SCAN ELECTRON MICROSCOPE AND XRD CHARACTERIZATION OF UNTAPPED CLAY DEPOSITS IN ITU LOCAL GOVERNMENT AREA AKWA IBOM STATE AND IT’S POTENTIALS AS RAW MATERIAL FOR PETROLEUM REFINING

Abstract

This work describesscan electron microscope (SEM) and X-ray diffraction (XRD)characterization of untapped clay deposits from Ikot UsoAkpan and EkimItam, Itu LGA, Akwa Ibom State Nigeria and its potential for development of zeolite for industrial applications. 50 g each of the kaolin clay samples were subjected to hydrothermal treatment, acid leaching with HCl and calcined at 1000 ^{O}C in a muffle furnace to produce metakaolin. The raw kaolin clay and metakaolin were characterized using XRD and SEM. XRD data indicated 48.0 % quartz, 30.0% kaolinite, 3.0 % chlorite, 16.0 % illite and 2.0% albite in the raw kaolin and 68.3 % quartz, 17.3 % orthoclase, 5.9 % muscovite, 1.8 % illite , 6.68 %, albite in the metakaolin from Ikot Uso Akpan. Also, 16.2 % kaolinite, 67.0% quartz, 2.5 % muscovite, 5.5 % orthoclase, 1.4 % chlorite, and 7.0 % albite were revealed in EkimItam raw kaolin samples while 66.0 % quartz, 10.0 % muscovite, 15.0 % orthoclase, 5.0 % illite, 5.0 % albite were recorded in the metakaolin. The XRD results confirmed the presence of quartz and alumina mineral phases from both kaolin deposits. Calcination at 1000 ^{o}C increased the crystalline structure of the metakaolin. The SEM results indicated heterogeneous size and spongy like porous shape. There was no significant change in the surface morphology of the heterogeneous size calcined kaolin compared with untreated kaolin. The SEM results of the metakaolin kaolin also indicated cubic crystalline structure with well-defined edges. Calcination at 650^{o}C for 2 hour did not significantly modify surface morphology of the kaolin indicating stability of kaolin structure one the desired property of a good zeolite. With adequate modification the studied kaolin could be a promising raw material for synthesis of zeolite suitable for bio and fossil fuel processing.

KEY Words: Characterization, Kaolin, Metakaolin, Calcination, kaolinite

INTRODUCTION

Kaolin is a white, soft, plastic clay composed mainly of kaolinite, $Al_4(OH)_8[Si_4O_{10}]$, and other related clay minerals such as nacrite and dickite (Baker & Uren, 2010). Kaolin deposits are classified as primary or secondary according to their genesis; primary deposits originating in situ by alteration, whereas secondary deposits are of sedimentary origin (Murray, 2012). Primary deposits are formed directly from hydrothermal alteration of volcanic and granitic rocks with examples as hydrothermal and volcanic clay types. Secondary clay deposits are products of weathering of pre-existing rocks, and subsequent alteration of the alumino-silicates into clays such as residual and sedimentary clays. Ideal conditions necessary to produce kaolinitic clays by means of chemical weathering are high rainfall, warm temperatures, lush vegetation, low relief and high groundwater table Cravero & Dominguez, 1999). Thus, kaolin is eroded and transported by streams to a quiet, fresh or brackish water environment. Post depositional leaching, oxidation, and digenesis can significantly modify the original clay mineralogy with improvement of kaolin quality (Hassan, 2014). Kaolin is an important raw material with widespread industrial applications such as water treatment, as porcelain, cement and ceramics production (Lima *et al.*, 2017)

Clays have extensive applications due to their swelling, adsorption and ion exchange properties and high surface areas (Jankovic *et al.*,2010). Starting from the beginning of petroleum refining and petrochemical industries, clays have been used as catalysts (Speight, 2006). The first hydrocracking process developed over 80 years ago was based on acid-modified clays, but later and still now, zeolites and aluminosilicates were used. However, in few cases such as in treating some heavy fractions, clays are still used. Clays with different acidities can be obtained by thermal treatment before preparing the catalyst. The temperature of the thermal treatment of the clay determines the type and concentration of the hydroxyl groups and thereby its acidity. The most important clay used in the manufacture of catalysts is kaolin and has many applications such as a catalyst substrate in the catalytic cracking of petroleum (Murray, 2007). Furthermore, kaolin is used to synthesize zeolite and alumina (Salahudeen *et al.*,2012). Kaolin or commonly referred as China clay is one type of mineralcontaining a crystal compound with the main content of kaolinite ($Al_2O_3.2SiO_2.2H_2O$). Kaolin can bedistinguished from other clay minerals due to its softness, white degree (whiteness) and easilydispersed in water or other solutions. Because of these physical properties, kaolin is widely used in thepaper industry as a filler or coating material. According to the theory, pure kaolin contains 46%silicate, 40% alumina and 14% water. Moreover, it is hardly found kaolin that meets thecomposition, since there are other impurities such as titan (TiO_2), iron (Fe_2O_3), lime (CaO) orpotassium (K_2O).

The demand for high value petroleum products such as middle distillate, gasoline and lube oil is increasing. Therefore, maximizing of liquid products yield from various processes and valorization residues is of immediate attention to refiners. At the same time, environmental concerns have increased, resulting in more rigorous specifications for petroleum products, including fuel oils. These trends have emphasized the importance of processes that convert the heavier oil fractions into lighter and more valuable clean products (Silvy, 2004). A number of technologies have been developed over the years for residual oil upgrading, which include process that are based on the catalyst, carbon rejection and hydrogen addition routes (Silvy, 2004). Besides, petroleum products are the basic materials used for the manufacture of synthetic fibers for clothing and in plastics, paints, fertilizers, insecticides, soaps, and synthetic rubber. The uses of petroleum as a source of raw material in manufacturing are central to the functioning of modern industry (Speight, 2006). Catalyst is the most powerful tools in the petroleum refining industry (Speight, 2006). Global capacity data of catalytic processing units in petroleum refineries collected by Silvy (Silvy, 2004) indicate that hydrotreating boasts the highest global capacity and fastest growth compared to other major catalytic processes such as fluid catalytic cracking (FCC), hydrocracking (HC), reforming, alkylation and isomerization (Samadhi *et al.*, 2011). Catalyst depends on the rate of deactivation by coke and metal deposits and sintering of the active phases (Bartholomew, 1994). Information regarding the activity, selectivity and deactivation of the individual catalyst is therefore highly desirable for optimizing the catalyst systems.

Kaolin catalysts are commercially used catalysts (Choudhury &Misra, 2011). Kaolin has extensive applications due to their swelling, adsorption and ion exchange properties and high surface areas (Jankovič *et al.,* 2010). Kaolin with different acidities can be obtained by thermal treatment before preparing the catalyst. The temperature of the thermal treatment of the kaolin determines the type and concentration of the hydroxyl groups (Herrero *et al.,* 2000), and thereby its acidity. Kaolin has many applications such as catalyst substrates in the catalytic cracking of petroleum (Murray, 2007). Further, kaolin is used to synthesis zeolite (Oghenejoboh&Ohimsor, 2011).

Zeolite is widely used as a catalyst in the petroleum and petrochemical industries because of its high concentration of active acid sites, its high thermal stability and high size selectivity. For example, ZSM-5 is widely used as a catalyst for isomerization, alkylation and aromatization processes (Oghenejoboh&Ohimsor, 2011). However, zeolite Y is the most important component in FCC catalysts (Htay & Oo, 2008). Today, synthetic zeolites are used commercially more often than natural due to the purity of crystalline products and the uniformity of particle sizes (Gonçalves *et al.*, 2009). Zeolites are usually synthesized from low cost silica-alumina sources in alkaline phase under hydrothermal conditions such as clays (Oghenejoboh&Ohimsor, 2011). The synthetic of zeolite from clay material is analogous to natural formation of zeolite from volcanic deposits or other high Si-Al material (Koukouzas, 2007)]. This is because both volcanic ash and natural clay are fine-grained and contain a large amount of alunimosilicate glass. The formation of natural zeolite may take thousands of years; however, laboratory preparation can shorten this period to hours (Oghenejoboh&Ohimsor, 2011). Kaolin is the most versatile industry mineral and is extensively used for synthetic zeolite (Wang *et al.*, 2007). The benefits of using kaolin as an aluminosilicate source in zeolite synthesis widely known (Oghenejoboh&Ohimsor, 2011).The analysis of the natural kaolin clay shows that the clay contains very low concentration of leachable metals (Pb, As, Zn) which negatively affects catalyst performance, thereby making the kaolin clay an excellent raw material for the production of zeolite for catalysis (Oghenejoboh&Ohimsor, 2011). Many variable parameters are strongly influenced on the formation of zeolite from kaolin. The important parameters are starting material composition, amount of added water, ageing temperature, ageing time crystallization temperature and crystallization time (Htay & Oo, 2008).

Kaolin is the most important clay used in the manufacture of catalysts. Because many catalysts are used at high temperatures and pressures, the refractory character of kaolin is appropriate for many applications. For most industrial applications kaolin must be refined and processed from the crude state to enhance its whiteness, purity and other important commercial characteristics (Naman *et al.*, 2012). The largest use of kaolin is in catalyst substrates in the catalytic cracking of petroleum (Murray, 2007). The purity of the kaolin is critical in this petroleum cracking operation so processed kaolin with low iron, titanium and alkali and alkaline earth compounds is preferred. It is estimated that over 200,000 tons of kaolin are used annually to produce petroleum cracking catalysts (Murray, 2007). Kaolin is the most important raw material in a matrix with zeolite as a catalyst in FCC process (Naman *et al.*, 2012), which kaolin clays modified the properties of catalytic cracking catalysts, such as reducing coke yield, improving attrition resistance, high tolerance to contaminated metal and high thermal stability (Campanati&Vaccari (2001). Kaolins are quite good catalysts for Diels-Alders reactions. They are also excellent supports for Lewis acids or for transition metals, to be applied in various organic reactions (Friedel-Crafts, acylation and alkylation of aromatics, etc.). Depending on the metal, the Brönsted versus Lewis acidity can be tuned, allowing obtaining a family of catalysts (Keith, 2002). In addition, kaolin has been identified as a potential raw material for the production of alumina, one of the most widely used catalyst support material for hydrotreating (Wang, 2009). Kaolin and halloysite are used to make cracking catalysts, as a polymerization catalyst, peptide bond formation, and others (Murray, 2007). Halloysite and metakaolin are used in the manufacture of molecular sieves used as petroleum cracking catalysts. The kaolin for this application must be low in iron and in alkalies and alkaline earth elements. The dry surface of kaolin is very acidic and is used to promote the polymerization of styrene, heterolytic breakdown of organic peroxides, dehydration of alcohols, hydrolysis of esters, and isomerization of alkenes (Murray, 2007).

Adsorption process is one of the simplest and efficient separation methods, because it can be achieved at ambient pressure, temperature and without the use of any expensive material (Emam, 2013). Additionally, it seems to be very promising and economical method and it saves energy consumption. Adsorption process is used to treat crude oil and petroleum fractions (Gawande&Kaware, 2016). It plays an important role in the treatment and finishing of petroleum fractions through desulfurization, deasphalting, bleaching and etc. (Dudasova*et al.,* 2008). Removal of traces of asphaltic materials and other compounds by clay that gives lubricating oils and waxes undesirable colors and odors. Naphtha treated with clay prevents gums formation in gasoline by removing diolefins (Speight, 2014). Clay minerals play significant role in petroleum refining processes, new catalyst are developed from kaolin clay to meet with increasing demand of petroleum products with human and environmental health in view.Despite being blessed with abundant deposits of untapped kaolin, an important raw material use for synthesis of zeolite. Nigeria still imports zeolite and other industrial materials produce from kaolin which is a locally available and untapped. Also,indigenous innovation and ingenuity in harnessing our natural resources should be appreciated regulated, and the products assessed if they meet local and international specifications to mitigate environmental pollution (Udo *et al.*, 2020).Naturally occurring zeolite is important in many industrial processes due to its environmentally benign nature, low cost and its relative abundance compared to deleterious, expensive and, imported synthetic zeolite (Udo *et al.*, 2023).Furthermore,the quest for a sustainable clean environment, has led to intensive research into alternative raw materials which will suit different industrial needs(Udo *et al.*, 2020).It is on this note that this research was designed to characterize some untapped clay deposits in Itu Local Government Area Akwa Ibom State using SEM and XRD. And assess potentials the investigated kaolin clay as raw material for petroleum refining, water treatment based on the SEM and XRD results.

MATERIALS AND METHOD

The kaolin samples used in this study was collected from clay deposits in IkotUsoAkpanItam and EkimItam, Itu L.G.A, Akwa Ibom State, using a clean garden fork. The sample was pulverized to enable its usability stored in clean dry plastic container. The study area is bounded in the North and North-East by Odukpani in Cross River State and Arochukwu in Abia State, in the West by IbionoIbom and Ikono L.G.A, in the South and South-east by Uyo and Uruan Local Government Areas respectively. Itu has a latitude of 5.203624(5o12'13.05oN) and a longitude of 7.968822(7o58'7.76oE) (Bassey *et al.*, 2020, Udo *et al.*, 2023)

Hydrothermal Treatment of Kaolin Clay

In hydrothermal process, 50 g of dried clay sample was added into a 200 ml conical flask containing 100 ml of deionized water. The mixture was heated at 150 ^{o}C for one (1) hour with constant stirring using hot plate with magnetic stirrer, the resulting mixture was filtered and oven dried at 120 oC stored in lid tight containers for further use. Hydrothermal methods can transform kaolin into an ultrafine powder under controlled thermal conditions. The benefits of hydrothermal treatment of kaolin include increased reactants reactivity, low energy consumption, reduced air pollution, easy to control the solution, formation of metastable phases, and unique condensed phases (Johnson and Arshad 2014, Udo *et al.*, 2023)

Acid Leaching of Mesoporous-Kaolin

The dried (mesoporous-kaolin) (50 g) prepared in the hydrothermal step was added to a 200 ml conical flask containing 100 ml of 11% hydrochloric acid (HCl). The resulting mixture was heated electrically at 150 oC with constant stirring using magnetic stirrer for one (1) hour and filtered. The solid residue was washed with deionized water until no chloride was detected using AgNO3 (Udo *et al*., 2023)

Calcination of the acidified mesoporous –kaolin

The acidified mesoporous -kaolin was oven dried at 120 oC for one (1) hour and calcinedto 650 ^{o}C for two (2) hours in a muffle furnace and later cooled. The calcined kaolin was stored in a lid tight container and properly labeled. The heating process eliminates water from the mineral kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), the main constituent of kaolin clay, and collapses the material structure, resulting in an amorphous aluminosilicate ($Al_2O_3 \cdot 2SiO_2$), metakaolinite. The process is known as dehydroxylation $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow Al_2O_3 \cdot 2SiO_2 + 2H_2O\uparrow$.

Results and Discursions

The results of the crystalline phases, percentage crystallinity, crystal structure of kaolin deposit from IkotUsoAkpanItam and EkimItam, Itu Local Government Area Akwa Ibom State Nigeria are presented Figure1 -Figure 8.

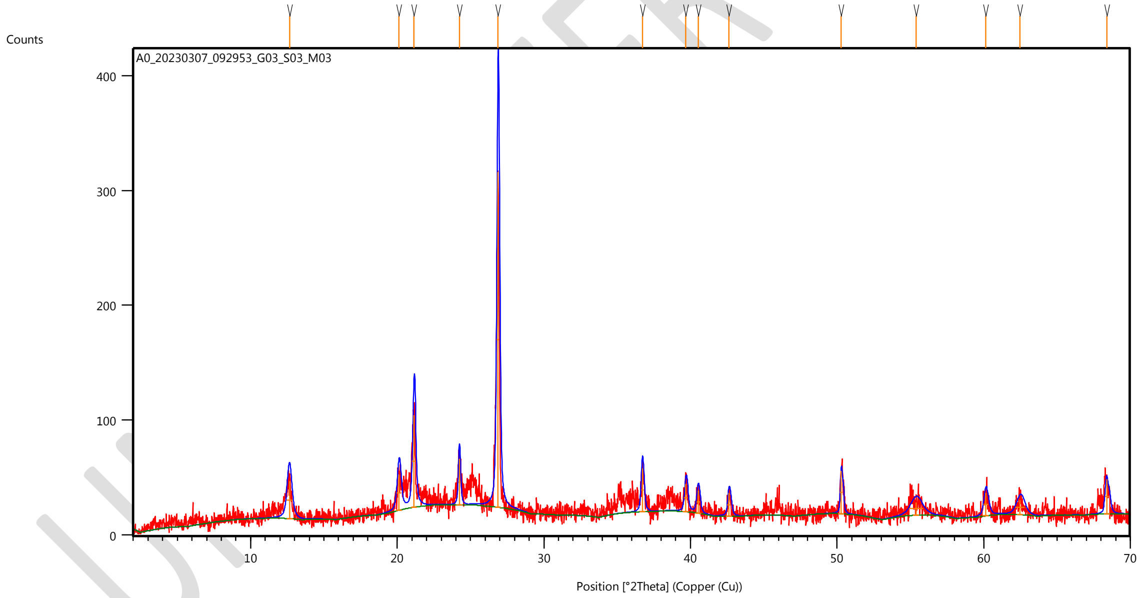
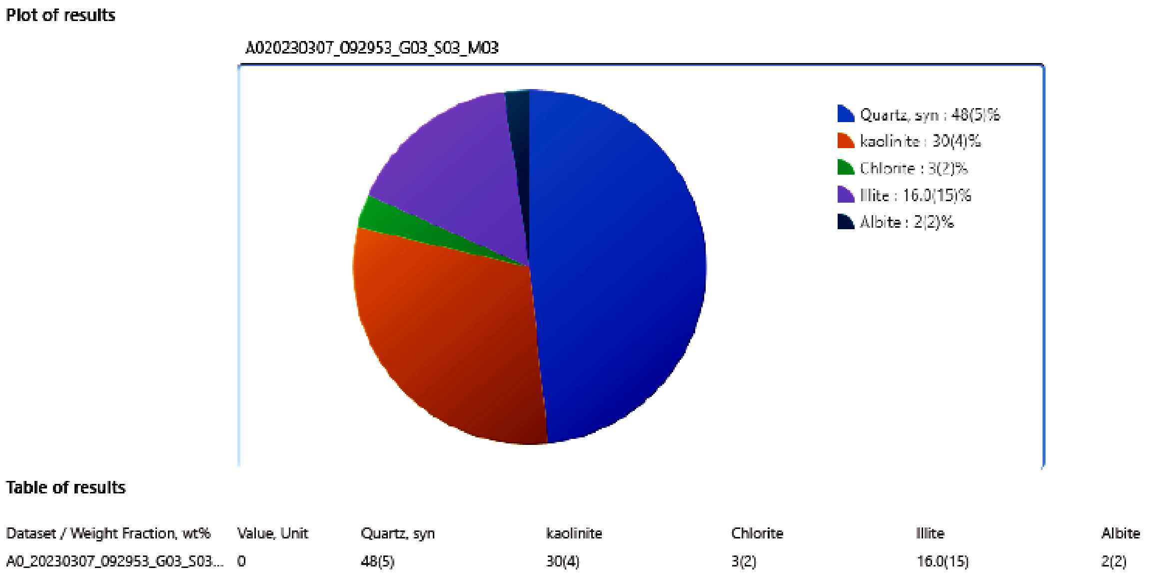


Fig. 1: XRD Pattern of IkotUsoAkpanItam Untreated Koalin



Plot of results

Table of results

Dataset / Weight Fraction, wt%	Value, Unit	Quartz, syn	kaolinite	Chlorite	Illite	Albite
A0_20230307_092953_G03_S03...	0	48(5)	30(4)	3(2)	16.0(15)	2(2)

Fig 2: Percentage quartz, kalonite, chlorite, illite and Albite for natural (untreated) kaolin sample from IkotUsoAkpanItam .

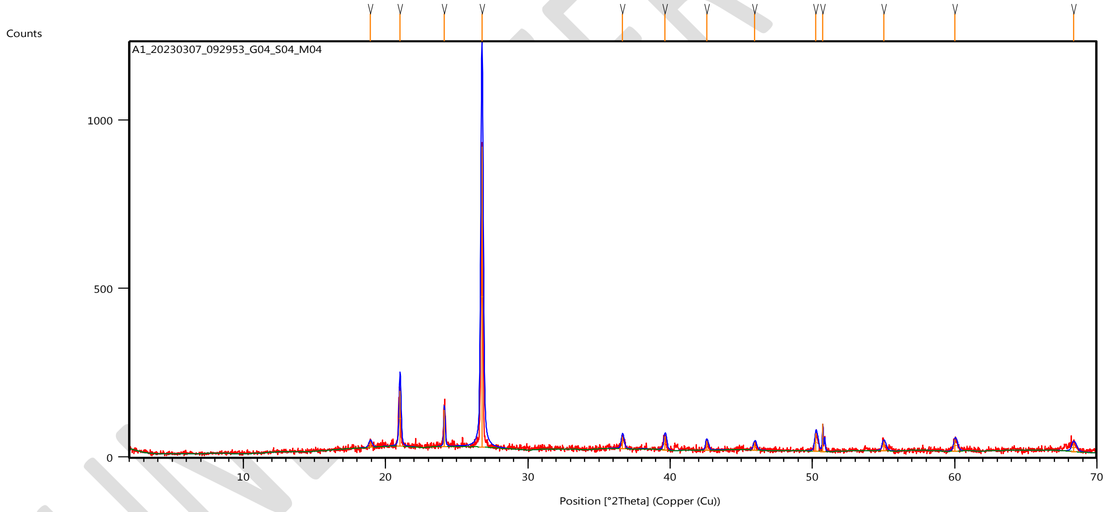


Fig. 3: XRD Pattern of IkotUsoAkpanItamCalcinedKoalin

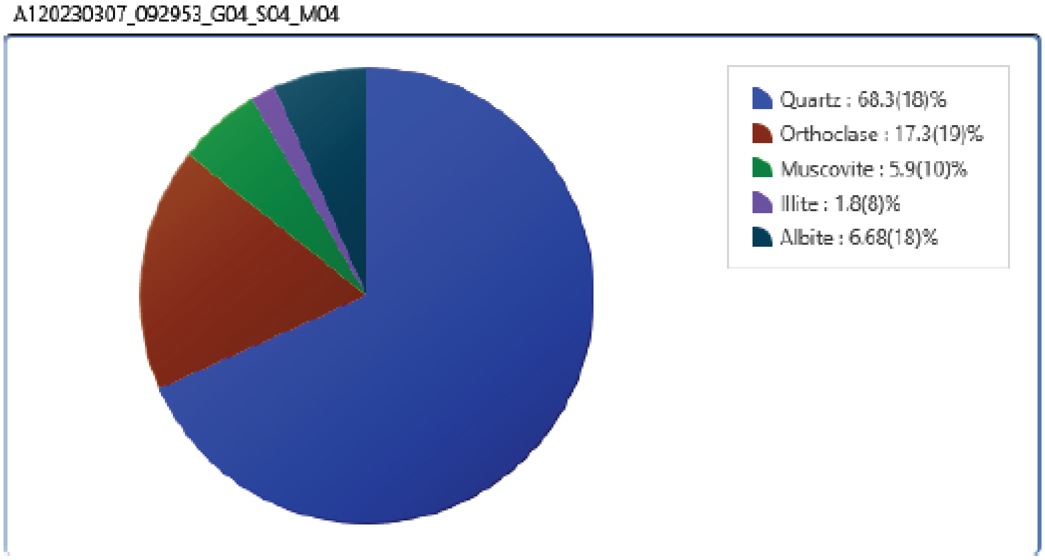


Fig 4: Percentage quartz, Orthoclase, Muscovite, illite and Albite in calcined kaolin from IkotUsoAkpanItamCalcined Kaolin

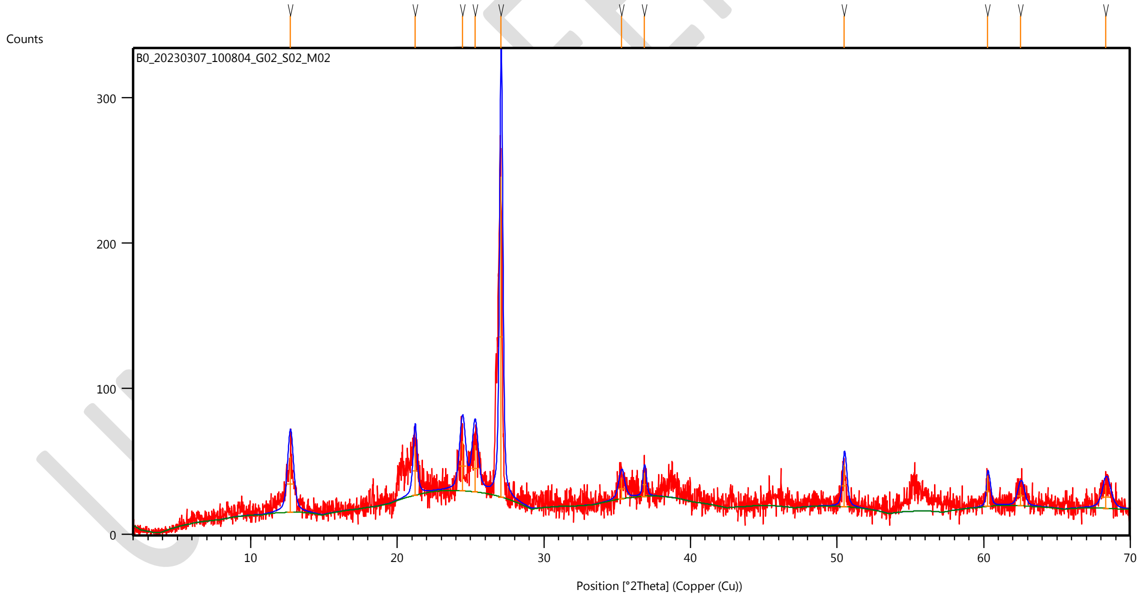
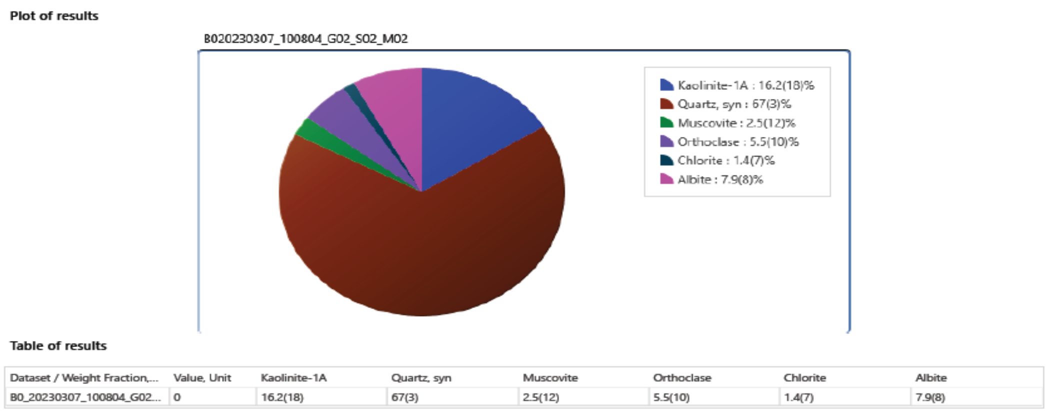


Fig. 5: XRD Pattern of EkimItam Untreated Koalin



Plot of results

Table of results

Dataset / Weight Fraction,...	Value, Unit	Kaolinite-1A	Quartz, syn	Muscovite	Orthoclase	Chlorite	Albite
B0_20230307_100804_G02...	0	16.2(18)	67(3)	2.5(12)	5.5(10)	1.4(7)	7.9(8)

Fig 6: Percentage quartz, Orthoclase, Muscovite, illite and Albite in untreated kaolin from IkotEkimItamCalcinedKoalin

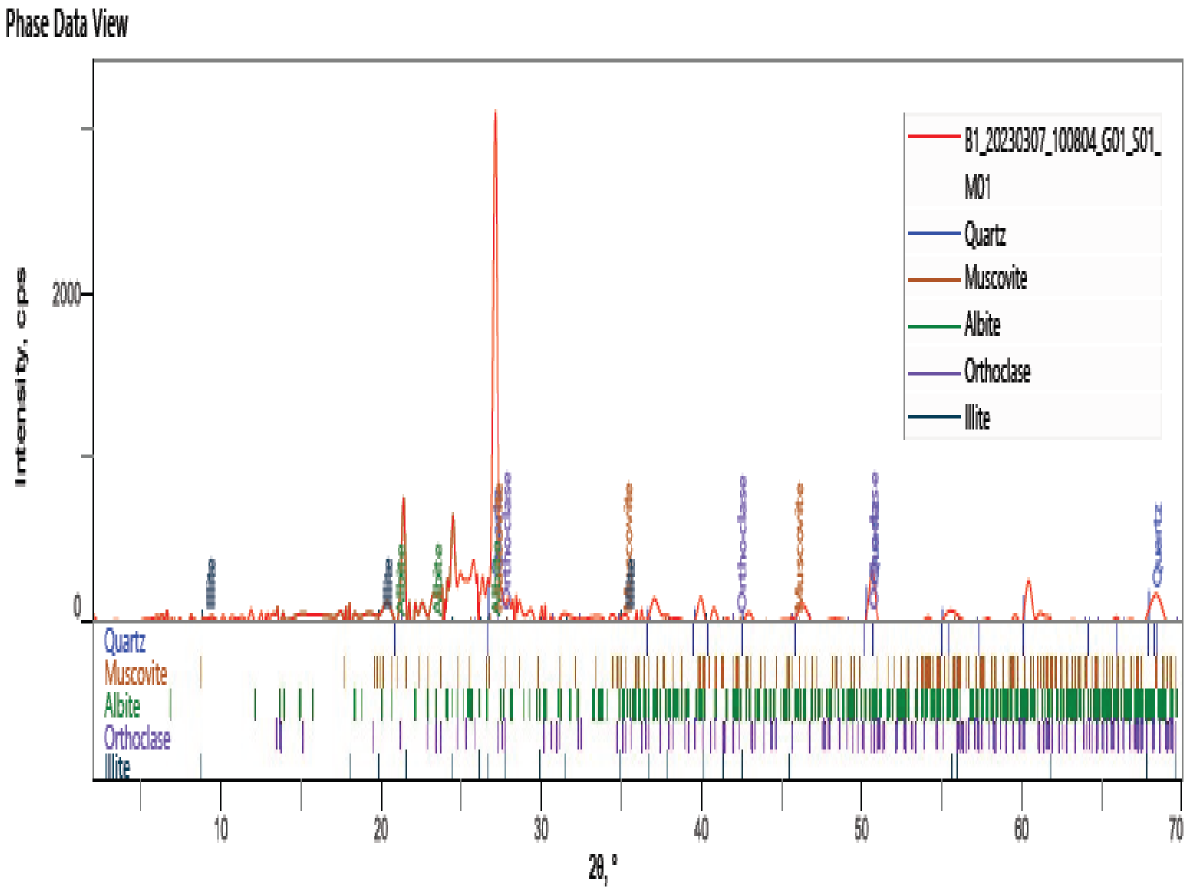


Fig. 7: XRD Pattern of EkimItamCalcinedKoalin

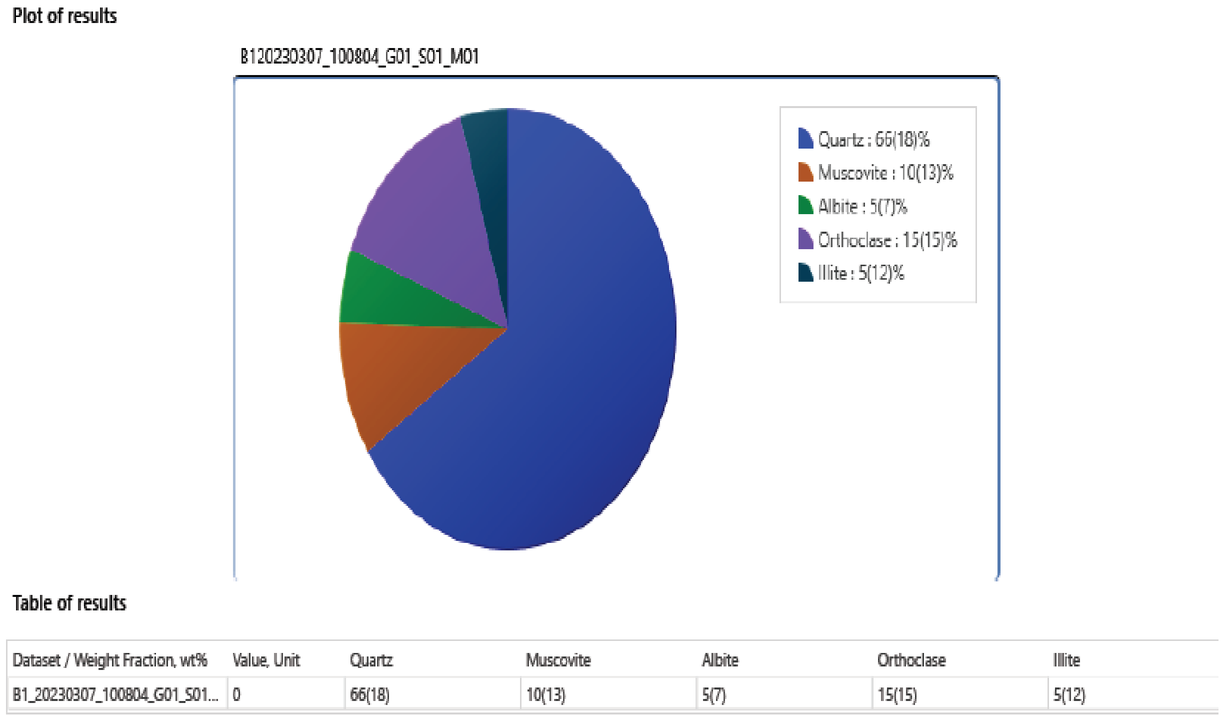

Plot of results

Table of results

Dataset / Weight Fraction, wt%	Value, Unit	Quartz	Muscovite	Albite	Orthoclase	Illite
B1_20230307_100804_G01_S01...	0	66(18)	10(13)	5(7)	15(15)	5(12)

Fig 8: Percentage quartz, Orthoclase, Muscovite, illite and Albite in calcined kaolin from IkotEkimItamCalcined kaolin.

Discussion

According to XRD data, the calcined kaolin from IkotUsoAkpanItam contained 68.3 % quartz, 17.3 % orthoclase, 5.9 % muscovite, 1.8 % illite , 6.68 %, albite and the natural (untreated) kaolin contained 48.0% quartz, 30.0% kaolinite, 3.0 % chlorite, 16.0 % illite and 2.0% albite while the calcined Kaolin from EkimItam contained 66.0 % quartz, 10.0 % muscovite, 15.0 % orthoclase, 5.0 % illite, 5.0 % albite and the natural (untreated) Kaolin contained 16.2 % kaolinite, 67.0% quartz, 2.5 % muscovite, 5.5 % orthoclase, 1.4 % chlorite, and 7.0 % albite, Fig. 1 - 8. The X-ray diffraction patterns of the untreated and calcined kaolin from the two kaolin deposits as presented in Fig 1 - 8 indicate sharp peaks implying that both samples are crystalline at natural and calcined stage. Konne, *et al* 2016 and Maciver, *et al* 2020 reported similar train for untreated and treated kaolin samples from Kono-Boue and Chokocho, Rivers State, Nigeria. The quartz was identified by its characteristics X-ray diffraction peaks at 20.96^o and 54.97^o 2-theta. There was increase in composition of quartz in Ikot Uso Akpan kaolin from 48.0% to 68.3% after calcination at 650 ^{o}C for 2 hours indicating higher crystallinity. Increase in calcination temperatureincreases activity and surface area of the metakoalinlinearly to a maximum temperature of 700 ^{oC}. Agglomeration of calcined kaolinite (metakoalinite) and formation of spinel phase occurs above 700 ^{oC}.The activation of kaolin should produce structural changes of its minerals composition hence promoting its activities (Gougazeh and Buhl, 2016).This investigation agrees with the work of (Adamu *et al.*, 2022, Udo *et al.*, 2023, Wang & Xie 2008). Calcination above 700 ^{o}c may result in disorderliness within the metakaolinite structure (Elimbi*et al.*, 2011). Activated kaolin and zeolite can increase the productivity of bio-oil. In a related study by (Gandidi*et al.*, 2018) kaolin proved a better ability for enhance pyrolysis process with improved yield bio-oil.

The results of SEM micrographs of the untreated and the metakaolin clay samples from Ikot Uso Akpan are presented in Figure 9 and Figure 10 respectively.

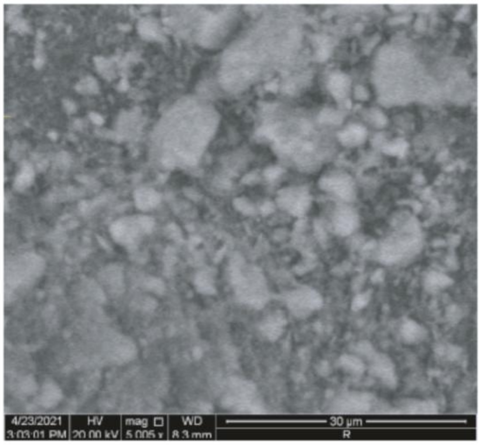


Figure 9: SEM Micrograph of Raw (Untreated) IkotUsoAkpanItamkaoline at 500x magnification

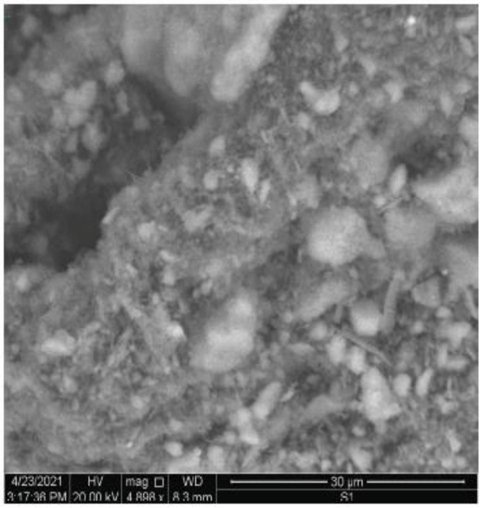


Figure 10: SEM Micrograph of Calcined IkotUsoAkpanItam kaolin at 500x magnification

SEM micrographs of the untreated clay and the metakaolin clay samples are presented in Figure 9 and 10 respectively. Micrograph resolutions were taken at 30µm. Both the untreated and the calcined surface morphologies were heterogeneous size and spongy-like porous shape. There was no significant change in the surface morphology heterogeneous size of the calcined kaolin from the untreated kaolin. This reveals that thermal treatment at 650°C for 2 hours did not significantly modify surface morphology of the kaolin. In accordance with the results of other analytical methods quartz was identified by SEM in the sample. Cubic crystalline structures with well-defined edges are observed on the micrographs of the calcined kaolin Fig 10. This is in line with the work of other researchers (Yusuf *et al* 2019, Adamu *et al* 2022).

Conclusion

Kaolin samples from IkotUsoAkpanItam and EkimItam, Itu local Government Area, Akwa Ibom State, Nigeria was successfully characterized using X-Ray Diffraction spectrophotometer technique to identify crystalline phase in the samples. This investigation has established the development of methakaolin through hydrothermal process and acid leaching. The characterization using XRD confirmed the presence of quartz and alumina mineral phases in from both kaolin deposits. It was also demonstrated that calcination of kaolin at 800 ^{o}C can increase its crystalline structure. Further work is required to synthesis zeolite catalyst from the kaolin for purification of biodiesel and cracking of hydrocarbons. Results of SEM indicated that the IkotUsoAkpanItam and EkimItam kaolin can be a promising raw material for zeolit production at appropriate processing conditions that can be a substitute imported zealite. This will reduce cost, increase employment and revenue

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