

Catalytic pyrolysis of mixed plastic wastes using commercial grade kaolin and Ukpor clay from Nigeria

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Abstract

The aim of this study is to convert mixed plastic waste into usable liquid fuel via pyrolysis technique using Ukpor clay as a low-cost catalyst and commercial grade kaolin. Waste plastic was catalytically degraded in a laboratory scale pyrolysis semi-batch reactor at a temperature of 400 °C, residence time of 45 min, and heating rate of 16 °C/min. The catalysts were characterized by XRF analysis while proximate analysis of the plastic feed carried out gave volatile materials content of 95.17 wt%, fixed carbon of 1.51 wt% and ash content of 2.6 wt%. Ukpor clay and kaolin were employed as catalysts in catalytic pyrolysis of the same feedstock for catalyst-to-plastic ratio of 1:1, 1:2, 1:3, and 1:4 and at the same operating parameters. Optimum yields were obtained at a catalyst-to-plastic ratio of 1:3 for both catalysts with a yield of 85.80, 3.58, and 10.62 wt% for Ukpor clay and 89.80, 6.33, and 3.87 wt% for kaolin for the liquid, gaseous, and solid products, respectively. The liquid products obtained for the catalytic cracking at optimum conditions were characterized for their suitability as fuel. The properties determined were density, viscosity, flash point, pour point, and calorific value. The results suggest that both catalysts produced liquid products, whose properties are comparable to conventional fuels (gasoline and diesel oil) with kaolin catalytic pyrolysis process producing higher liquid yield. GC-MS analysis found that most of the liquid oil produced a high aromatic content with some aliphatic and other hydrocarbon compounds, FTIR analysis of the liquid product from catalytic pyrolysis also shows that it contains hydrocarbons with different functional groups such as aromatics, olefins, carbonyl, amines, sulphides, and hydroxyl.

Keywords: Catalytic pyrolysis; Ukpor clay; Pyrolytic oil; Kaolin; Plastic waste

1. Introduction

Plastics are high molecular weight organic substances or polymers and have a variety of uses recently. According to Raja and Murali (2011), global breakthroughs in science and technology have altered patterns of material consumption, energy demand, and energy use; as a result, traditional materials like metal and steel are increasingly being replaced by plastics. Over the past century, the use and use of plastic has expanded from 10 million tons annually to over 50 billion tons in 2013. According to Thahir et al. (2019), more than 70% of these enormous plastics have a single usage or application before ending up in the waste stream as plastic debris. Researchers are looking for strategies to turn these waste plastics into high-quality oils that could replace fossil fuels due to the depletion of oil resources and rise in energy demand (Kalargaris et al., 2017). Waste plastics are one of the most promising sources for fuel production, according to Syamsiro and Mufrodi (2020), due to their high heat of combustion and growing availability in local communities. Plastics do not absorb much moisture, in contrast to paper and wood, and their water content is significantly lower than that of biomass, such as crops and food scraps (Miandad et al., 2019). Types of plastic affect how waste plastics are converted into fuel. Additionally, choosing the right technology in accordance with the local economy, environmental, social, and technical requirements is necessary for an effective conversion.

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Thermal treatments are among the most widely utilized procedures for treating the millions of plastic wastes produced each year and converting them into energy products, according to Mumbach et al. (2019). Three different sorts of this approach include incineration, gasification, and pyrolysis. The goods produced by digesting plastic trash include biogas, oil, wax, and char that can be utilized as a solid fuel as well as thermal energy for heating systems in the winter (De Weerd et al., 2020). Pyrolysis oil product offers a higher calorific value and superior economic performance when compared to all of these energy products. In addition, even though chemical and mechanical treatments have a high yield and strong economic performance, the products are thought to be the most realistic technique (Dunkle et al., 2021). As a result, numerous writers have researched the pyrolysis-based valorization of plastic waste. Their research centered on determining the ideal parameters that would result in the highest oil output possible, and the conditions discovered were the pyrolysis temperature, pyrolysis time, heating rate, and nitrogen flow rate. Additionally, it was discovered that each form of plastic waste requires a separate set of pyrolysis conditions due to its varied composition. The two primary forms of plastic trash that can be pyrolyzed are pure plastic waste and metallized plastic waste (Rodríguez-Luna et al., 2021). Polymeric waste made out of only pure plastic garbage is polymeric waste that solely contains layers comprised of bags, containers, or other polymer components (such as mechanical parts, spines, etc.). During the pyrolysis process, this type of waste can break down into oil and a trace quantity of char. The second type, known as "metallized plastic waste," is made up of single or multiple polymeric layers that have been coated or bonded with a metal layer and have a significant negative environmental impact. While this category, which includes MFPW, contains a high amount of volatile matter (up to 99.5 weight percent), it is regarded as the most complex component of plastic trash and has a low recycling rate.

Currently, plastic trash poses a threat to the global economy, as well as to people, animals, and the environment. This is particularly true for emerging and underdeveloped nations, which lack sophisticated recycling facilities and lax laws governing the creation, use, and control of plastics (Srivastav et al., 2015). Plastic may contain some, if not all, of the following additives, including plasticizers, fire retardants, antioxidants, light stabilizers, lubricants, pigments, antistatic agents, and thermal stabilizers, depending on its kind, application, and service condition. Research has demonstrated that many of these additives enter the systems of humans and animals and have the potential to imitate, block, or interfere with hormones in the body's endocrine system. As a result, they are categorized as endocrine disrupting chemicals (EDCs), according to Schuga et al. (2011). Moreover, a significant portion have been categorized as persistent organic pollutants (POPs), also referred to as "forever chemicals". They are organic substances that can't be destroyed by chemical, biological, or photolytic processes in the environment.

Plastic trash is a significant issue for many nations worldwide. Plastic is produced in large quantities and is durable, which has caused a surge in non-biodegradable plastic garbage that is polluting the environment and harming people and wildlife. Additionally, the beauty of our surroundings—which are also aquatic life's habitats—are diminished by plastic garbage. Therefore, it is essential to recycle plastic trash into usable goods, which would then offer a long-term solution to the issue. Global plastic output has substantially expanded over time, and if the trend continues, it is predicted that by 2050, there will be more plastic debris in the ocean than fish. Negative effects of plastic trash on the environment and human health are occurring. The main problem with plastic waste is that it is not biodegradable, which means that it slowly fractures into tiny bits known as microplastics (Jiang et al., 2019). The accumulation of these microscopic particles in water bodies puts aquatic life in danger. Marine animals become entangled in plastic garbage, which prevents them from moving and foraging, finally causing their demise. Additionally, as plastic breaks down into tiny pieces, it releases hazardous compounds that could harm both people and wildlife.

Plastic garbage has accumulated in landfills and oceans as a result of the high manufacturing rate of plastic products and their low recycling rate. Plastic garbage creates a problem for human health and the environment since it is hazardous to dispose of and releases dangerous compounds into the environment. Furthermore, plastic garbage clogs drainage systems, causing flooding during the rainy season and severe effects on infrastructure in addition to property damage.

Plastic garbage has harmful environmental effects when it is dumped in landfills or the ocean. The development of technology aimed at recycling waste plastic into valuable items has taken center stage in recent years. Devy et al. (2016) claim that destructive thermal treatment, such as controlled combustion or pyrolysis, is the only approach to completely get rid of plastic waste. A technique used to turn plastic waste into energy in the form of solid, liquid, and gaseous fuels is pyrolysis of plastic wastes. This method uses a comprehensive close-loop approach. According to Miandad and Barakat (2016), it is the thermal breakdown of plastic at various temperatures (300-900 °C), without oxygen, that yields liquid and gaseous fuel. Pyrolysis appears to be a suitable method of recovery, In contrast to mechanical recycling, pyrolysis appears to be a suitable method for recovering materials and energy from waste plastic without component separation, selectivity of plastic type (thermoplastic or thermosetting), or sorting into different plastic types (Eze et al., 2021). This is assuming a successful method for reducing toxic compounds is used. The yield of liquid fuel has been

shown to increase both quantitatively and qualitatively when catalysts are used in the pyrolysis of plastics (Dimitris and Achilias, 2014). By lowering the reaction temperature or length of time, adding catalysts eliminates the drawbacks of thermal pyrolysis. Catalyst addition increases conversion, lowers pyrolysis activation energy, and improves fuel quality. Zeolites, polyciliate components, and clays are the most often utilized catalysts for the pyrolysis of plastics. The catalytic process has several advantages over thermal pyrolysis, including a lower process temperature, a decrease in solid residues such carbonized char and volatile fraction, a shorter processing time, good product selectivity, and high-octane-number products. The best alternative for pyrolyzing plastic waste and co-pyrolyzing mixed plastic waste/biomass is zeolite-based catalysts. The rate of global plastic manufacturing vastly outpaces recycling rates, which have been continuously rising over the past 30 years. As a result, an increasing amount of plastic is ending up in landfills, dump sites, and ultimately the environment, where it harms the ecosystem. In order to complement present recycling efforts and reverse the tide of plastic waste, better end-of-life choices for plastic trash are required. Plastic pyrolysis, a chemical process that reduces plastics to their component parts, is a promising developing technology. In recent years, synthetic catalysts for catalytic pyrolysis have included zeolites, silica alumina, zinc oxides, calcined dolomite, and synthetic fly ash. The use of locally obtained catalyst is advocated because these synthetic catalysts are not widely available and have a high production cost, making catalytic cracking rather expensive.

It is impossible to overestimate the significance of catalytic pyrolysis of plastic trash in the modern world. The energy needed to break down the waste polymers is significantly decreased via catalytic pyrolysis compared to thermal pyrolysis, and the process's time and temperature requirements are also significantly reduced. According to Anene et al. (2018), catalytic pyrolysis may increase product yield or cause other favorable reactions to enhance the product's quality.

Additionally, a less rodent-infested and microbially active environment is achieved, along with a cleaner environment devoid of plastic trash. By creating jobs and bringing in money for the public and private sectors, this effort fosters economic growth and advances environmental sustainability. It also offers a path toward a circular economy. Additionally, it would add to the fuel supply, lessening or halting the nation's lack or scarcity of petroleum products.

For the conversion of plastic waste into liquid oil and char, microporous and mesoporous catalysts have been used, according to several research. Gaca et al. (2008) used modified MCM-41 and HZSM-5 to pyrolyze plastic waste, and they found that using HZSM5 resulted in lighter hydrocarbons (C3-C4) with the most aromatic chemicals. According to Lin et al. (2004), who employed a variety of catalysts, combining HZSM-5 with mesoporous SiO₂-Al₂O₃ or MCM-41 produced the most liquid oil with the least amount of gas. According to Aguado et al. (1997), the catalytic pyrolysis of PE with HZSM-5 resulted in the synthesis of aromatic and aliphatic compounds; however, the introduction of mesoporous MCM-41 reduced the amount of aromatic compounds produced due to its weak acid catalytic activity. The whole pyrolysis process was improved by the employment of synthetic catalysts, which also increased the quality of the liquid oil that was generated. However, the price of the pyrolysis process increased with the inclusion of synthetic catalysts.

This study aims to confirm Ukpore clay's potential as a catalyst for the pyrolysis of mixed waste plastic into useful fuel because no prior attempt has been made to investigate it. The cost of catalytic pyrolysis from the use of commercial-grade catalysts will be greatly reduced by using kaolin from Ukpore clay. Ukpore clay is a naturally occurring substance that has been shown to have a high mesoporous surface area, excellent acidic characteristics, and a large pore volume. It has also been reported by Nnaneme et al., 2020, to include Si/Al in a ratio that is extremely similar to that of zeolites. These characteristics make it a superior substance for catalytic pyrolysis.

2. Material and methods

2.1. Materials

Clay samples and mixed waste plastics from trash cans were collected from Awka and Ukpore in Anambra State, Nigeria, respectively. While phosphoric acids and commercial grade kaolin were purchased from Springboard Scientific Laboratory and a market in Awka, Anambra. All chemicals are of analytical grade.

2.2. Methods

The plastic wastes were cleaned, dried, and shred into little pieces after being sorted. A sample of the feedstock was subjected to proximate analysis. X-ray fluorescence (XRF) was used to analyze ukpore clay and commercial grade kaolin. A laboratory-scale semi-batch reactor for pyrolysis was used, together with an electric heater, condenser, pump, and collecting bottle. The reactor's circular bottle has two necks and is made of glass that can endure extreme temperatures.

The second inlet is utilized for the exit of the gas product that leaves the reactor and goes to the condenser, while the first neck is used as the input for the plastic waste. Cool water is utilized in the condenser, a shell and tube heat exchanger, to condense the generated gases.

2.3. Preparation and characterization of catalyst

Commercially bought kaolin and locally sourced clay (Ukpor clay) were used as catalyst. Grinding of the catalyst was done to have fine sized particles. The catalyst was then activated with the use of acid (Acid activation).



Figure 1 Sample of Catalysts used

2.4. Acid activation of Ukpor clay and Kaolin

The surface acidity, porosity and high specific surface area of the catalyst play an important role in producing liquid products instead of gas products. The 1000 g of Ukpor clay catalyst was soaked in 4 litres of 95 % distilled water and 1 litre of 5 % 0.1 M solution of Phosphoric Acid. The mixture was heated for 6 hours at a temperature of 95 °C. The sample was then washed with de-ionized water until a normal pH was obtained. The same procedure was followed in the activation of kaolin.

2.5. Catalytic pyrolysis of the plastic waste

50 g each of mixed plastic waste and Ukpor clay catalyst were inserted into the semi-batch reactor and mixed at the beginning of the first run. The catalytic pyrolysis was carried out at a temperature of 400 °C with a heating rate of 16 °C/min and pressure maintained at 1 atm. The vapour arising from the pyrolysis was condensed to liquid, collected and weighed. The process lasted for 45 minutes. The reactor was allowed to cool and solid residue left inside the reactor removed and weighed. Material balance of the system was done to calculate the gaseous product. Each run was repeated for thrice times and the average value evaluated. The procedure was also repeated for plastic waste/catalyst ratio of 1:2 (50 g of plastic waste and 100 g of Ukpor clay catalyst), 1:3 (50 g of plastic waste and 150 g of Ukpor clay catalyst) and 1:4 (50 g of plastic waste and 200 g of Ukpor clay catalyst) respectively. Furthermore, the entire process was repeated using kaolin as catalyst.

2.6. Characterization of the liquid fuel

After the acid activation, Ukpor Clay and commercially purchased kaolin were analyzed using X-ray fluorescence (XRF). The fuel qualities of the resultant pyrolysis oils were evaluated using the accepted techniques, such as bomb calorimetry, ASTM D1298 for density, and ASTM D445, for kinematic viscosity at 20 °C. By using Fourier Transform Infrared spectroscopy (IRTracer-100), the functional groups of the oil were identified. The method of FTIR applied was Transmission /wavenumber at 30 sample scans and 16 background scans. The range was 4000-650 and resolution of 8. The Gas Chromatography Mass Spectrometry was used to examine the liquid fraction.

3. Results and discussion

3.1. Proximate analysis of waste plastic feed

Table 1 shows the findings of the proximate analysis of pyrolytic oil from plastic trash. The amount of material that can be thermally broken down in a given substance is known as its volatile content. This gauges how much material can be extracted after cracking (Sharma et al., 2014). High volatile content in a substance denotes high energy and matter recovery. The plastic feedstock has a sufficient amount of volatile material (95.17 %). This result indicates that high amount of products can be obtained upon thermal cracking.

Table 1 Proximate analysis of waste plastics

Composition	Amount (wt%)
Moisture content	0.72
Volatile matter	95.17
Ash content	2.60
Fixed carbon	1.51

3.2. X-ray fluorescence (XRF) analysis of kaolin and Ukpor clay catalysts

From the result obtained, the compounds and elements present indicate the catalyst samples are more kaolinite clay. XRF analysis of the Ukpor clay after acid activation revealed the presence of SiO₂ (52.151 %), Al₂O₃ (30.808 %), Fe₂O₃ (3.169 %), Pb₂O₃ (8.109 %), CaO (0.150 %), K₂O (0.214 %), TiO₂ (3.781 %). The result indicated that the major compounds present in kaolin and Ukpor clay are alumina (Al₂O₃) and silica (SiO₂), and this is expected, because the major constituents of sand for which clay is a type are silica and alumina. Variation in the ratio of silica to alumina is the basis for different types of clay (Panda et al., 2010). The presence of other metal oxides is as a result of special properties of kaolin which gave it wide acceptance as a catalyst. The silica/alumina ratio (SiO₂/Al₂O₃) for Ukpor clay is 1.7 while that of Kaolin is 3.2. Eman and Mustapha, (2018) characterized commercial kaolin Procured from Alara mining Corporation, and reported 55 % SiO₂, 29 % Al₂O₃, 2.49 % Fe₂O₃, 0.2 % MgO, 0.80 % CaO, 0.79 % K₂O, and 10.2 % LOI at 1000 °C. Most of the values reported are in close range to the one obtained in this study.

3.3. Effect of the catalyst on product yield

The product yield for both Catalyst used in the pyrolysis process are presented in figure (2) and tables (2 and 3). From the table it can be seen that the liquid oil yield increased with increase in catalyst-to-plastic ratio up to 1:3 for both catalysts and decreased at a ratio of 1:4. The solid residue decreased with increase in catalyst-to-plastic ratio, before a sudden increase at 1:3 catalyst-to-plastic ratio was recorded for the Ukpor clay but at 1:4 ratio for kaolin. The gaseous product also decreased with increase in catalyst-to-plastic ratio for both catalysts. The highest product yield was obtained at a catalyst-to-plastic ratio of 1:3 with liquid oil yield of 85.80 wt% for Ukpor clay and 89.80 wt% for the kaolin, gaseous yield of 3.58 wt% for Ukpor clay and 6.33 wt% for kaolin, and solid residue of 10.62 wt% for Ukpor clay and 3.87 wt% for kaolin. This increase in liquid yield during catalytic cracking is a substantial improvement over thermal cracking due to the catalytic nature of kaolin and Ukpor clay which aided the cracking process. The behaviour in the cracking process in the presence of kaolin and Ukpor clay as a catalysts can be explained by its mesoporous surface area, acidity, and high Si/Al ratio which facilitated the cracking reaction. The yield of the liquid oil products increased from 68.60 wt% to 85.80 wt% for Ukpor clay and 73.64 wt% to 89.80 wt% for kaolin when catalyst-to-plastic ratio was increased from 1:1 to 1:3. Thus, an increment of about 17 wt% and 16 wt% in oil yield for Ukpor clay and kaolin respectively was observed for an increment in catalyst-to-plastic ratio of 1:3. However, further increase in catalyst-to-plastic ratio to 1:4 led to a decrease in the oil yield. This behaviour might be due to the high plastic-to-catalyst ratio as the catalyst effect is no longer significant for the process, thus decreasing the yield of liquid product and increasing the gas and char yields. The presence of catalyst in the ratio 1:3 is significant for the optimum product yield for both catalysts. Kaolin gave a higher yield than Ukpor clay showing that it is a better catalyst for the catalytic pyrolysis of mixed plastics. Nevertheless, Ukpor clay proved effective in catalyzing the process. Furthermore, from figure 3 and Table 2, it can be observed that the char yield showed an interesting pattern with slight decrease between ratio 1:1 and 1:2 (from 9.4 to 9.21 wt%); however, beyond this ratio up to ratio 1:3, abrupt increase was observed (from 9.21 to 10.62 wt%). Also beyond the optimum ratio, the char yield experienced a gradual decrease (from 10.62 to 8.05 wt%) and a drop in the liquid product which is indicative of a reduction in catalyst activity. Gaseous products yield decreased steadily throughout the process, a sudden increase then occurs after the optimum catalyst-to-plastic ratio (1:3).

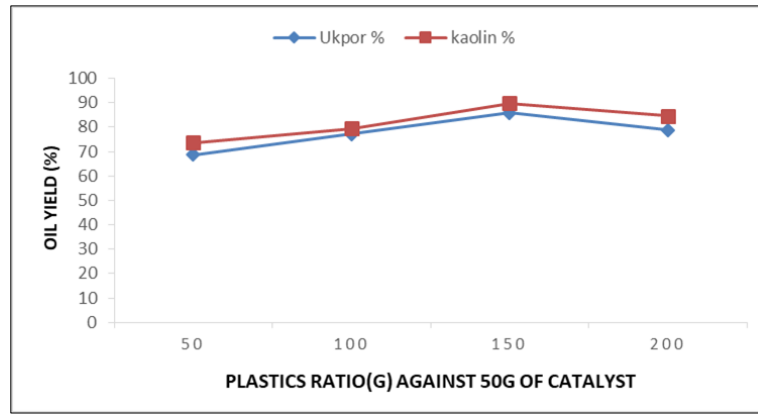


Figure 2 Oil Yield versus Catalyst – Plastic Ratio

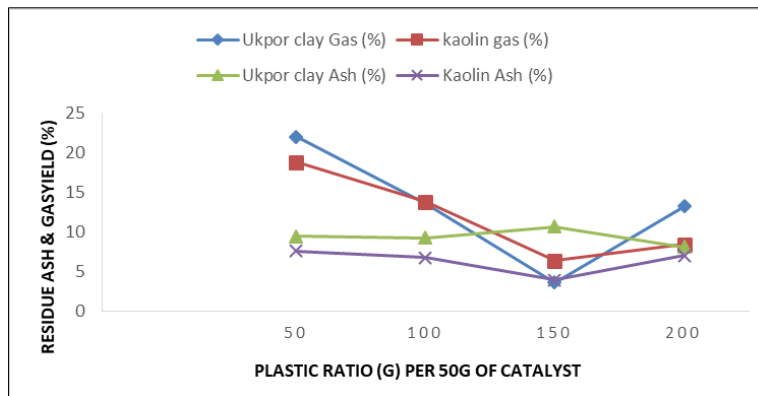


Figure 3 Gas Yield and Residue Ash % versus Catalyst-Plastic ratio

Table 2 Yield for Catalytic pyrolysis at Different Plastic to catalyst ratio using Ukpore clay

Plastic: catalyst ratio	Liquid oil yield (%)	Solid yield (%)	Gas yield (%)
1:1	68.60	9.40	22.00
1:2	77.16	9.21	13.63
1:3	85.80	10.62	3.58
1:4	78.75	8.05	13.20

Table 3 Yield for Catalytic pyrolysis at Different Plastic to catalyst ratio using Kaolin

Plastic: catalyst ratio	Liquid oil yield (%)	Solid yield (%)	Gas yield (%)
1:1	73.64	7.54	18.82
1:2	79.47	6.72	13.81
1:3	89.80	3.87	6.33
1:4	84.62	6.99	8.39

3.4. Determination of physio-chemical properties of the liquid fuel

The physio-chemical properties of the liquid oil products obtained from the catalytic pyrolysis at optimum conditions are determined and are shown in Tables (4 and 5). The liquid fuels obtained from kaolin and Ukpore clay catalyzed process at optimum conditions of catalyst-to-plastic ratio of 1:3, temperature of 400 °C and 45 min were characterized to determine their suitability for use as fuel. The liquid products gotten from catalytic pyrolysis are highly volatile and pale yellow in colour. The results prove that the use of catalyst in pyrolysis of plastic helps to improve quality and increase yield and the catalyst-plastic ratio of 1:3 produced a higher volume of liquid fuel. Similar oil colour (brownish yellow) was observed by Sonawane et al., (2015) when 10 % NZ catalyst was used in the pyrolysis of polypropylene. Density is the weight occupied by a substance per unit volume; it is a property which determines the injection and ignition quality of a fuel (Bilal et al., 2013). The density of the optimum product yield of the kaolin catalytic cracking process is 0.784 g/Cm³ and that of Ukpore clay is 0.797 g/Cm³. Thus, the density of the liquid product from kaolin catalytic cracking process is lower than that of the Ukpore clay. On comparing with gasoline with a reported density range of 0.72–0.78 g/ml and diesel oil with density range of 0.82–0.90 g/ml, the catalytic liquid product density is between the reported density ranges of gasoline and diesel. The two liquid product densities from these studies indicate that there are more breaking of the plastic C–C covalent bonds to a remarkable extent during the kaolin catalytic cracking than during Ukpore clay catalytic cracking. The density of the catalytic pyrolytic liquid obtained is in consonance with that of other pyrolytic oils, 0.875 g/cm³ and 0.778 g/ml, as reported by Budsareechai et al., (2019) and Panda et al., (2013) respectively. The very little variations could be as a result of differences in pyrolysis condition, catalyst used, polymeric material and method of evaluation. The density of the liquid product obtained from kaolin catalyzed pyrolysis in this study suggests that it can be suitable for use as fuel.

Viscosity is an important property which measures the resistance of fluid flow which is related directly to pressure, temperature, and film formation (Gao, 2010). Viscosity is the most crucial property of any lubricating oil or fuel oil which signifies how well a fuel will flow in automobile engines (Kumar et al., 2011). A high viscous fluid is not good for automobile engines as it can cause mechanical inefficiency, also a low viscous fluid is not also recommended as the fuel will drain away faster in engines (Musa et al., 2015). The viscosity of the highest yield of catalytic pyrolysis of liquid product obtained in this work for kaolin and Ukpore clay are 5.141 Mm²/s and 5.227 Mm²/s respectively. Ibrahim et al., (2018) observed that liquid oil from thermal cracking has a higher viscosity as a result of the waxy nature. Table 6 shows the viscosity and density values of standard diesel and it can be seen that the viscosity and density level of the liquid fuel are within these ranges. Different pyrolytic oils have been documented with viscosities similar to the one obtained in this study. All the values reported were within similar range; however, the little discrepancies observed might be due to differences in methods of evaluation, polymer feedstock cracked, and pyrolysis condition.

Table 4 Characterization of liquid oil at Different Amounts of Plastic: catalyst ratio (Ukpore clay)

Plastic: catalyst ratio	Colour	Density at 15 °C, g/ Cm ³	Viscosity at 20 °C, Mm ² / s
1:1	Greenish yellow	0.795	5.801
1:2	Greenish yellow	0.795	5.850
1:3	Pale yellow	0.797	5.227
1:4	Brownish yellow	0.800	5.225

Table 5 Characterization of liquid oil at Different Amounts of Plastic: catalyst ratio (kaolin)

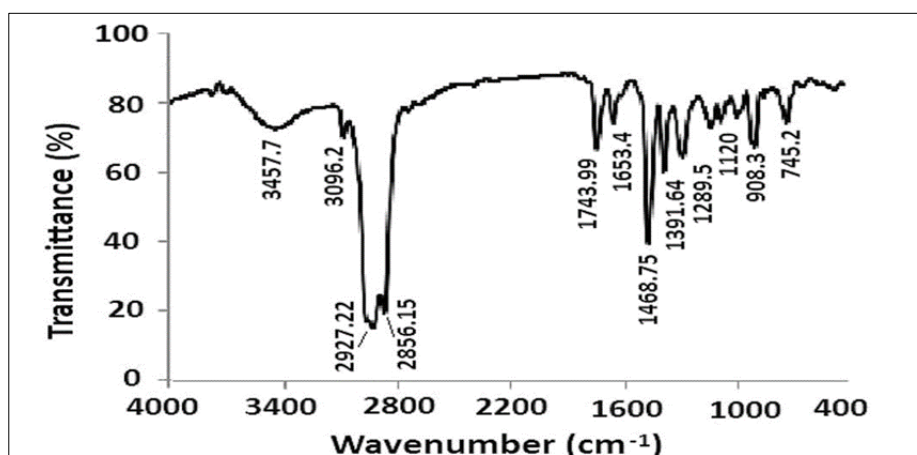
Plastic: catalyst ratio	Colour	Density at 15 °C, g/ Cm ³	Viscosity at 20 °C, Mm ² / s
1:1	Greenish yellow	0.762	5.034
1:2	Greenish yellow	0.768	5.088
1:3	Pale yellow	0.784	5.141
1:4	Brownish yellow	0.815	5.113

Table 6 Comparison between standard diesel fuel and liquid pyrolysis product

Properties	Standard diesel	Liquid pyrolysis product (Ukpor clay :plastic = 1:3)	Liquid pyrolysis product (kaolin :plastic = 1:3)
Density at 15°C, g/Cm ³	0.8	0.797	0.784
Viscosity at 20°C, Mm ² / s	2.2-8.8	5.227	5.141

3.5. FTIR characterization of the liquid fuel

The presence of several functional groups within the waveband of 650-4000 cm⁻¹ was discovered by FTIR analysis of liquid fuel under ideal conditions. The results given in tables (7 and 8) reveal that several hydrocarbons were present in the products together with other organic compounds. It was discovered from the oils' FTIR spectra that the liquid oil products made by the kaolin and Ukpor clay catalytic cracking procedures varied in composition. In the kaolin catalytic process, mono-substituted aromatics showed a medium peak intensity, indicating a higher amount of this component in the final product. In Figures (4 and 5) the FTIR spectra curves of the liquid fuel are shown. Short wave band 2929.37–3068.85 cm⁻¹ denotes the presence of aromatic alkyl groups (C–H stretch); this is expected as the oil is obtained from degradation of plastic which contains carbon and hydrogen (Coates, 2000). There are both CH₃ and CH₂ groups on the spectrum, as well as potent C=C groups. The presence of amine, phosphate, and organohalogen functional groups may have been caused by impurities in the unaltered kaolin utilized.

**Figure 4** FTIR spectrum of the pyrolytic oil for Ukpor clay**Table 7** Interpretation of FTIR Spectra of Liquid oil for Ukpor clay

Peak value	Peak Intensity	Group and class	Bonds
2911.818	Medium-Strong	-CH ₃ and CH ₂ in aliphatic compounds	CH antisym and sym stretching
2678.061	Weak-medium	CHO in aldehydes	Overtone of CH bending
2553.132	Broad	-NH ₃ ⁺ in amine hydrohalides	NH ₄ stretching modes
2446.047	Very broad	-OH in carboxylic acids	H-bonded OH stretch
2273.714	Medium	-PH in phosphines	P-H stretch; sharp peak
2086.489	Medium	N=N=N in azides	N=N=N antisym stretch
1843.948	Strong	C=O in β-lactone	C=O stretch
1618.791	Strong	C=C in vinyl ethers	C=C stretch
1444.479	Very strong	CH ₃ in aliphatic compounds	CH ₃ antisym deformation

1384.615	Very strong	SO ₂ in sulfonyl chloride	SO ₂ antisym stretch
1176.327	Very strong	P=O in phosphorus oxyacid and phosphate	P=O stretch
1019.327	Strong	CH-O-H in cyclic alcohol	C-O stretch
826.8491	Very strong	p-disubstituted benzene	CH out of plane deformation
698.7069	Strong	O-C=O in carboxylic acids	O-C=O bending

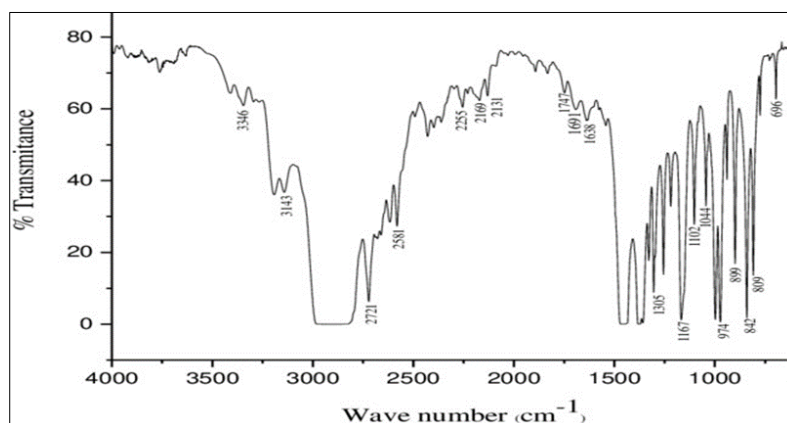


Figure 5 FTIR spectrum of the pyrolytic oil for Kaolin

Table 8 Interpretation of FTIR Spectra of Liquid oil for Kaolin

Peak value	Peak Intensity	Group and class	Bonds
3023.470	Medium-Strong	-CH ₃ and CH ₂ in aliphatic compounds	CH antisym and sym stretching
2738.115	Weak-medium	CHO in aldehydes	Overtone of CH bending
2681.108	Broad	-NH ₃ ⁺ in amine hydrohalides	NH ₄ stretching modes
Peak value	Peak Intensity	Group and class	Bonds
2449.926	Very broad	-OH in carboxylic acids	H-bonded OH stretch
2369.227	Medium	-PH in phosphines	P-H stretch; sharp peak
2299.653	Medium	N=N ⁺ =N ⁻ in azides	N=N=N antisym stretch
2026.193	Strong	C=O in β -lactone	C=O stretch
1814.921	Strong	C=C in vinyl ethers	C=C stretch
1744.815	Very strong	CH ₃ in aliphatic compounds	CH ₃ antisym deformation
1394.295	Very strong	SO ₂ in sulfonyl chloride	SO ₂ antisym stretch
1279.022	Very strong	P=O in phosphorus oxyacids and phosphate	P=O stretch
1011.624	Strong	CH-O-H in cyclic alcohol	C-O stretch
842.519	Very strong	p-disubstituted benzene	CH out of plane deformation
720.4025	Strong	O-C=O in carboxylic acids	O-C=O bending

3.6. Chemical Analysis of the liquid fuel Using GC–MS

As shown in GC–MS analysis (Figure 6), the peak area of 3,3-dimethyl-Octane (2.54 %) and Pentadecane compounds (2.47 %). Meanwhile, the peak area of 11-Methyldodecanol is seen to be 7.6 %. In addition, other compounds appeared at high concentration of catalyst (1:3), e.g., n-Pentadecanol (7.313 %), xylic acid, bis (2-ethyl-)(17.92 %) and more which can be seen in Table 9. In addition, there was strong presence of other compounds generated from the catalytic pyrolysis process which were typical energy products.

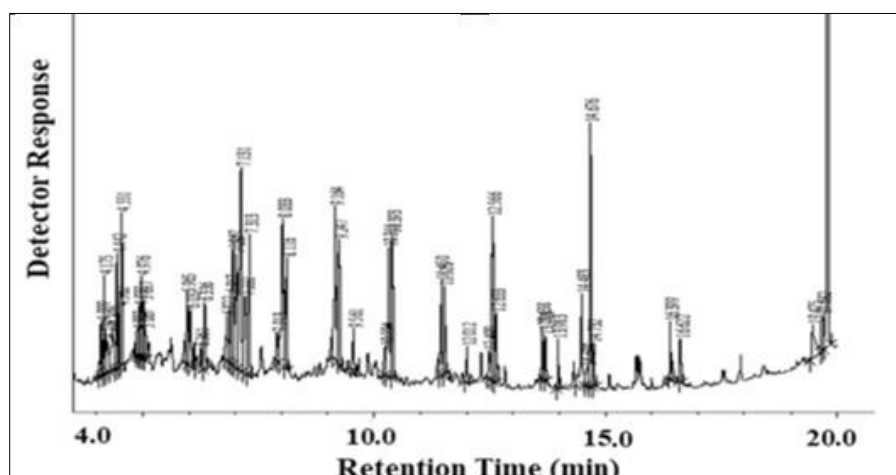


Figure 6 GC-MS of liquid fraction of highest yield

Table 9 Interpretation of GC-MS Chromatogram of Liquid Oil

Retention time	Constituent (% peak area)	Name of constituents	Chemical formula
4.342	2.54	3,3 dimethyl Octane	C ₁₀ H ₂₂
6.037	0.71	Dodecane	C ₁₂ H ₂₆
7.039	2.53	Tridecane	C ₁₃ H ₂₈
8.117	2.22	Tetradecane	C ₁₄ H ₃₀
9.247	2.47	Pentadecane	C ₁₅ H ₃₂
11.526	4.48	1-Pentadecene	C ₁₅ H ₃₀
15.719	0.82	1-Nonadecene	C ₁₉ H ₃₈
12.633, 13.703	0.52	7-methyl-1-Undecene	C ₁₂ H ₂₄
10.393	3.57	2-Ethyl-1-hexanol	C ₈ H ₁₈ O
6.917	7.6	11-Methyldodecanol	C ₁₃ H ₂₈ O
7.908	1.36	n-Pentadecanol	C ₁₅ H ₃₂ O
6.958	17.92	xylic acid, bis(2-ethyl-	C ₂₄ H ₃₈ O ₄
8.033	6.117	11-Methyldodecanol	C ₁₃ H ₂₈ O
9.164, 10.311	2.11	phthalate	C ₂₄ H ₃₈ O ₄
14.675	7.225	11-Methyldodecanol	C ₁₃ H ₂₈ O
12.566, 16.622	7.133, 7.313	n-Pentadecanol	C ₁₅ H ₃₂ O
16.776	1.89	Phenol	C ₆ H ₆ O

4. Conclusion

Pyrolysis presented itself as a sustainable and an efficient treatment method to treat solid waste accumulation which is an important issue nowadays in overcoming landfilling and pollution control. Pyrolysis has environmental advantages compared to other PSW treatment methods as it takes place in an atmosphere free of oxygen, thus does not produce dioxins and has reduced carbon monoxide and dioxide emissions. Mixed plastic wastes were converted into usable liquid fuel through catalytic pyrolysis process at an optimum temperature of 400 °C and catalyst-to-plastic ratio of 1:3 for 45 minutes. Ukpore clay was found to be effective as a low-cost catalyst for the degradation of plastic to gasoline/diesel grade fuel. The Ukpore clay and kaolin used has selectivity for liquid product than solid and gaseous products of pyrolysis. The quality of the oil obtained from the kaolin catalyzed pyrolysis reaction is better than that the Ukpore clay catalyzed pyrolysis reaction because the modification of kaolin catalysts was carried out by novel thermal (TA) and acidic (AA) activation that enhanced their catalytic properties. Physico-chemical properties of the catalyzed pyrolytic oil confirmed the suitability of the mixed plastic liquid product as fuel with most properties comparable to those of conventional fuels with similarity peculiar to gasoline. The chemical composition of the pyrolysis oil was analyzed using GC-MS, and it was found that most of the liquid oil produced a high aromatic content with some aliphatic and other hydrocarbon compounds. These results were further confirmed by the FTIR analysis showing clear peaks corresponding to aromatic and other hydrocarbon functional groups. Scaling up this process will contribute greatly to the energy need of the society and equally reducing the environmental challenges caused by these waste plastics.

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

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