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A REVIEW OF THE PROPERTIES OF NIGERIAN KAOLIN FOR CONVERSION OF POLYMER WASTES TO PYROLYTIC FUEL

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ABSTRACT

Nigeria faces a mounting plastic waste crisis, generating over 32 million tons of solid waste annually, with plastics comprising a growing proportion that overwhelms inadequate landfills, open dumps, and natural ecosystems. Conventional disposal methods like open burning release toxic dioxins and contribute to environmental degradation, while imported synthetic catalysts for advanced waste conversion remain prohibitively expensive. This comprehensive review explores Nigerian kaolin—an abundant, locally sourced clay mineral—as a cost-effective alternative for catalytic pyrolysis of polymer wastes, transforming non-recyclable plastics (HDPE, LDPE, PP, PS, PET) into valuable pyrolytic fuels. Derived primarily from kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), Nigerian kaolin exhibits favorable physicochemical properties including 45-55% SiO_2 , 25-35% Al_2O_3 , moderate Brønsted/Lewis acidity, and layered structure that supports zeolite Y synthesis and direct catalytic applications. Major deposits span states like Abia, Anambra, Bauchi, Edo, Ekiti, and Katsina, offering vast reserves for industrial utilization. The review details kaolin's transformation into metakaolin via calcination (500-700°C), enhancing surface area ($10-30 \text{ m}^2/\text{g} \rightarrow \text{higher}$) and catalytic activity for pyrolysis at reduced temperatures (350-500°C vs. 450-600°C thermal), achieving 60-75 wt% liquid yields with gasoline/diesel-range hydrocarbons (40-45 MJ/kg calorific value). Environmental benefits include landfill diversion, lower emissions than open burning, and char-based carbon sequestration, while economic advantages encompass 25% catalyst cost savings, job creation across waste-to-fuel value chains, and reduced fossil fuel imports. However, challenges persist: deposit variability requiring beneficiation, catalyst deactivation (coke deposition, pore blockage), scaling from bench to industrial reactors, feedstock contamination from real-world mixed plastics, and policy gaps hindering commercialization. Future research directions emphasize advanced catalyst modifications (metal doping,

hierarchical porosity), process optimization (fluidized-bed reactors, kinetic modeling), feedstock flexibility (co-pyrolysis with biomass), product upgrading for fuel standards compliance, comprehensive life cycle assessments, and pilot demonstrations. Supportive policies—tax incentives, extended producer responsibility, and national standards—are essential. Nigerian kaolin-based pyrolysis represents a circular economy cornerstone, converting waste liabilities into sustainable energy assets while advancing environmental protection and energy security.

KEYWORDS: Nigerian kaolin; Polymer waste pyrolysis; Waste-to-fuel conversion; Catalytic pyrolysis; Fuel production.

1. INTRODUCTION

The global plastic waste crisis has reached alarming proportions, with millions of tons of plastic ending up in landfills, oceans, and natural ecosystems each year (UNEP, 2010). Plastic pollution contributes to environmental degradation, threatens marine life, and generates microplastics that enter the food chain, posing significant risks to human health (Ates, 2013). In developing countries like Nigeria, waste management systems are often inadequate, leading to widespread open dumping, burning, and environmental contamination (Bloodworth et al., 1993).

Pyrolysis has emerged as a promising thermochemical recycling method that can convert plastic waste into valuable products such as liquid fuels, gases, and char (Gushit et al., 2010). Unlike incineration, pyrolysis operates in an oxygen-limited environment, reducing harmful emissions and producing usable hydrocarbons (Ajayi et al., 2010). Compared to mechanical recycling, pyrolysis can handle mixed, contaminated, and non-recyclable plastics, offering a more flexible waste-to-energy pathway (Adeniyi et al., 2020).

Catalytic pyrolysis further enhances the process by lowering reaction temperatures, improving fuel quality, increasing liquid yield, and reducing undesirable byproducts such as wax and coke (Qoniah et al., 2005). While synthetic catalysts like zeolites and silica-alumina are effective, they are often expensive and not locally available in many regions (Pan et al., 2013). Natural clays, such as kaolin, offer a cost-effective, abundant, and environmentally friendly alternative (RMRDC, 2003).

Nigeria is endowed with substantial kaolin deposits across multiple states, presenting a unique opportunity to utilize locally sourced materials for catalytic pyrolysis (Gushit et al., 2010). Nigerian kaolin possesses favorable physicochemical properties, including high silica and alumina content, layered structure, and natural acidity, making it suitable for catalytic applications (Adeniyi et al., 2020). This review aims to synthesize existing knowledge on the use of Nigerian kaolin in polymer waste pyrolysis, identify research gaps, and propose future directions to advance this sustainable technology in Nigeria and beyond (Hakeem et al., 2018).

2. Polymer Waste Landscape in Nigeria

Nigeria generates significant volumes of polymer waste, primarily from packaging, household goods, agriculture, healthcare, and industrial sectors (UNEP, 2010). Common plastic types include high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), and polyethylene terephthalate (PET) (Ates, 2013). Despite growing awareness, waste management remains a challenge due to inadequate collection systems, limited recycling infrastructure, and low public participation in waste segregation (Bloodworth et al., 1993).

Current disposal methods include landfilling, open burning, and indiscriminate dumping, which contribute to soil contamination, air pollution, and public health risks (Gushit et al., 2010). Open burning of plastics releases toxic gases such as dioxins and furans, while landfilling leads to long-term environmental persistence and microplastic leakage (Ajayi et al., 2010). There is a clear need to transition from linear waste disposal to circular economy models that view plastic waste as a resource (Adeniyi et al., 2020).

The conversion of polymer waste into pyrolytic fuel presents a viable opportunity for energy recovery, reducing dependence on imported fossil fuels and providing a locally sustainable energy source (Hakeem et al., 2018). This aligns with Nigeria's goals for energy security, waste reduction, and environmental sustainability (RMRDC, 2003).

3. Properties and Characteristics of Nigerian Kaolin

Kaolin is a clay mineral predominantly composed of kaolinite $[Al_2Si_2O_5(OH)_4]$, formed through the weathering of aluminosilicate minerals (Bloodworth et al., 1993). In Nigeria, kaolin deposits are widespread, with significant reserves in states such as Abia, Anambra, Bauchi, Edo, Ekiti, and Katsina (Table 1) (Gushit et al., 2010).

Physicochemical Properties:

Chemical Composition: Nigerian kaolin typically contains 45–55% SiO_2 and 25–35% Al_2O_3 , with trace amounts of Fe_2O_3 , TiO_2 , K_2O , and MgO (Gushit et al., 2010).

Mineralogy: Kaolinite is the dominant mineral, though some deposits contain quartz, illite, feldspar, and montmorillonite (Adeniyi et al., 2020).

Structure: Kaolinite has a layered 1:1 phyllosilicate structure, with alternating tetrahedral silica and octahedral alumina sheets, providing natural acidity and ion-exchange capacity (Bloodworth et al., 1993).

Surface Area and Porosity: Raw kaolin has moderate surface area (10–30 m^2/g), which can be enhanced through thermal treatment or acid activation (Ajayi et al., 2010).

Acidity: Kaolin exhibits both Brønsted and Lewis acid sites, which can be modified through calcination or metal impregnation to enhance catalytic activity (Qoniah et al., 2005).

Thermal Stability: Kaolin is stable up to $\sim 600^\circ\text{C}$, beyond which it transforms into metakaolin, an amorphous phase with increased reactivity (Pan et al., 2013)..

Characterization Techniques:

Common methods include X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and Brunauer–Emmett–Teller (BET) surface area analysis (Adeniyi et al., 2020).

Compared to synthetic catalysts like zeolite Y or HZSM-5, Nigerian kaolin is less acidic and has smaller pores, but its abundance, low cost, and ease of modification make it a competitive alternative for pyrolysis applications (Ajayi et al., 2010).

Kaolin is often produced through the weathering of hydrated aluminum silicates in the earth's crust. The term "kaolin" may refer to either unprocessed clay or finished commercial products (Bloodworth et al., 1993). There is a preponderance of the clay mineral kaolinite, which has the chemical formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, in this clay-rich rock. Optimal kaolin characteristics include a specific gravity of 2.58–2.63, a refractive index of 1.56–1.62, and a plastic or slippery texture (Gushit et al., 2010). Because of its inert chemical nature under normal conditions, kaolin is in high demand as a raw material for the production of a broad range of goods, including paper, ceramics, paint, chalk, cosmetics, pharmaceuticals, and agrochemicals. As a catalyst for the pyrolysis of plastic waste, it might be useful (Qoniah et al., 2005).

Hydrogen bonds hold together the silicate (Si_2O_5) and aluminum oxide/hydroxide ($\text{Al}_2(\text{OH})_4$) sheets that form gibbsite, a layered silicate mineral. Each alumina octahedron is connected to a tetrahedral alumina sheet through oxygen atoms. The aluminum layers in kaolinite share a similar structure with gibbsite, consisting of alternating silicate and gibbsite layers held together by weak interlayer forces, known as s-g layers. Due to these weak bonds, kaolinite is brittle and easily cleaved (Bloodworth et al., 1993).

Pure kaolin is primarily formed through intense weathering processes. It is the most common clay mineral in tropical soils and the second most abundant in marine sediments. Other minerals with the same chemical composition as kaolinite include halloysite, dickite, and nacrite. These minerals are polymorphs, meaning they share the same chemical formula but crystallize differently. Kaolinite is typically formed by the chemical alteration of aluminum-rich silicate minerals, such as feldspar. Other possible sources include sedimentary deposits and the hydrothermal alteration of alumino-silicate-rich rocks. As a key industrial mineral, kaolinite has numerous applications across various sectors (Adeniyi et al., 2020).

Research by Adeniyi et al. (2020) highlights the extensive applications of kaolinite, a primary clay mineral in kaolin clays, due to its high silica and alumina content. Recently, kaolinite (or metakaolinite) has gained significant attention for its potential use as a catalyst precursor, carbon-sequestering material, cement additive, and geopolymers feedstock. The synthesis of catalytic aluminosilicate compounds using both raw and thermally treated kaolin clays has been successfully demonstrated (Qoniah et al., 2005; Pan et al., 2013).

Therefore, the underestimation of the economic and industrial values of Nigeria's kaolin resources may have been attributable to a lack of local expertise, implying that Nigeria's manufacturing industry must depend on imported kaolin due to its inability to match the required industrial criteria. RMRDC (2003) reports that many kaolin deposits totaling billions of tons have been discovered in Nigeria.

Table 1. Primary kaolin resources and reserves found in Nigeria - (revised from Gushit et al., 2010).

State	Major Locations	Estimated Reserve (million-tonnes)
Abia	Isikwuato, Nneochi, Obingwa, Umuahiaarea, Ikwuano	Very large
Anambra	Anambra-East, Ayamelum, Ekwusigo, Njikoka, Aguata, Ihiala, Nnewi-South	4.2
Bauchi	Alkaleri, Bauch, Damban, Darazo, Ganjuwa, Kirfi, Misau, Ningi	18

Benue	Obi, Ogbadibo, Apa, Oturkpo	10
Borno	Gwoza, Chibok, Damboa	Large
Edo	Esan, Ovia and Etsako areas, Ikpoba Okha, Akoko-Edo, Egor, Igueben, Oredo, Orhionmwon, Uhunmwonde, Owan-East	Very large
Ekiti	Ikere, Ijero-Ekiti, Isan-Ekiti	Very large
Enugu	Enugu	50
Kaduna	Maraban-Rido	5.5
Katsina	Batagarawa, Batsari, Dan-Musa, Danja, Dutsin-Ma, Ingawa, Kankara, Kankia, Safana, Malumfashi, Musawa,	Very large
Kebbi	Bagudo, Suru, Wasagu/Danko	Very large
Kwara	Baruten, Edu, Ifelodun, Ilorin, Ilepodun, Isin, Kaiama, Pategi	Large
Niger	Bosso, Edati, Gbako, Katcha, Lapai, Lavun, Mashegu, Mokwa, Paikoro, Shiroro, Wushishi	Very large
Ogun	Abeokuta area, Ado-Odo/Ata, Idarapo, Ifo, Igbadoarea, Ijebuarea, Ipokia, Obafemi-Owode, Odeda, Odogbolu, Remo-North	Large
Ondo	Irele, Odigba	Not available
Oyo	Atisbo, Ifedayo, Iseyin, Saki West and East.	1.5
Plateau	Barkin-Ladi, Bassa, Bokkos, Jos-North, Kanke, Pankshin	8.0
Zamfara	Gumi, Gusau, Kaura-Namoda, Maradun, Maru, Talata-Mafara, Zurmi	Not available

Zeolites, crystalline microporous aluminosilicate minerals, are widely recognized for their high thermal stability and ion-exchange capabilities across various temperature ranges. Zeolite Y, a highly porous faujasite-type zeolite with a Si/Al ratio of 1.5–3.8, is extensively used in industrial processes, particularly for catalytic cracking of heavy hydrocarbons in the petroleum and petrochemical industries. While synthetic zeolites are dominant in these sectors, natural zeolites are also produced.

The synthesis of zeolites from clay, a rich source of both silica and alumina, is a well-established and cost-effective practice (Ajayi et al., 2010). Studies have shown that using Arobeye clay from Nigeria can reduce zeolite production costs by 25% compared to commercial chemical alternatives. With abundant kaolin clay deposits across Nigeria, scientific research supports its viability as a cost-effective substitute for alumina in industrial applications.

4. Pyrolysis of Polymer Wastes: Principles and Mechanisms

Pyrolysis is a thermochemical decomposition process that occurs in the absence of oxygen, converting polymeric materials into smaller molecular fragments through the breaking of

chemical bonds under controlled heating (Ajayi et al., 2010). This section details the fundamental principles, mechanisms, and influencing factors of both thermal and catalytic pyrolysis, with particular emphasis on how these processes transform polymer wastes into valuable fuel products (Hakeem et al., 2018).

Thermal Pyrolysis

Thermal pyrolysis involves heating polymers in the absence of oxygen to break long-chain hydrocarbons into shorter ones (Bloodworth et al., 1993). Key factors include temperature (typically 350–600°C), heating rate, residence time, and polymer type (Gushit et al., 2010). Products include liquid oil (pyrolytic oil), gas (methane, ethylene, propylene), and solid char; however, thermal pyrolysis often yields low-quality oil with high wax content and requires high energy input (Adeniyi et al., 2020).

Catalytic Pyrolysis

Catalytic pyrolysis introduces a catalyst to lower activation energy, reduce reaction temperature, and improve product selectivity (Qoniah et al., 2005). Catalysts facilitate cracking, isomerization, deoxygenation, and aromatization reactions, leading to higher yields of gasoline- and diesel-range hydrocarbons (Pan et al., 2013). The catalyst's acidity, pore structure, and surface area significantly influence product distribution and quality (RMRDC, 2003).

Common pyrolysis reactors include batch, fixed-bed, fluidized-bed, and rotary kiln systems, each with distinct advantages for scalability and product control (Ajayi et al., 2010).

Thermal Pyrolysis: Fundamentals and Limitations

Thermal pyrolysis involves heating polymer materials in an inert atmosphere (typically nitrogen or argon) to temperatures between 350°C and 900°C (Gushit et al., 2010). Under these conditions, the long-chain hydrocarbon polymers undergo random scission, depolymerization, and rearrangement reactions, breaking down into shorter-chain hydrocarbons (Bloodworth et al., 1993).

Key Degradation Mechanisms:

Random Chain Scission: C-C bonds break at random positions along the polymer backbone (Adeniyi et al., 2020).

End-Chain Scission (Depolymerization): Polymer chains unzip from their ends (Qoniah et al., 2005).

Side-Group Elimination: Functional groups attached to the main chain (e.g., chlorine in PVC) are eliminated (Pan et al., 2013).

Cross-Linking and Char Formation: At higher temperatures or longer residence times (RMRDC, 2003).

Factors Affecting Thermal Pyrolysis:

- Temperature: The most critical parameter. Higher temperatures generally increase liquid and gas yields but can promote excessive cracking to light gases or secondary reactions leading to char (Ajayi et al., 2010).
- Heating Rate: Fast heating (flash pyrolysis) minimizes secondary reactions and maximizes liquid yield, while slow heating favors char formation (Hakeem et al., 2018).
- Residence Time: Longer residence times allow more complete decomposition but can also lead to overcracking and gas formation (Gushit et al., 2010).
- Polymer Type: Different polymers exhibit distinct degradation behaviors:
- Polyethylene (PE) and polypropylene (PP) primarily undergo random scission
- Polystyrene (PS) predominantly depolymerizes to styrene monomer
- Polyethylene terephthalate (PET) decomposes to produce terephthalic acid and ethylene glycol
- Polyvinyl chloride (PVC) releases HCl gas during early-stage decomposition (Bloodworth et al., 1993)

Products of Thermal Pyrolysis:

- Liquid Oil (Pyrolytic Oil): A complex mixture of aliphatic and aromatic hydrocarbons typically containing 55-85% of the product mass (Adeniyi et al., 2020)
- Gas: C1-C4 hydrocarbons (methane, ethane, ethylene, propylene) constituting 10-30% of yield (Qoniah et al., 2005)
- Char: Carbonaceous solid residue representing 5-20% of original mass (Pan et al., 2013).
- Limitations of Thermal Pyrolysis:
 - Requires high temperatures (often $>500^{\circ}\text{C}$), leading to substantial energy input
 - Produces a broad distribution of hydrocarbons, including heavy waxes (C20+) that require further upgrading
 - Often yields oils with poor fuel properties: low octane/cetane numbers, high aromatic content, and poor cold flow properties

- Limited control over product selectivity (RMRDC, 2003).

Catalytic Pyrolysis: Enhanced Mechanisms and Selectivity

Mechanism of Catalysis:

Catalysts function by providing alternative reaction pathways with lower activation energies, facilitating specific bond-breaking and rearrangement reactions. In polymer pyrolysis, catalysts primarily act through:

1. Acid-Catalyzed Cracking: Brønsted and Lewis acid sites on catalyst surfaces protonate hydrocarbon chains, promoting β -scission reactions that break C-C bonds (Ajayi et al., 2010).
2. Isomerization: Rearrangement of carbon skeletons to form branched hydrocarbons with improved fuel properties (Hakeem et al., 2018).
3. Aromatization: Cyclization and dehydrogenation reactions leading to aromatic compound formation (Gushit et al., 2010).
4. Deoxygenation: Particularly relevant for oxygen-containing polymers or biomass co-feeds (Bloodworth et al., 1993).

Influence of Catalyst Properties:

- Acidity: Stronger acidity generally increases cracking activity but can promote excessive gas formation and coke deposition. Optimal acidity balances cracking with product quality (Adeniyi et al., 2020).
- Pore Structure:
- Microporous catalysts (e.g., zeolites) provide shape selectivity, favoring specific product ranges
- Mesoporous materials allow diffusion of larger molecules, reducing pore blockage
- Hierarchical pore structures combine advantages of both micro- and mesoporosity
- Surface Area: Higher surface area provides more active sites but must be balanced with pore accessibility
- Thermal Stability: Critical for maintaining activity at pyrolysis temperatures (Qoniah et al., 2005; Pan et al., 2013).

Reaction Pathways in Catalytic Pyrolysis:(Adeniyi et al., 2023; Cheng et al., 2024)

1. Primary Cracking: Initial breakdown of polymer chains into smaller fragments (oligomers)
2. Secondary Cracking: Further decomposition of oligomers to gasoline- and diesel-range hydrocarbons

3. Oligomerization/Cyclization: Formation of cyclic and aromatic compounds
4. Hydrogen Transfer: Redistribution of hydrogen among reaction intermediates
5. Coke Formation: Polyaromatic condensation leading to catalyst deactivation

Kaolin-Specific Behavior

Nigerian kaolin exhibits moderate acidity from Al^{3+} Lewis sites; calcination to metakaolin increases acidity/surface area (RMRDC, 2003). Layered structure accommodates intermediates; controls cracking severity vs. HZSM-5 (Ajayi et al., 2010).

Reactor Configurations

Batch: Laboratory research (Hakeem et al., 2018).

Fixed-Bed: Catalyst performance studies (Gushit et al., 2010).

Fluidized-Bed: Best heat/mass transfer; ideal for kaolin (Bloodworth et al., 1993).

Screw/Kiln: Continuous viscous feedstocks (Adeniyi et al., 2020).

Fluidized-beds minimize kaolin deactivation via abrasion/regeneration (Qoniah et al., 2005).

Product Distribution with Kaolin

Liquid: 60-75 wt% C5-C20 hydrocarbons (Pan et al., 2013).

Gas: 15-30 wt% propylene/butenes (RMRDC, 2003).

Char: 5-15 wt% (Ajayi et al., 2010).

Mechanistic Considerations

Moderate acidity prevents excess gas (Hakeem et al., 2018).

Layered structure traps intermediates (Gushit et al., 2010).

Metakaolin transformation at 500-700°C (Bloodworth et al., 1993).

Trace oxides modify sites (Adeniyi et al., 2020).

Particle morphology affects reactor efficiency (Qoniah et al., 2005).

Table 2. Comparative Analysis: Thermal vs. Catalytic Pyrolysis with Kaolin

Parameter	Thermal Pyrolysis	Kaolin-Catalyzed Pyrolysis
Temperature	450-600°C	350-500°C
Liquid Yield	50-70%	60-75%
Gas Yield	20-40%	15-30%
Char Yield	10-25%	5-15%
Oil Quality	Heavy, waxy, high aromaticity	Lighter, lower viscosity, improved fuel properties
Energy	High	Reduced by 20-

Requirement		40%
Product Control	Limited	Enhanced through catalyst modification

The principles and mechanisms of polymer pyrolysis reveal a complex interplay of thermal and catalytic processes that determine product yields and qualities. While thermal pyrolysis provides a foundation for polymer decomposition, catalytic pyrolysis with materials like Nigerian kaolin offers significant advantages through reduced reaction temperatures, improved product selectivity, and enhanced fuel properties. The moderate acidity, thermal stability, and structural characteristics of Nigerian kaolin make it particularly suited for controlling the balance between cracking severity and product quality. Understanding these mechanisms provides the basis for optimizing pyrolysis conditions and catalyst modifications to maximize the efficiency and economic viability of polymer waste conversion to valuable fuels.

5. Exploiting Nigerian Kaolin in Polymer Pyrolysis: State-of-the-Art

Several studies have explored the use of Nigerian kaolin in the pyrolysis of various polymers. Evident from Table 3 is the summary of previous work done by some great scholars, their earlier research work done on Nigerian **Kaolin Catalyst** in different regions, the researcher(s) identity, the number of specific areas studied of location and experiment done, the year these research works were conducted for the records was indicated.

Table 3. Studies conducted on Nigerian kaolin catalyst by Nigerian researchers.

Researcher (s)	Specific areas studied or locations	Research conducted
Hakeem et al	Ahoko, Nigeria	Catalytic pyrolysis of waste polypropylene using Ahoko kaolin from Nigeria.
Ogundiran, M. and Winjobi, F	Ijero-Ekiti	The potential of binary blended geopolymers binder containing Ijero-Ekiti calcined kaolin clay and ground waste window glass.
Ojo et al	Ifon, Ondo State, Nigeria	Geotechnical Properties and Geochemical Composition of Kaolin Deposits in Parts of Ifon, Southwestern Nigeria.
OlaOlorun, O. and Oyinloye, A	Ijero-Ekiti, southwestern Nigeria	Geology and Geotechnical Appraisal of Some Clay Deposits Around Ijero-Ekiti

		Southwestern Nigeria: Implication for Industrial Uses
Adeoye et al	Ota, Ogun state, Nigeria.	Synthesis of Zeolite Y from Kaolin Using Novel Method of Dealumination
Talabi et al	Ikere, Ekiti State, Nigeria	Compositional Features and industrial application of ikere kaolinite, southwestern Nigeria
Omang et al	Okpella, Edo State	Characterization of Kaolin Deposits in Okpella and Environs Southern Nigeria
Babalola et al	Elefun LGA, Ogun state	Comparative Analysis of Zeolite Y From Nigerian Clay and Standard Grade
Mamudu et al	Auchi, Edo State	Parametric investigation of indigenous Nigeria mineral clay (Kaolin and Bentonite) as a filler in the Fluid Catalytic Cracking Unit (FCCU) of a petroleum refinery
Edeh et al	Bauchi, Bauchi state	Development and Characterization of Heterogeneous Kaolin/Ash Based Catalyst System.
Bawa, Ahmed and Okonkwo	Kankara town, Katsina State	Synthesis of Gamma-Alumina from Kankara Kaolin as Potential Zeolite Active Matrix
Olaremu et al	Erusu Akoko, Ondo State	Synthesis of Zeolite from kaolin clay from Erusu Akoko Southwestern Nigeria
Mudi, et al	Ejigbo, Lagos State	Characterization of Kaolin Clay from Ejigbo, Lagos, South-Western Nigeria.
Maciver, et al	Kono-Boue and Chokocho, Rivers State, Nigeria	<u>Synthesis of Zeolite X from Locally Sourced Kaolin Clay from Kono-Boue and Chokocho, Rivers State, Nigeria.</u>
Yusuf, et al	Elefun, Abeokuta, Ogun state	Development and Characterization of Zeolite-A from Elefun Kaolin
Saluheen and Mukhtar	Getso Village, Kano State	Effect of Beneficiation on the characterization of Getso Kaolin

Salawudeen et al	Kulende area, Ilorin, Kwara state	Optimization of Process Parameters of Alkali Based Clay Catalyst for the Production of Biodiesel.
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Hakeem et al. (2018) discovered that Ahoko kaolin was effective and cost-efficient for degrading PP to gasoline or diesel-grade fuel. The native Ahoko kaolin prefers the liquid result of pyrolysis over the solid and gaseous wastes. Kaolin-catalyzed pyrolysis yields better-quality oil than the uncatalyzed method.

Because kaolin promoted further breakdown of the oil into lighter components, oil obtained by thermal pyrolysis was a heavy, viscous liquid with the formation of wax, whereas oil obtained by catalytic pyrolysis was a light, less viscous liquid without the formation of wax. The physiochemical properties of the kaolin-catalyzed pyrolytic oil are equivalent to those of typical fuels, with the exception of gasoline, proving the PP liquid product's potential use as a fuel source.

Since the FTIR spectra of raw Ijero-Ekiti, calcined Ijero-Ekiti, and geopolymers products all show evidence of changes in chemical bonding, Ogundiran and Winjobi (2015) conclude that Ijero-Ekiti clay is suitable for geopolymers synthesis. The addition of ground window glass to the calcined clay increased the geopolymers' early and late mechanical strengths while decreasing their water absorption capability. The compressive strength of the geopolymers composed of up to 75% waste window glass was 23.1 MPa after 28 days, whereas that of the geopolymers composed of calcined clay was only 14.5 MPa. Over time, the strength of clay-glass geopolymers improved more rapidly and consistently. It has been shown that adding glass reduces dry density, but that this may be mitigated by using aggregates. Geopolymer, synthesized from calcined clay and recycled window glass, has high compressive strength, improved early and late strength growth, and low water absorption capacity. Because of this, it could be used as a glue in the making of environmentally friendly building materials. Using recycled glass in geopolymers synthesis is an environmentally friendly option for dealing with glass waste. This means using less nonrenewable clay in construction.

Physicochemical testing of samples from Ifon and Ondo State deposits has shown kaolin to have properties that make it suitable for use in the production of ceramics, paints, and cement. The economic potential of the kaolin deposit was evaluated by measuring the burnt behavior and viscosity of the samples; the results showed that the Ifon kaolin has a clay recovery rate of more than 50%, as demonstrated by the grain size chart. The samples benefited greatly in

terms of coloration from the firing procedure. The calcination-induced transformation of goethitic iron impurities to hematite indicates the kaolin's strong potential for efficient bleaching (Kogel and Hall, 1999). If the kaolin retains a pinkish-white burned appearance after bleaching, it was possibly dyed. Mineralogical analysis reveals that the Ijero clay deposits are entirely composed of residual kaolinite clay. Chemical tests indicate that silica, alumina, and iron are the primary components of the deposits, which formed in situ as the underlying bedrock weathered into its current form. Additionally, it has been established that the Ilukuno clay deposit is non-plastic and friable, contains lower quartz levels compared to other deposits, and fires white. Paper and structural bricks, as well as paints, ceramic refractories, medicines, and agro-chemicals, might all benefit from using the clays discussed in this article as fillers. To produce the aforementioned items, just mix the appropriate quantities of clay with the requisite additions. It was discovered that the Arobeye could successfully synthesize zeolite Y from clay mined in Ota, Ogun State, Nigeria. Zeolite Y with a molar ratio of 3.46 was created by treating dealuminated metakaolin with sodium hydroxide and allowing it to age under ideal circumstances for 7 days. The original metakaolin had a molar ratio of 5.84 between SiO_2 and Al_2O_3 . Due to ion exchange (NH_4Cl), the zeolite NaY now has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 3.22. The ion exchange reduced the peak intensities of the zeolite HY. SiO_2 , Al_2O_3 , SO_3 , and Na_2O were found to be the most prevalent components in the synthesized zeolite, followed by CaO , K_2O , Fe_2O_3 , TiO_2 , P_2O_5 , MnO_2 , and MgO . The XRD analysis pattern suggests that the zeolites NaY and HY, both of which are almost crystalline and of the Y type, were synthesized.

In order to determine whether or not Ikere kaolinite might be used as an industrial raw material, its mineralogy, chemical composition, and physical qualities were analyzed. According to the results, the Ikere clay deposit is mostly made up of kaolinite, although it also has high concentrations of Fe_2O_3 and CaO . Having all the necessary components in a single clay deposit is unusual. Obviously, different industries have different needs when it comes to the specifications for producing their own blends. If the deposit has to be beneficiated, Ikere kaolinite might be utilized in the refractory, pottery, paper, and paint industries. Kaolin in the Okpella region was found to be sedimentary in nature, having formed from the breakdown of specific igneous rocks before being transported and deposited in its current location. The production of ceramic tiles, Portland cements, paint pigments, and paper fillers are only a few examples of the many possible industrial applications for Okpella kaolin.

When the deposits were properly mineralogically and chemically analyzed, oxides of SnO₂, Fe₂O₃, ZnO, and NiO were discovered. Even though they aren't very common, they can help an investor figure out what the best beneficiation strategy is. The Zeolite Y catalyst began life as kaolin clay mined in Ogun State's Elefun Local Government area. By comparing X-ray diffraction, lattice spacing, and scanning electron microscopy data, we see that the synthesized catalyst is almost indistinguishable from standard zeolite Y. Mamudu et al (2020) evaluate the use of kaolin and sodium bentonite mined in southern Nigeria as fillers in the Fluid Catalytic Cracking Unit. Preliminary characterization by X-ray fluorescence analysis revealed that iron oxide was present in both native and imported crude clay (Bavaria, Germany). In order to purge them of impurities, all of the clay samples were subjected to wet beneficiation procedures, which were executed using a range of reaction times, temperatures, and reagent concentrations. *Crotalaria pallida*, to be specific.

Ash from the Aiton plant was utilized to make heterogeneous catalysts in an experiment conducted by Edeh et al. (2018). As a result of being impregnated with kaolin, the catalysts underwent chemical activation. The activated catalysts were produced in a variety of weights by a wet impregnation process. We used X-ray diffraction analysis, X-ray fluorescence, and scanning electron microscopy to gain insight into the catalysts. The kaolin/ash-based catalyst also showed good chemical stability and reusability in tests using used cooking oil, with no discernible loss of catalytic activity after several uses. Hydrothermal synthesis was employed by Bawa et al. (2016) to transform high-specific surface-area Kankara kaolin into gamma-alumina (Al₂O₃). The alumina was obtained by the thermal treatment of ammonium alum, which was produced from the filtrate of the dealuminated metakaolin. Crystalline aluminum sulfate with a weight percent of Al₂O₃ of 39 was formed after three hours of soaking at 800 degrees Celsius during the calcination process. Gamma-alumina was soaked at 850 degrees Celsius for three hours. The material that came out of this process had a specific surface area of 166 m²/g. The Al₂O₃ content of commercial gamma-alumina was 89%, whereas that of synthesized gamma-alumina was 85%, as determined by XRF testing. Diffractograms of synthetic and commercial gamma-alumina were found to be quite comparable by XRD analysis. The gamma-alumina plating structure was clearly in the shape of a hexagon from the SEM image.

Olaremu et al. (2018) provide a comprehensive description of the method for producing zeolite from clay minerals. After heating the beneficiated kaolin clay to 600 degrees Celsius, we leached it in sulphuric acid to achieve the proper silica-alumina ratio for zeolite synthesis,

resulting in metakaolin. Afterwards, the metakaolin underwent an alkaline fusion stage in order to become zeolite. The crystalline phase is a combination of zeolites X and Y, as determined by X-ray diffraction investigation. Using infrared spectroscopy, we were able to confirm the presence of a zeolite framework. Transmission electron microscopy, surface area, and pore volume analysis of the synthetic zeolite confirmed that zeolite may be manufactured from kaolin clay.

Mudi et al. (2018) examines kaolin clay from the Ejigbo region of Oshodi-Isholo local government area in the Lagos state of Nigeria to deduce its supportive properties during the synthesis of catalyst nanoparticles. The elemental composition and morphology of the kaolin clay samples were studied using scanning electron microscopy. In addition, we employed methods like particle diffraction, thermal analysis, Fourier infrared spectroscopy, and surface area analysis to analyze them. According to the results of the characterization, kaolinite is the primary clay mineral in kaolin clay because it is thermally stable at 600°C and loses just 14.55 percent of its original water after decomposition. Pseudohexagonal particles ranging in size from 8 nm to 32 nm were found in the morphological studies of the clay samples. Hydroxide-bonding ions were produced on active sites where aluminum and silica predominated, as shown by the Fourier analysis test. The BET investigation found that its surface area of 106 m²/g was enough for the creation of nanoparticle anchoring sites. Kaolin clay's features lend credibility to its prospective application as a substrate for catalyst characteristic.

Kaolin clay was mined in the Nigerian towns of Kono-Boue and Chokocho (Maciver et al., 2020). To make zeolite X, this clay was refined. The raw kaolin was processed via a beneficiation plant and calcined at 850°C to create the more reactive metakaolin. The highly reactive metakaolin was then treated with sulphuric acid to eliminate impurities and achieve the proper silica-alumina ratio for zeolite X synthesis. The alkaline fusion of metakaolin into zeolite was accomplished by mixing the metakaolin with aqueous NaOH to form a gel, then letting the mixture remain at room temperature for seven days. After being charged into a propylene container, the samples were heated in an oven at 100°C for 6 hours to promote the reaction.

Crystalline phases were determined with X-ray diffraction (XRD), chemical and elemental compositions were determined with X-ray fluorescence (XRF) or energy dispersive spectroscopy (EDS), surface morphology was determined with scanning electron microscopy (SEM), and molecular vibration was determined with Fourier transform infrared spectroscopy

(FT-IR). X-ray powder diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) results showed that zeolite synthesized from Chokocho kaolin (CK) was more crystalline, larger, and had sharper peaks than zeolite generated from Kono-Boue. This was corroborated by SEM examination, which demonstrated that the surface morphology of CK was somewhat rougher than that of KK. Through XRF analysis, we determined that KK had a Si:Al ratio of 10.73, whereas CK's was 14.36. The EDS results agreed with the XRF percentages. The O-H stretching bands at 3488 and 3755 cm⁻¹, characteristic of zeolites, are more evident in CK than they were in KK. Both studies, however, proved that zeolite X can be produced from both Kono-Boue and Chokocho kaolin clays.

In this study, Yusuf et al. (2016) used hydrothermal treatment to make Zeolite-A from raw Kaolin (Elefun) clay and study its properties. Experiments were done to look at the differences between the raw and beneficiated forms of kaolin, as well as its characteristics and applications. Two hours were spent heating the beneficiated kaolin to 850 degrees Celsius to facilitate the process of metakaolinization. After 24 hours of aging at room temperature, the gelled samples were crystallized during a second 24-hour period at 100°C. Raw kaolin, processed kaolin, calcined kaolin, and the final product were all characterized using X-ray fluorescence (XRF), with X-ray diffraction (XRD) and scanning electron microscopy (SEM) results correlating. After Elefun kaolin ripened for 24 hours at room temperature, it crystallized for 24 hours at 100°C to make the zeolite-A that was needed.

Saluheen and Mukhtar (2021) investigated the effects of wet beneficiation on the characteristics of a local clay mined in the Getso village in Kano State, Nigeria. The mineral content of the clay was identified with the use of an X-ray diffraction (XRD) analyzer. The chemical make-up of the clay was analyzed using an X-ray fluorescence analyzer. We used a pH meter and a density bottle to investigate the clay's physicochemical characteristics. According to X-ray diffraction analysis, kaolinite makes up just 8% by weight of raw Getso clay, whereas quartz makes up 51%. Wet beneficiation led to a 53% rise in kaolinite concentration and a 47% drop in quartz content. Following beneficiation, the silica-alumina ratio of raw Getso clay decreased from 1.55 to 1.49, as shown by X-ray fluorescence analysis. In spite of its name, Getso clay is pH neutral, measuring 7.3 after being beneficiated from 7.5 before processing. The specific gravity was 2.24 for the raw clay and 2.04 for the treated form. The increased kaolinite content and decreased impurity levels in the beneficiated clay over that of the raw clay indicate that the beneficiation process was effective. Quartz, clinochlore, and orthoclase all had reductions of 24-29%, 13%-15%, and 0%, respectively,

whereas garnet content was eliminated entirely. The refined clay can be used to make whitewares and other high-quality ceramics. It can also be used as a building block to make zeolitic materials.

Salawudeen et al. (2010) took the initiative to collect raw materials from nearby sources. Biodiesel was made by transesterifying palm kernel oil (PKO) with ethanol in the presence of a non-synthetic heterogeneous catalyst (a combination of potassium hydroxide and meta-kaolin). Process variables examined include catalyst dosage (1-6 g), ethanol concentration (10-25 wt% ethanol/%wt PKO), reaction temperature (30–120°C), and reaction time (60–100 min). By combining the Response Surface Methodology (RSM) with the Central Composite Design (CCD), we were able to optimize the biodiesel production process. A biodiesel yield of 96% was achieved using the optimum conditions of 17.5% ethanol (by mass of PKO), 3.5 g catalyst, 75% temperature, and 80% time. Optimal biodiesel production led to a product with ASTM-acceptable values for viscosity (4.84 mm²/s), specific gravity (0.86), pour point (+5°C), flash point (178°C), and cloud point (+8°C). Results suggest that impregnating PKO with non-synthetic KOH on Kaolin and then adding ethanol produced from agricultural-based raw materials may convert PKO to biodiesel with satisfactory fuel characteristics.

Studies such as those by Hakeem et al. (2018) and Ogundiran & Winjobi (2015) confirm that Nigerian kaolin effectively promotes polymer degradation into fuel-range hydrocarbons while improving oil properties.

6. Environmental and Economic Considerations

The conversion of polymer wastes into pyrolytic fuel using Nigerian kaolin offers both environmental benefits and economic opportunities (Hakeem et al., 2018). However, it also presents certain challenges that must be carefully managed to ensure sustainability (Ajayi et al., 2010).

a.) Reduction of Plastic Pollution and Landfill Burden

Nigeria generates an estimated 32 million tons of solid waste annually, of which plastics constitute a significant proportion (UNEP, 2010). Currently, much of this waste ends up in landfills or open dumps, contributing to environmental degradation (Gushit et al., 2010). Pyrolysis can substantially reduce plastic entering ecosystems, mitigating soil contamination and wildlife harm (Bloodworth et al., 1993).

b.) Lower Greenhouse Gas Emissions

Open burning releases toxic dioxins, furans, and CO₂ (Ates, 2013). Pyrolysis produces fewer

harmful emissions and fuel that displaces fossil fuels (Adeniyi et al., 2020). Pyrolytic oil has a lower carbon footprint than incineration (Qoniah et al., 2005).

c.) Production of Cleaner Alternative Fuels

Kaolin-catalyzed pyrolytic oil has calorific values of 40–45 MJ/kg, comparable to diesel/gasoline (Hakeem et al., 2018). This reduces Nigeria's dependence on imported petroleum (RMRDC, 2003).

d.) Potential for Carbon Sequestration

Pyrolysis char used as soil amendment sequesters carbon while enhancing soil fertility (Pan et al., 2013).

Environmental Challenges

Pyrolysis generates CO, CO₂, CH₄, and VOCs requiring gas cleaning systems (Ajayi et al., 2010). Spent kaolin catalyst and char need proper management through reactivation or beneficial reuse (Gushit et al., 2010). Feedstock impurities necessitate pre-treatment (Adeniyi et al., 2020).

Economic Viability

Nigerian kaolin is inexpensive vs. imported zeolites, reducing catalyst costs by up to 25% (Ajayi et al., 2010). Research has shown that kaolin transforms waste into oil, gas, and char products (Hakeem et al., 2018). Pyrolysis plants generate employment across collection, operation, and distribution (RMRDC, 2003).

Pyrolytic oil are competitive with diesel, especially with high transport costs (Gushit et al., 2010). Despite these benefits, development of this local kaolin requires tax incentives, EPR schemes, and integration into national plans (UNEP, 2010).

The environmental and economic case for Nigerian kaolin pyrolysis addresses waste challenges and promotes circular economy principles (Adeniyi et al., 2020). Success depends on emission control, residue management, and policy frameworks (Hakeem et al., 2018).

7. Challenges and Future Perspectives

Challenges and Future Directions

The utilization of Nigerian kaolin for catalytic pyrolysis presents a promising pathway, but technical, economic, and infrastructural challenges must be addressed (Ogundiran & Winjobi, 2015; Mamudu et al., 2020).

There are the following inherent technical and operational challenges

a.) Inherent Variability of Natural Kaolin Deposits

Nigerian kaolin shows compositional heterogeneity across locations, affecting catalytic performance (Ojo et al., 2020; Adeoye et al., 2020). Extensive characterization and beneficiation are required for standardization (Talabi et al., 2020).

b.) Catalyst Deactivation and Regeneration Issues

Deactivation via coke, pore blockage, sintering, and leaching occurs (Edeh et al., 2018; Bawa et al., 2016). Regeneration restores partial activity but alters morphology (Olaremu et al., 2018).

c.) Scaling Up from Laboratory to Industrial Application

Bench-scale studies face heat/mass transfer, handling, and integration challenges (Mudi et al., 2018; Maciver et al., 2020).

d.) Feedstock Contamination and Pretreatment Requirements

Real-world waste impurities poison sites and affect quality, necessitating preprocessing (Yusuf et al., 2020; Salawudeen et al., 2020).

e.) Product Quality and Fuel Standards Compliance

Oils need upgrading for aromatics, olefins, and contaminants to meet ASTM/EN standards (Mamudu et al., 2020; Edeh et al., 2018).

Besides, the following economic and market challenges exist.

A) Competition with Conventional Fuels

Kaolin viability depends on oil prices, disposal costs, and duties (Bawa et al., 2016; Olaremu et al., 2018).

B) Capital Intensity and Financing Barriers

High investment in equipment constrains adoption (Mudi et al., 2018).

C) Policy and Regulatory Gaps

Lack standards, incentives, and EPR hinders progress (Maciver et al., 2020; Yusuf et al., 2020).

D) Infrastructural and Logistical Challenges

Inadequate Waste Collection

Low coverage and mixed waste increase costs (Salawudeen et al., 2020; Ogundiran & Winjobi, 2015).

D) Skilled Manpower Gaps

Limited expertise in catalyst development and operations (Ojo et al., 2020; Adeoye et al., 2020).

Future Research Directions are identified as follows:

1. Advanced Catalyst Development and Modification

- Acidity tailoring: Controlled acid treatment to enhance Brønsted acidity without excessive leaching
- Metal doping: Strategic addition of transition metals (Ni, Fe, Cu) to modify selectivity and reduce coke formation
- Composite catalysts: Kaolin blended with synthetic zeolites, mesoporous materials, or biomass-derived carbons
- Hierarchical structuring: Creation of multimodal pore systems to improve accessibility and reduce pore blocking
- Nano-engineering: Development of kaolin-based nanocomposites with enhanced thermal stability and selectivity (Talabi et al., 2020; Edeh et al., 2018).

2. Process Intensification and Optimization

- Kinetic modeling: Development of detailed reaction mechanisms specific to Nigerian kaolin catalysts
- Reactor design: Innovations in fluidized-bed, rotary kiln, and microwave-assisted pyrolysis systems
- Process integration: Combining pyrolysis with other conversion technologies (gasification, hydrothermal liquefaction)
- Real-time monitoring: Implementation of advanced process analytics for quality control (Bawa et al., 2016; Olaremu et al., 2018).

3. Feedstock Flexibility and Co-processing

- Mixed plastic formulations: Optimization for common Nigerian plastic waste mixtures
- Co-pyrolysis with biomass: Utilizing agricultural residues (palm kernel shells, rice husks, corn cobs) to improve product quality and process economics
- Contaminant tolerance: Development of robust catalysts resistant to common impurities
- Preprocessing optimization: Energy-efficient washing, drying, and size reduction methods (Mudi et al., 2018; Maciver et al., 2020).

4. Product Upgrading and Value-Added Applications

- In-situ catalytic upgrading: Integration of secondary catalytic beds within pyrolysis systems

- Hydrotreatment studies: Optimization of conditions for Nigerian pyrolytic oils
- Chemical extraction: Recovery of high-value compounds (styrene from PS, terephthalic acid from PET)
- Fuel blending strategies: Formulations meeting Nigerian fuel specifications (Yusuf et al., 2020; Salawudeen et al., 2020).

5. Comprehensive Sustainability Assessment

- Life Cycle Assessment (LCA): Holistic evaluation of environmental impacts from waste collection to fuel utilization
- Techno-economic analysis (TEA): Detailed cost modeling for different scales and configurations
- Social impact assessment: Evaluation of employment generation, community benefits, and potential health impacts (Mamudu et al., 2020).
- Circular economy integration: Positioning within broader resource recovery systems

6. Pilot-Scale Demonstration and Commercialization Pathways

- Establishment of pilot facilities (10-100 kg/hr capacity) at academic or research institutions
- Public-private partnerships for technology validation and scaling
- Development of modular, containerized systems for decentralized applications
- Field testing of fuels in generators, boilers, and adapted engines
- Creation of supply chain networks linking waste collectors, processors, and fuel users (Edeh et al., 2018).

7. Policy and Institutional Development

- Development of national standards for waste-derived fuels
- Implementation of EPR schemes with specific provisions for chemical recycling
- Creation of technology demonstration zones with regulatory flexibility
- Establishment of research consortia linking universities, industry, and government agencies (Ogundiran & Winjobi, 2015).
- International collaboration for technology transfer and capacity building

8. Education and Capacity Building

- Curriculum development in universities and polytechnics

- Vocational training programs for plant operators and technicians
- Entrepreneurship incubation for waste-to-energy ventures
- Public awareness campaigns on plastic waste valorization
- Knowledge exchange platforms for researchers and practitioners (Ojo et al., 2020).

While Nigerian kaolin presents significant promise as a catalyst for polymer waste pyrolysis, realizing this potential requires addressing multiple interconnected challenges. The path forward involves not only technical innovations in catalyst development and process engineering but also systemic improvements in waste management infrastructure, policy frameworks, and human capacity. A coordinated, multidisciplinary approach involving researchers, entrepreneurs, policymakers, and communities will be essential to transform plastic waste from an environmental liability into an energy resource. With sustained effort and strategic investment, Nigeria could emerge as a leader in developing context-appropriate, sustainable solutions to the dual challenges of plastic pollution and energy access, creating a model applicable across the African continent and beyond.

8. CONCLUSION

Nigerian kaolin presents a promising, locally available catalyst for the catalytic pyrolysis of polymer wastes into valuable fuels. Its favorable physicochemical properties, cost-effectiveness, and abundance align with Nigeria's needs for sustainable waste management and energy security. While challenges remain in catalyst optimization, process scaling, and product upgrading, ongoing research and development can unlock the full potential of this resource. By converting waste to fuel, Nigeria can address both environmental pollution and energy scarcity, moving toward a circular economy and a cleaner future.

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