as a catalyst in the production of biodiesel" Petroleum & Coal 52 (4) 261-272.

Lahijani, P. & Zainal, Z.A., (2011). Gasification of palm empty fruit bunch in a bubbling fluidized bed: a performance and agglomeration study. Bioresource technology, 102 (2), pp.2068–76.

Blissett R. S. and N. A. Rowson, (2012) “Review article A review of the multi-component utilisation of coal fly ash,” Fuel, 97,1–23.

Dwivedi, S. et al., (2012). Characterization of coal fly ash nanoparticles and induced oxidative DNA damage in human peripheral blood mononuclear cells. The Science of the total environment, 437, pp.331–8.

Mohammed, M. (2012)," Gasification of oil palm empty fruit bunches: a characterization and kinetic study". Bioresource technology, 110, pp.628–36.

Ahmed, R., & Chandra, M. S. (2013). Equilibrium Modeling in Updraft Gasifier for Refinery Sludge Gasification Using ASPEN PLUS Simulator. Applied Mechanics and Materials, 393, 729–734.

Jain, D., Hada, R. & Rani, A., (2013). Surface Modification of Fly Ash for Active Catalysis.

Sarmah M., B. P. Baruah, and P. Khare, (2013) “A comparison between CO_2 capturing capacities of fly ash based composites of MEA/DMA and DEA/DMA,” Fuel Process. Technol. , 490–497.

Shen, Y. & Yoshikawa, K., (2013). Recent progresses in catalytic tar elimination during biomass gasification or pyrolysis—A review. Renewable and Sustainable Energy Reviews, 21, pp.371–392.

Wongsiriamnuay. T, N. Kannang, and N. Tippayawong (2013) “Effect of Operating Conditions on Catalytic Gasification of Bamboo in a Fluidized Bed,”.

Yaumi, A.L., Hussien, I. a. & Shawabkeh, R. a., (2013). Surface modification of oil fly ash and its application in selective capturing of carbon dioxide. Applied Surface Science, 266, pp.118–125.

Udomsirichakorn. J.and P. A. Salam, (2014) “Review of hydrogen-enriched gas production from steam gasification of biomass: The prospect of CaO-based chemical looping gasification,” Renew. Sustain. Energy Rev., vol. 30, pp. 565–579.

Lwee Kui Choo. (2016). Partial replacement of cement with incinerated sewage sludge ash in mortar brick with natural calcium carbonate as additive.

Amir Fauzia,c, Muhd Fadhil Nuruddina,*, Ahmad B. Malkawia, Mohd Mustafa Al Bakri Abdullah ,(2016) " Study of Fly Ash Characterization as a Cementitious Material" Procedia Engineering 148 487 – 493

Maciej. Ż, Rui C. Neto. L F.Santo.Witkowski. K.(2016)" Characterization of fly-ash cenospheres from coal-fired power plant unit" Volume 174, Pages 49-53.

Shuo Cheng, Yuhua Wang, Ningbo Gao, Fumitake Takahashi, Aimin Li, Kunio Yoshikawa, (2016) "Pyrolysis of oil sludge with oil sludge ash additive employing a stirred tank reactor", Journal of Analytical and Applied Pyrolysis, Volume 120, Pages 511-520.

Ramírez.F, Jose & Galeano, Luis Alejandro & Vicente, Miguel Angel. (2019). Fly Ash as Photo-Fenton catalyst for the degradation of amoxicillin. Journal of Environmental Chemical Engineering. 7. 103274. 10.1016/j.jece.2019.103274.