ORIGINAL PAPER



The effect of Kankara zeolite-Y-based catalyst on some physical properties of liquid fuel from mixed waste plastics (MWPs) pyrolysis

Wilson Uzochukwu Eze¹ · Innocent Chimezie Madufor² · Godwin Nkemjika Onyeagoro² · Henry Chinedu Obasi²

Received: 1 February 2019 / Revised: 22 April 2019 / Accepted: 7 May 2019 © Springer-Verlag GmbH Germany, part of Springer Nature 2019

Abstract

The effect of Kankara zeolite-Y-based catalyst on some physical properties of liquid fuel obtained from the pyrolysis of mixed waste plastics has been investigated. Combination of zeolite-Y, metakaolin, aluminum hydroxide and sodium silicate all synthesized from Kankara kaolin from Kankara in Katsina State, Nigeria, was used as catalysts. In this study, fifteen experiments were conducted: fourteen set of 200 g of the mixed waste plastics comprising 27 wt% HDPE, 33 wt% LDPE, 13 wt% PP, 18 wt% PS, 9 wt% PET were de-polymerized with catalyst and a set without catalyst (thermal pyrolysis) in a batch reactor. The maximum temperatures for catalyzed and thermal pyrolysis in this study are 350 °C and 490 °C, respectively. The catalyst components were characterized by XRF analysis, while their textural properties were determined from BET technique by N₂ adsorption at −196 °C. A constant catalyst-to-plastic ratio of 1:10 was used for all the catalyzed reactions. The catalyzed liquid sample with the optimum yield of 46.7 wt% was obtained using 10.49 wt%, 32.42 wt%, 27.09 wt% and 30 wt%, of zeolite-Y, metakaolin, aluminumhydroxide and sodium silicate, respectively, while the thermal pyrolysis gave a liquid yield of 66.9 wt%. Furthermore, the liquid products obtained for both thermal and catalytic cracking at optimum yield were characterized for their suitability as fuel. The properties determined were density, viscosity, fire point, and calorific value. The results suggest that catalytic pyrolysis produced liquid products whose properties are comparable to conventional fuels (gasoline and diesel oil) and more suitable for use as liquid fuel than that produced through thermal pyrolysis.

 $\textbf{Keywords} \ \ Pyrolysis \cdot Mixed \ waste \ plastics \cdot Kankara \ zeolite-Y \cdot Catalyst \cdot Liquid \ fuel \cdot Physical \ properties$

Published online: 11 May 2019

Extended author information available on the last page of the article



Wilson Uzochukwu Eze wilstyrene@yahoo.ca

Introduction

The choice of plastics over other traditional materials is indispensable in today's world, due to their lightweight, durability, ease of processing, design flexibility, resistance to corrosion, and energy efficiency [1-3]. As a result of these inherent properties, plastics have become essential materials. Plastics are now considered as vital materials in several areas such as packaging, construction, aerospace, engineering applications, medical, automotive, leisure, electronics, food, and others [4]. Furthermore, high demand on plastic articles and their feedstock chemicals used in their production have been necessitated due to economic growth and increase in population. However, one great challenge of these synthetic plastics is their nondegradability [5, 6] over a reasonable period after disposal which has created a very serious environmental concern. They constitute a higher proportion of municipal solid wastes in the environment because of their huge quantities and their disposal problems. The presence of these plastic wastes undoubtedly affects living organisms throughout the ecosystem, with an increasingly high impact on marine life at both macro- and microscale. In this regard, conventional plastics waste management practices (such as landfill, incineration, and recycling) have been seen to be inadequate in managing these wastes [7]. The landfill and incineration methods of waste plastics are undesirable due to non-biodegradability and harmful gas emissions [8, 9], whereas effective recycling of waste plastics is restricted by the economic barrier caused by the low quality of recycled waste plastics [10]. However, mechanical recycling of plastic wastes seems to be a "green" process; the reprocessing operation is somewhat expensive as it desires high energy for cleaning, sorting, transportation and processing besides the additives used to provide a useable product [11].

Most governments around the world, therefore, have adopted partial or total ban on plastics usage in their localities as a way to circumvent this perennial disposal problem and to have a greener environment. In this regard, many researchers and industrialists are working on the exploitation of waste plastics as a source of fuel or chemical feedstock [7]. Again, the high heating values associated with consumable plastics also suggest the prospective value of waste plastics as a source of energy or fuel recovery [12, 13]. For this reason, pyrolysis, a thermal decomposition reaction of plastics at temperatures in the range of 350 and 600 °C in the absence of oxygen [14–16], could be considered as a suitable technique for both the treatment of plastics wastes and fuel production or chemical feedstock from plastics wastes.

Currently, pyrolysis is receiving attention for its flexibility to produce a combination of solid, liquid, and gaseous materials in different proportions by varying the operating parameters such as temperature or heating rate [17]. The process provides an opportunity of converting materials of low-energy density into biofuels of high-energy density and, at the same time, recovering high-value chemicals [18, 19]. Pyrolysis could be achieved through hydrocracking, thermal cracking, and catalytic cracking processes. Nevertheless, the thermal degradation of polymers to low molecular weight materials requires high temperatures. The output has been a major limitation as a very broad product range is obtained [15]. But catalytic pyrolysis process attempts to address these problems. The presence of



catalyst lowers the reaction temperature and time [20], inhibits the creation of unwanted products, and increases product yield and production of liquid products with a lower boiling point [21, 22]. Furthermore, catalytic degradation produces a much narrower product distribution of carbon atom number having peaks at lower amount of hydrocarbons and at significantly lower temperatures [15, 23]. This process can be optimized by reuse of catalysts and the use of effective catalysts in lesser quantities. Many studies on the catalytic pyrolysis of plastic wastes have been reported.

Seo et al. [24] reported the effect of a catalyst (ZSM-5) on the degradation of high-density polyethylene (HDPE) at 450 °C in a batch reactor. A gas yield of 65 wt% and a liquid yield of 35 wt% were obtained. Gas chromatography-mass spectrometry (GC-MS) analysis of the liquid product gave a carbon distribution of 99% of C_6 – C_{12} (gasoline) and 1% of C_{13} – C_{23} (diesel). Li et al. [25] also reported the catalytic activity of different kinds of catalysts in the pyrolysis of waste polyethylene (PE) and polypropylene (PP) mixture using a batch reactor at 500 °C. Three microporous catalysts (HUN-ZSM-5, C-ZSM-5, and β-zeolite) and three mesoporous catalysts (Al-MCM-41, KFS-16B, and Al-SBA-15(wo)) were used. The highest gasoline fraction was produced by HUN-ZSM-5 (96%) followed by β-zeolite (85%). The Al-SBA-15 catalyst has an excellent selectivity for diesel $(C_{13}-C_{20})$ fractions (54%). They concluded that the acidity and textural properties of the catalysts determined the yield, and the catalytic pyrolysis products could be a potential alternative to fossil fuel. Uemichi et al. [26] investigated the catalytic pyrolysis of PE using HZSM-5 catalyst which revealed that the catalyst promoted the formation of hydrocarbon fractions within the gasoline range comprising isoalkanes and aromatic compounds in a fixed-bed flow reactor system at 526 °C and 450 °C pyrolysis and catalyst temperatures, respectively. Aguado et al. [27] employed a two-stage, pyrolysis—catalysis reactor for processing polyethylene (PE) using zeolite HZSM-5 and MCM-41 catalysts at temperatures range 425-475 °C. They reported that the oil yield product (75 wt%) in the absence of catalyst comprised of alkanes and alkenes, but in the presence of HZSM-5 catalyst, oil yield decreased and gas yield increased to 73.5 wt%. The oil consisting of aromatic and branched aliphatic compounds with a carbon number ranges from C_5 to C_{12} .

In addition, the use of kaolin clay or its derived zeolite as catalyst in plastic pyrolysis is gaining attention largely as a result of its high silica-to-alumina ratio which makes it suitable for use as catalyst and has been reported as used on single plastic type [28, 29]. Currently, the use of these catalysts on mixed plastics pyrolysis has not received adequate attention by researchers; using mixed plastics as feed will potentially lower the cost associated with pre-recycling operation (sorting). Nigeria has abundance of kaolin deposit in different geographical locations, it is important to state that the properties and elemental composition of these raw kaolin vary with their geographical source or mining location; Hakeem et al. [29] reported silica alumina ratio (SiO₂/Al₂O₃) of 3.8 for Ahoko kaolin from Kogi State of Nigeria, Ajibola et al. [28] reported SiO₂/Al₂O₃ of 1.45 for Arobieye kaolin from Sango Ota, Ogun State of Nigeria, and Babalola et al. [30] reported silica/alumina molar ratio of 3.90, 2.287, 3.03, 2.55, and 2.76 for raw kaolinite clay from Eket, Etinan, IbionoIbom, Ikot Abasi, and UdungUko clay deposits, respectively, in Akwa Ibom State, Nigeria.



In this study, we explore the potentials of combining zeolite-Y, metakaolin, aluminum hydroxide, and sodium silicate from Kankara kaolin from Katsina State of Nigeria as catalyst for the pyrolysis of mixed waste plastics. This research presents an investigation of the catalytic performance of modified near-microporous catalysts; zeolite-Y from Kankara kaolin as base catalyst, in combination with mesoporous catalyst; and metakaolin, aluminum hydroxide, and sodium silicate all from Kankara kaolin at varying proportion.

The focus in this study is to explore the potential and suitability of the catalyst for the pyrolysis of mixed waste plastics into usable liquid fuels. The use of Kankara kaolin-derived materials from naturally abundant Kankara clay will reduce significantly the cost associated with catalytic pyrolysis from the use of analytical grade catalysts and also open a new market for abundant kaolin deposit in Nigeria and Africa at large.

Materials and methods

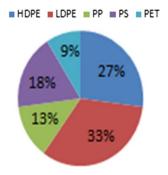
Mixed waste plastics (MWPs)

The MWPs were collected from the disposal site located in Sabon Gari market, Zaria, Kaduna State Nigeria. These MWPs consisted of various used plastic wastes such as polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), low-density polyethylene (LDPE), and high density polyethylene (HDPE) wastes. Samples were cleaned, washed severally with distilled water, and sun-dried for 4 days. The dried MWPs were then chopped into pieces smaller than 4 mm to provide proportional size with reactor capacity. The composition of MWPs used per batch for each pyrolysis is shown in Fig. 1.

Catalysts preparation for pyrolysis

The zeolite-Y synthesized from Kankara kaolin used for this research was obtained from the petroleum trust fund chair laboratory, Ahmadu Bello University, Zaria, Nigeria. The metakaolin, aluminum hydroxide, and sodium silicate used in this

Fig. 1 The composition of mixed waste plastics as used in this study





study were synthesized from Kankara kaolin, a local source in Kankara Local Government Area in Katsina, Nigeria.

The following process was used in preparing the metakaolin, aluminum hydroxide, and sodium silicate from raw kankara kaolin;

Beneficiation of Kankara kaolinite clay

The beneficiation procedure followed was adapted from the literature [31]. Raw kaolin clay from Kankara community in Katsina State, Nigeria, was beneficiated by soaking it in water for 3 days in a plastic container, with periodic stirring, and the suspended impurities were decanted daily. The resulting mixture was sieved using 75-micron sieve and allowed to settle for 24 h. After settling, it was decanted and dried atmospherically for 2 days. The beneficiated clay was ground and sieved.

Calcination of beneficiated Kankara kaolin clay

The dried kaolinite powder was then placed into crucibles and calcined in an electric furnace at 750 for 5 h to obtain the more reactive phase of kaolin known as metakaolin. The resulting metakaolin was characterized, for elemental composition.

Part of the metakaolin was used for synthesis of sodium silicate and aluminum hydroxide; the procedure was adapted from the literature [31–33].

Dealumination of metakaolin using sulfuric acid

Metakaolin of 150 g was mixed with 3000 ml of distilled water and stirred to achieve homogenous mixture. Calculated quantity of 98% sulfuric acid that will give acid concentration of 60 wt% was measured and then added to the metakaolin suspension in the conical flask, and the exothermic reaction was left for 30 min, after which additional distilled water was then added to quench the reaction.

The resulting mixture consists of silica component which was inert to the sulfuric acid used during the reaction and was obtained as a solid product, while the alumina which reacted with the sulfuric acid was obtained in liquid form as aluminum sulfate, known as alum. The two components were separated, and the solid silica washed with distilled water several times was filtered and dried for further processing into sodium silicate. The aluminum sulfate (alum) was collected for further processing into aluminum hydroxide.

Processing aluminum hydroxide and sodium silicate

Aluminum hydroxide was precipitation from aqueous solutions of aluminum sulfate by alkaline solution of sodium hydroxide; the precipitation was carried out at 25 °C and pH below 9. The precipitate was characterized.

Hundred grams of silica were dissolved in 2.5 M of sodium hydroxide in distilled water and placed in a bottle and heated at 90 °C with constant stirring on a magnetic stirrer for 1–3 h. The resulting mixture was allowed to cool to room temperature



and then filtered. Hot deionized water at $100~^{\circ}\text{C}$ was used to wash the residue. The resulting product was characterized.

Characterization of the catalysts components

X-ray fluorescence mineralogical compositions of the samples were confirmed using spectrometer X-Supreme 8000 XRF (Oxford Instrument).

The textural properties of the catalyst components were determined from BET technique by N_2 adsorption at -196 °C using Tristar 3000 Micrometrics equipment.

The various catalyst components and the design of experiment (DOE) for the fourteen runs and uncatalyzed experiment are shown in Table 1.

Pyrolysis experiment

A diagram of the experimental setup is as shown in Fig. 2. The setup consists of a stainless steel (reactor) heated with gas source, a galvanized steel container, two condensers, and fuel sample collectors. The maximum loading capacity of the reactor is 1 kg. The reactor consists of inner stainless-steel container, an outer galvanized steel container, and clay in between as lagging material. A cast iron pipe of 17 cm diameter and 60 cm length is connected to the top cover of the reactor. A double-pipe counter flow heat exchanger of length 90 cm was connected in series functions as the condenser. Water at 28 °C (room temperature) was used as the coolant

Table 1 Catalyst formulations

Run	Component 1	Component 2	Component 3	Component 4
	A: zeolite	B: metakaolin	C: aluminum hydroxide	D: sodium silicate
	%	%	%	%
1	23.22	30.00	16.78	30.00
2	10.49	32.43	27.09	30.00
3	10.00	35.00	30.00	25.00
4	17.32	36.25	21.44	25.00
5	30.00	30.00	15.00	25.00
6	10.00	41.16	21.64	27.20
7	15.50	41.95	17.28	25.28
8	10.99	43.52	15.49	30.00
9	12.14	47.86	15.00	25.00
10	13.66	37.01	19.33	30.00
11	20.24	37.42	15.00	27.39
12	17.14	30.00	25.91	26.96
13	10.00	41.16	21.64	27.20
14	17.14	30.00	25.91	26.99
*C	0	0	0	0



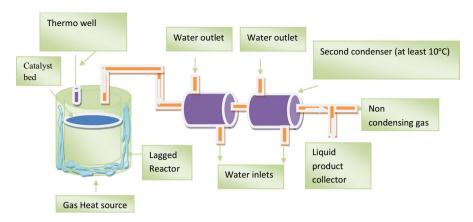


Fig. 2 Setup for the pyrolysis



Fig. 3 Mixed waste plastic liquid samples from the fourteen catalysts

in the first condenser, and the temperature of water being supplied to the second heat exchanger was not more than $10\,^\circ\text{C}$. The waste plastic was placed inside the stainless-steel container of $15\,^\circ\text{cm}$ diameter and $20\,^\circ\text{cm}$ height.

An amount of 200 g of MWPs and 20 g of the compounded catalyst was put into reactor locked to airtight. The reaction time was for 120 min for thermal pyrolysis (uncatalyzed) and 90 min for catalyzed pyrolysis experiments. Heat was supplied from external gas source; the temperature was monitored using a digital thermocouple and regulated from the gas cylinder. The temperature range for the uncatalyzed pyrolysis was between 450 and 490 °C, while for the catalyzed pyrolysis the maximum temperature was 350 °C. The gas produced was flowed into the first shell and tube condensers at 28 °C, while the second condenser was maintained at 10 °C maximum. The experiments were conducted for fourteen different catalyst combinations and one uncatalyzed sample (*C) as indicated in Table 3 to determine the catalyst composition that gives optimum yield. The char remaining in the reactor was collected after each pyrolysis reaction was finished. The various liquid fuels are shown in Fig. 3.

The solid (S), gaseous (G), and liquid product (L) yields were calculated using the formula given below as shown in Eqs. 1, 2, and 3 [34] (Fig. 4):



Fig. 4 Mixed waste plastic liquid-uncatalyzed (control/thermal pyrolysis) sample and sample 2 (optimum yield)



$$L(\text{wt\%}) = \frac{\text{weight of liquid product}}{\text{weight of plastic feed}} \times 100,$$
 (1)

$$L(\text{wt\%}) = \frac{\text{weight of solid product}}{\text{weight of plastic feed}} \times 100,$$
 (2)

$$G(wt\%) = 100 - (L(wt\%) + S(wt\%)).$$
 (3)

Results and discussion

Results of mineralogical composition and textural analysis

The mineralogical composition of the zeolite-Y and other catalyst components is shown in Table 2. The high amount of SiO_2 and $\mathrm{Al}_2\mathrm{O}_3$ in the zeolite-Y and metakaolin showed that they are proper to use as a catalyst. These compounds could increase the cracking efficiency and improve the properties of liquid pyrolytic products. The results also confirmed the other synthesized compound to be aluminum hydroxide and sodium silicate.

Table 3 shows the textural properties of the catalyst components. The results indicate that zeolite-Y had specific surface area of 321 m²/g as revealed from the BET analysis and has pore size and pore volume of 3.4 nm and 0.271 cm³/g. The zeolites had good BET properties, generally having surface areas higher than the products reported by many other researchers [26, 35, 36]. The pore size is large enough to



Table 2 Elemental compositions of catalyst components. *Source*: Eze et al. (this study)

Analyte concentration table					
Element	Zeolite-Y	Metakaolin	Aluminum hydroxide	Sodium silicate	
	Concentration (wt%)				
Na ₂ O	10.118	0.000	0.307	32.217	
MgO	0.349	0.743	0.803	0.185	
Al_2O_3	29.070	41.536	91.437	5.887	
SiO_2	57.597	55.284	3.354	58.510	
P_2O_5	0.00	0.000	0.000	0.000	
SO ₃	0.689	0.150	2.064	0.335	
Cl	0.069	0.010	0.000	0.020	
K_2O	0.145	1.123	0.013	2.129	
CaO	0.669	0.229	0.015	0.179	
TiO_2	0.058	0.084	0.032	0.151	
Cr ₂ O ₃	0.015	0.002	0.008	0.000	
Mn_2O_3	0.017	0.011	0.006	0.003	
Fe_2O_3	1.081	0.815	1.926	0.374	
ZnO	0.119	0.009	0.035	0.005	
SrO	0.005	0.004	0.000	0.005	
SiO ₂ /Al ₂ O ₃	3.37	1.331			

Table 3 Textural properties of the catalyst components

Properties	Zeolite-Y	Metakaolin	Aluminum hydroxide	Sodium silicate
Surface area (m ² /g)	321	15.5217	166	426
Pore size (nm)	3.4	25.96991	24.5	15.8
Pore volume (cm ³ /g)	0.271	0.059222	0.39	0.9

accommodate molecules of larger diameter mostly found in the heavy gas oil feedstock. This implies that diffusion resistance will not be a much challenge.

BET analysis of the clay prepared at 750 °C gave a surface area of $9.1217 \text{ m}^2/\text{g}$, pore volume of $0.059222 \text{ cm}^3/\text{g}$, and pore size of 25.96991 nm. The textural properties of aluminum hydroxide and sodium silicate are also shown in Table 3.

Yield of MPWs liquid fuel

Table 4 shows the percentage yield of uncatalyzed and catalyzed pyrolysis; it is evident that the yield of liquid fuel decreased significantly with the use of the catalyst at all combinations under investigation. The uncatalyzed pyrolysis (thermal pyrolysis) has a percentage yield of 69.9%, while the maximum yield for the catalyzed pyrolysis is 46.7%. This decrease in yield for catalyzed reaction is in agreement with



Run	Component 1	Component 2	Component 3	Component 4	Response 1
	A: zeolite	B: metakaolin	C: aluminum hydroxide	D: sodium silicate	Percentage yield
	%	%	%	%	%
1	23.22	30.00	16.78	30.00	13
2	10.49	32.43	27.09	30.00	46.7
3	10.00	35.00	30.00	25.00	32.2
4	17.32	36.25	21.44	25.00	18.3
5	30.00	30.00	15.00	25.00	7.4
6	10.00	41.16	21.64	27.20	45.6
7	15.50	41.95	17.28	25.28	44
8	10.99	43.52	15.49	30.00	37.2
9	12.14	47.86	15.00	25.00	25.4
10	13.66	37.01	19.33	30.00	14.7
11	20.24	37.42	15.00	27.39	22.2
12	17.14	30.00	25.91	26.96	35.1
13	10.00	41.16	21.64	27.20	45.6
14	17.14	30.00	25.91	26.96	35.1
*C	0	0	0	0	66.90

findings of Rehan et al. [37] who studied the effect of zeolite catalysts on pyrolysis liquid oil and reported that thermal pyrolysis produced maximum liquid oil (80.8%) with gases (13%) and char (6.2%), while catalytic pyrolysis using synthetic and natural zeolite decreased the liquid oil yield (52%) with an increase in gases (17.7%) and char (30.1%) production.

Table 4 shows that the optimum yield (Sample 2) was obtained at a 10.4902%:32.4225%:27.0872%:30% of zeolite-Y, metakaolin, aluminum hydroxide, and sodium silicate catalyst composition, respectively.

Similar observation as above was also reported by Seo et al. [24] who studied the catalytic degradation of HDPE using a batch reactor at a temperature of 450 °C and noted that the pyrolysis performed with the zeolite ZSM-5 had higher yield of the gaseous fraction and smaller liquid fraction when compared with thermal cracking.

Figure 5a, b shows the combined effects of catalyst component on the yield of waste plastic fuel; it is clear from the 3D response surface plot (Fig. 5a) that the variation of the catalyst components has significant effect on the yield. The yield increased significantly with increase in volume of aluminum hydroxide; zeolite-Y caused insignificant increase in yield while very sharp increase in yield was caused by increasing volume of metakaolin, and this indicates that metakaolin had a better selectivity for liquid product due to its higher active site and mesoporosity.

The effect of the individual catalyst components is even clearer on the contour plot (Fig. 5b). The blue region around the zeolite-Y region indicates regions of lower fuel yield promoted by the zeolite component in the catalyst due to its poor selectivity for liquid fuel. High yield of liquid fuel was obtained around the aluminum



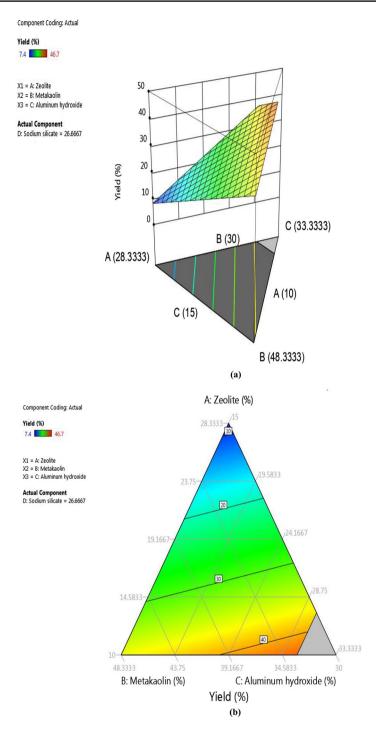


Fig. 5 a 3D response surface plot of percentage yield of fuel versus catalyst components. **b** Contour surface plot of percentage yield of fuel versus catalyst components

Table 5. Thysical properties of the thermal and eathly the pyrolytic on at optimum condition						
Physical property	Method	Thermal MWPs fuel	Catalyzed MWPs fuel	Gasoline	Diesel	
Color		Dark brown	Light yellow			
Odor		Chocking smell	Choking smell			
Density @ 23 °C (g/cm ³)	ASTM D4052	0.8945	0.8336	0.70-0.78 ^a	0.82-0.87 ^a	
Dynamic viscosity @ 32 °C (mPa s)	ASTM D445	2.03	1.0	1.0–2.1	2.0-4.1 ^d	
Fire point (°C)	ASTM D93	90	84	$42-47^{c}$	60–90°	
Calorific value (J/g)	ASTM D4809	14,751	24,919	42.702 ^b	45.814 ^b	

Table 5 Physical properties of the thermal and catalytic pyrolytic oil at optimum condition

hydroxide and metakaolin components denoted by the red regions. The aluminum hydroxide and metakaolin had high selectivity for liquid fuel.

The lower yield of liquid fuel through catalytic pyrolysis is due to catalytic features of the zeolites used such as near-microporous structure and high BET surface area. However, the larger pore size of aluminum hydroxide and metakaolin lowers molecular sieving activity and tends to favor more liquid yield.

Characterization of the liquid fuel

The liquid product obtained from both the thermal and catalytic pyrolysis at optimum yield was characterized for some of its physical properties, namely density, viscosity, fire point, and calorific value, according to American Standard for Testing and Materials (ASTM). The physical properties of the liquid products obtained from thermal and catalytic pyrolysis at optimum yield are shown in Table 5.

The liquid fuels obtained in this study from both thermal and catalyzed process at optimum yield (10.4902%:32.4225%:27.0872%:30% of zeolite-Y, metakaolin, aluminum hydroxide, and sodium silicate catalyst composition, respectively), temperature range of 400–450 °C, and 90 min were characterized to investigate their acceptance for use as fuel. Significant variation in color was observed with the change in catalyst composition. The liquid product from thermal cracking is more viscous, dark brown in color, while that from catalytic pyrolysis (optimum yield) is light yellow in color. The difference in color can be attributed to the activity of catalyst which promotes the secondary cracking of the plastic to lighter products. The results prove that the use of catalyst in pyrolysis of MWPs decreased the yield of liquid fuel but improved the usability as an alternative fuel. Similar oil color (dark brown) was observed by Songcha et al. [41] in their study on Distillation of Pyrolytic Oil Obtained from Fast Pyrolysis of Plastic Wastes.



^aGandidi et al. [38]

^bMiandad et al. [39]

^cHakeem et al. [29]

^dWongkhorsub and Chindaprasert [40]

According to Barabas and Todorut [42], fuel density is the mass of unit volume, measured in a vacuum. Fuel density directly affects fuel performance, as some of the engine properties, such as cetane number, heating value, and viscosity, are strongly connected to density. The density of the thermal cracking liquid product obtained in this study is 0.8945 g/cm³, while that of catalytic cracking process (optimum yield) is 0.8336/cm³. Consequently, the density of the liquid product from thermal cracking process is higher than that of the catalytic process. This is expected as the liquid product obtained from catalytic cracking is light and wax-free. On comparing with gasoline with a reported density range of 0.70-0.78 g/cm³ and diesel oil with density range of 0.82-0.87 g/cm³, 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 C-C covalent bonds in the plastics during the catalytic cracking than during thermal cracking as secondary cracking is facilitated by the use of the catalyst. The density of the catalytic pyrolytic liquid obtained in this work is within the range reported for other pyrolytic oils; polypropylene pyrolytic oil has density of 0.81 g/cm³ [43]. Low-density polyethylene pyrolytic oil was reported to have 0.815 g/ml as density [44]. Rehan et al. [37] reported a density of 0.9 g/cm³ for zeolite-catalyzed and thermal polypropylene pyrolysis. The very slight variation can be due to differences in pyrolysis condition, catalyst used, differences in polymeric material, and differences in the method of evaluation. The density of the liquid product obtained from zeolite, metakaolin, aluminum hydroxide, and sodium silicate combination-catalyzed pyrolysis in this study suggests that it can be used as alternative for gasoline fuel.

Viscosity is a very important fuel property for the automobile engine. Viscosity affects the atomization of a fuel upon injection into the combustion chamber and the transport resistance in the fuel injection systems [45]. The viscosity of fuel oil is a very important parameter; moderate viscosity is desirable as too low viscosity leads to high fuel consumption and too high viscosity causes blockage of nozzle and poor of ignition during cold weather [46]. The viscosity of the catalytic pyrolysis liquid product obtained in this work is 1.0 mPa s, while that of thermal pyrolysis is 2.03 mPa s. The higher viscosity value of the liquid product from thermal cracking is due to its waxy nature. These viscosity values are within the viscosity value reported for different plastic pyrolytic oils; 1.77–1.90 mPa s was reported as the viscosity range for polystyrene (PS), polyethylene (PE), polypropylene (PP), and polyethylene terephthalate (PET) pyrolytic oils [38]. Rehan et al. [29] reported 1.9 for zeolite catalyzed PS pyrolysis oil.

When compared with 1–4.1 mPa s reported by Wongkhorsub and Chindaprasert [40] as the dynamic viscosity range for diesel oil, it suggests that the viscosity of the catalyzed pyrolytic oil obtained in this work is comparable to that of diesel oil.

All the values reported were within similar range; however, the little discrepancies observed might be due to differences in methods of evaluation, differences in polymer feedstock cracked, and differences in pyrolysis condition.

Furthermore, fire point of a fuel is the temperature at which it will continue to burn for at least 5 s after the source of ignition has been removed. The fire point is used to measure the risk of materials ability to support combustion. Generally, the fire point of any liquid oil is about (5-10) °C higher than the flash point [47]. Fire



points of 90 and 84 °C were obtained for the thermal and catalytic pyrolytic liquid, respectively. It is expected that the catalytic pyrolytic liquid which is light and less viscous should be more volatile and ignites in open flame at lower temperature than the thermally pyrolytic liquid which is viscous. The thermal and catalyzed pyrolytic liquid fire points were within the fire points range of 60–90 °C reported for diesel oil. However, significant variation exists in the values of the fire points obtained in this work compared with that reported for different plastic types: Hakeem et al. [29] reported 47 °C and 85 °C as fire points for kaolin-catalyzed and thermal pyrolysis of polypropylene, respectively. Arunkumar and Nataraj [48] reported 45 °C for bentonite-catalyzed low-density polyethylene pyrolysis oil. The discrepancies observed can be largely attributed to differences in polymer feedstock used and differences in pyrolysis condition.

The result of this study confirms the suitability of the liquid product as fuel for automobile engines.

Lastly, the standards measure of the energy content of a fuel is its heating value (HV), sometimes called the calorific value or heat of combustion. The energy content is one of the most important characteristics of any fuel in its applications, and it can be characterized by its HV. The higher the HV value of a fuel, the higher the energy content of the fuel, meaning the required performance can be achieved with less fuel quantity [49].

The calorific value of the catalytic pyrolytic liquid is 24,919 J/g, while that of thermal pyrolytic liquid is 14,751 J/g. Heating or energy or calorific value of a fuel refers to the amount of heat evolved during combustion of a given amount of it [42]. High calorific values indicate that such substance would release great amount of heat energy during complete combustion with air under standard conditions. For a substance to be suitable for use as fuel, it must have considerably high amount of heating value which would make it burn in the air for a very long time [50]. The calorific value (CV) of the catalytic and thermal pyrolysis liquid obtained in this work is remarkably lower than gasoline CV of 42,702 J/g and that of diesel oil with CV of 45,814 J/g; this can be attributed to the feedstock used. However, the catalyst improved the CV of the liquid fuel significantly such that the catalytic pyrolytic liquid would function well as fuel in automobile engines.

Conclusion

Several factors affect the physical properties and suitability of plastic pyrolysis liquid for use as fuel. Feedstock composition has shown to be very influential, as the properties obtained in this work differ from the results reported for other single plastic feed. However, the use of mixed plastics as feedstock will potentially increase the elimination of plastics waste in the environment and circumvent the huge cost of sorting associated with plastic waste recycling. The physical properties obtained in this work for the catalyst that gave the optimum yield (10.49 wt%, 32.42 wt%, 27.09 wt%, and 30 wt%, of zeolite-Y, metakaolin, aluminum hydroxide, and sodium silicate, respectively) are close to that of conventional diesel oil.



The yield decreased significantly for the catalyzed pyrolysis liquid with optimum yield (46.7%) when compared with the thermal pyrolysis liquid (66.9%), but the former had better and improved physical properties which make it more suitable for use as fuel. Finally, the addition of mesoporous metakaolin, aluminum hydroxide, and sodium silicate into near-microporous zeolite-Y has shown a marked increase in yield compared to that reported for only zeolite-catalyzed pyrolysis. The Kankara zeolite-Y-based catalyst was very effective in cracking mixed waste plastics into usable fuel.

Acknowledgements The authors acknowledge the support of Dr. Solomon Gajere Bawa of Petroleum Technology Laboratory, Ahmadu Bello University Zaria, Nigeria, for providing us with the zeolite-Y and assistance in the synthesis of the other catalyst components. The authors also acknowledge the valuable contributions of Dr. Bashir of the Multi-User Laboratory, Ahmadu Bello University, Zaria, Nigeria.

Compliance with ethical standards

Conflict of interest The authors declare no conflict of interest.

References

- 1. Crawford RJ (1998) Plastics engineering. Elsevier, Amsterdam
- 2. Curcio M, Picci N (2008) Polymer in agriculture: a review. Am J Agric Biol Sci 3(1):299-314
- 3. Scott G (2013) Degradable polymers: principles and applications. Springer, New York
- 4. Al-Salem S, Antelava A, Constantinou A, Manos G, Dutta A (2017) A review on thermal and catalytic pyrolysis of plastic solid waste (PSW). J Environ Manag 197:177–198
- 5. Behera AK, Avancha S, Basak RK, Sen R, Adhikari B (2012) Fabrication and characterizations of biodegradable jute reinforced soy based green composites. Carbohyd Polym 88(1):329–335
- 6. Singh P, Sharma V (2016) Integrated plastic waste management: environmental and improved health approaches. Procedia Environ Sci 35:692–700
- 7. Lee H, Park Y-K (2018) Catalytic pyrolysis of polyethylene and polypropylene over desilicated beta and Al-MSU-F. Catalysts 8(11):501
- 8. Hafeez S, Manos G, Al-Salem S, Aristodemou E, Constantinou A (2018) Liquid fuel synthesis in microreactors. React Chem Eng 3:414–432
- 9. Wang T, Xiao F, Zhu X, Huang B, Wang J, Amirkhanian S (2018) Energy consumption and environmental impact of rubberized asphalt pavement. J Clean Prod 180:139–158
- 10. Scott G (2000) 'Green' polymers. Polym Degrad Stab 68(1):1-7
- 11. La Mantia F (2002) Handbook of plastics recycling. Smithers Rapra Publishing, Akron
- 12. Sharuddin SDA, Abnisa F, Daud WMAW, Aroua MK (2016) A review on pyrolysis of plastic wastes. Energy Convers Manag 115:308–326
- 13. Sim J-W, Kim S-S (2017) Recovery of polyethylene telephthalate monomer over Cu or Mn/gamma-Al₂O₃ catalysts. Appl Chem Eng 28(4):485–489
- 14. Lee H, Kim Y-M, Lee I-G, Jeon J-K, Jung S-C, Do Chung J, Park Y-K (2016) Recent advances in the catalytic hydrodeoxygenation of bio-oil. Korean J Chem Eng 33(12):3299–3315
- Panda AK, Singh RK, Mishra D (2010) Thermolysis of waste plastics to liquid fuel: a suitable method for plastic waste management and manufacture of value-added products—a world prospective. Renew Sustain Energy Rev 14(1):233–248
- Shafaghat H, Rezaei PS, Ro D, Jae J, Kim B-S, Jung S-C, Park Y-K (2017) In-situ catalytic pyrolysis of lignin in a bench-scale fixed bed pyrolyzer. J Ind Eng Chem 54:447–453
- Czajczyńska D, Anguilano L, Ghazal H, Krzyżyńska R, Reynolds A, Spencer N, Jouhara H (2017) Potential of pyrolysis processes in the waste management sector. Therm Sci Eng Prog 3:171–197
- Biswal B, Kumar S, Singh R (2013) Production of hydrocarbon liquid by thermal pyrolysis of paper cup waste. J Waste Manag 2013:731858. https://doi.org/10.1155/2013/731858



- Chowdhury R, Sarkar A (2012) Reaction kinetics and product distribution of slow pyrolysis of Indian textile wastes. Int J Chem React Eng. https://doi.org/10.1515/1542-6580.2662
- 20. Zhang X, Lei H, Yadavalli G, Zhu L, Wei Y, Liu Y (2015) Gasoline-range hydrocarbons produced from microwave-induced pyrolysis of low-density polyethylene over ZSM-5. Fuel 144:33–42
- Almeida D, Marques MDF (2016) Thermal and catalytic pyrolysis of plastic waste. Polímeros 26(1):44–51
- López A, De Marco I, Caballero B, Laresgoiti M, Adrados A, Aranzabal A (2011) Catalytic pyrolysis of plastic wastes with two different types of catalysts: ZSM-5 zeolite and Red Mud. Appl Catal B 104(3–4):211–219
- Auxilio AR, Choo W-L, Kohli I, Srivatsa SC, Bhattacharya S (2017) An experimental study on thermo-catalytic pyrolysis of plastic waste using a continuous pyrolyser. Waste Manag 67:143–154
- 24. Seo Y-H, Lee K-H, Shin D-H (2003) Investigation of catalytic degradation of high-density polyethylene by hydrocarbon group type analysis. J Anal Appl Pyrol 70(2):383–398
- 25. Li K, Lee SW, Yuan G, Lei J, Lin S, Weerachanchai P, Wang J-Y (2016) Investigation into the catalytic activity of microporous and mesoporous catalysts in the pyrolysis of waste polyethylene and polypropylene mixture. Energies 9(6):431
- 26. Uemichi Y, Hattori M, Itoh T, Nakamura J, Sugioka M (1998) Deactivation behaviors of zeolite and silica–alumina catalysts in the degradation of Polyethylene. Ind Eng Chem Res 37(3):867–872
- 27. Aguado J, Serrano D, San Miguel G, Castro M, Madrid S (2007) Feedstock recycling of polyethylene in a two-step thermo-catalytic reaction system. J Anal Appl Pyrol 79(1–2):415–423
- 28. Ajibola AA, Omoleye AJ, Efeovbokhan VE (2018) Catalytic cracking of polyethylene plastic waste using synthesized zeolite Y from Nigerian kaolin deposit. Appl Petrochem Res 8:211–217
- 29. Hakeem IG, Aberuagba F, Musa U (2018) Catalytic pyrolysis of waste polypropylene using Ahoko kaolin from Nigeria. Appl Petrochem Res. https://doi.org/10.1007/s13203-018-0207-8
- Babalola R, Bassey EN, Brown IL, Salahudeen N (2017) Identification of kaolinite clay in five local government areas of Akwa Ibom State, Nigeria for zeolite synthesis as a way of import substitution.
 J Emerg Trends Eng Appl Sci 8(5):215–218
- Ajayi AO, Atta AY, Aderemi BO, Adefila SS (2010) Novel method of metakaolin dealuminationpreliminary investigation. J Appl Sci Res 6(10):1539–1546
- 32. Aderemi BO, Edomwonyi-Otu L, Adefila SS (2009) A new approach to metakaolin dealumination. Aust J Basic Appl Sci 3(3):2243–2248
- 33. Bawa SG, Ahmed AS, Okonkwo PC, Waziri SM (2017) Development of pilot scale dealumination unit of 2.5 kg metakaolin per batch capacity. Niger J Technol 36(3):829–834
- 34. Francis AA, Fredriksen SB, Sætre KA, Tokheim L-A (2018) Experimental study of thermal and catalytic pyrolysis of plastic waste components. Sustainability 10(11):3979
- 35. Liu X, Yan Z, Wang H, Luo Y (2003) In-situ synthesis of NaY zeolite with coal-based kaolin. J Nat Gas Chem 12:63–70
- Ratnasari DK, Nahil MA, Williams PT (2017) Catalytic pyrolysis of waste plastics using staged catalysis for production of gasoline range hydrocarbon oils. J Anal Appl Pyrolysis 124:631–637
- 37. Rehan M, Miandad R, Barakat MA et al (2017) Effect of zeolite catalysts on pyrolysis liquid oil. Int Biodeterior Biodegrad 119:162–175
- Gandidi IM, Susila MD, Rustamaji H (2018) Effect of natural zeolite and kaolin as a catalyst in the isothermal-catalytic cracking of real municipal solid waste (MSW) for bio-oil production. IOP Conf Ser Earth Environ Sci 160:012018
- Miandad R, Barakat MA, Rehan M, Aburiazaiza AS, Ismail IMI, Nizami AS (2017) Plastic waste to liquid oil through catalytic pyrolysis using natural and synthetic zeolite catalysts. Waste Manag. https://doi.org/10.1016/j.wasman.2017.08.032
- 40. Wongkhorsub C, Chindaprasert N (2013) A comparison of the use of pyrolysis oils in diesel engine. Energy and Power Engineering 5(4B):350–355. https://doi.org/10.4236/epe.2013.54B068
- 41. Wiriyaumpaiwong S, Jamradloedluk J (2017) Distillation of pyrolytic oil obtained from fast pyrolysis of plastic wastes. Energy Procedia 138:111–115
- 42. Barabás I, Todorut A, Baldean D (2010) Performance and emission characteristics of an CI engine fueled with diesel-biodiesel-bioethanol blends. Fuel 89(12):3827–3832
- 43. Sarker M et al (2013) Petroleum production from polystyrene waste. Science and Technology Publishing Inc, New York, pp 1–40. ISBN 978-0-9886890-1-5
- Na J-G, Jeong B-H, Seong-Soo Kion SH (2006) Pyrolysis of low density polyethylene using synthetic catalyst produced from fly ash. J Mater Cycles Waste Manag 8:126–132



- Technical Information ASTM D975 Diesel Fuel Specification Test (1996) Syntek Global Inc, pp 1–3
- 46. Musa U, Mohammed IA, Sadiq MM, Aberuagba F, Olurinde AO, Obamina R (2015) Synthesis and characterization of trimethylolpropane-based biolubricants from castor oil. In: Proceedings of the 45th annual conference of NSCHE, Warri, Nigeria, 5–7 November 2015
- Khan MZH, Sultana M, Al-Mamun MR, Hasan MR (2016) Pyrolytic waste plastic oil and its diesel blend: fuel characterization. J Environ Public Health 2016:7869080. https://doi. org/10.1155/2016/7869080
- 48. Arunkumar BY, Nataraj CN (2017) Conversion of waste plastic into fuel oil in the presence of bentonite as a catalyst. Int Res J Eng Technol 4(9):114–119
- 49. Saptoadiand H, Pratama NN (2015) Utilization of plastics waste oil as partial substitute for kerosene in pressurized cook stoves. Int J Environ Sci Dev 5(6):363–368
- 50. Ituen E, Ijioma C (2012) Fuel properties of palm oil biodiesel and its blends with diesel. J Mater Resour 7(1&2):38–48

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Affiliations

Wilson Uzochukwu Eze¹ · Innocent Chimezie Madufor² · Godwin Nkemjika Onyeagoro² · Henry Chinedu Obasi²

- Department of Polymer Technology, Nigerian Institute of Leather and Science Technology, Zaria, Nigeria
- Department of Polymer and Textile Engineering, Federal University of Technology, Owerri, Nigeria

