

## Research Article

# Catalytic Pyrolysis of Plastic Waste to Liquid Fuel Using Local Clay Catalyst

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Plastics are nonbiodegradable, and safe disposal of this waste poses an environmental challenge all over the world. Catalytic pyrolysis is superior to thermal pyrolysis as it uses lower temperatures and hence less energy. The main objective of this study was to produce liquid fuel from plastic waste using indigenous clay as a catalyst through catalytic pyrolysis. The clay from Kisumu County was characterized through an X-ray fluorescence spectrometer (XRFS) and an X-ray diffractometer (XRD). The reaction setup consisted of a round-bottom flask reactor through which plastic feed and catalyst were heated in a temperature-controlled furnace. Vapor product was condensed using a Liebig type water condenser to give pyrolysis liquid product. Solid char was recovered from the flask at the end of the reaction. Optimization studies using central composite design (CCD) and response surface methodology (RSM) were performed in design expert software to predict optimal conditions of the operating variables for maximum yield of the liquid fuel. Results show that clay has a composition of silica and alumina at 64.5 wt% and 16.3 wt%, respectively, indicating high acidity of the clay, being a requirement for a good pyrolysis catalyst. For high-density polyethylene and polypropylene, the highest liquid yield of 87.23 wt% and 60.36 wt%, respectively, was at 300°C and a catalyst concentration of 10 wt%. Indigenous clay was established to be a suitable catalyst for catalytic pyrolysis of plastic waste, with the potential to replace imported catalysts since high yields of liquid fuel were obtained at lower reaction temperatures of 300-450°C, as compared to the 600°C required for thermal pyrolysis. In conclusion, waste plastics can be used to generate alternative fuel for industrial use. The liquid fuel can be used in diesel engines as a transport fuel, in turbines for electricity generation, and as a heating source in boilers and furnaces. Further studies on the modification of the surface and structure of clay are suggested to enhance its catalytic performance in the pyrolysis process for a better fuel yield.

## 1. Introduction

Plastic is one of the major toxic pollutants of present time being composed of toxic chemicals and, most importantly, nonbiodegradable; plastic pollutes the Earth, air, and water. This also mixes with the food chain, affecting the environment, humans, and animals. The global production of plastics was reported to be 299 million tons in the year 2013, and an increase of 4% has been reported over the years, reaching a production rate of 367 million tons in the year 2020 [1]. The impact of plastic pollution has been felt across

the world, with 8 million tons of plastic finding its way into oceans every year. It is estimated that only 9% of all plastic waste ever produced has been recycled, while 79% ends up in landfills, dumps, or the natural environment [2]. Landfills are health hazards, causing air and water pollution with mercury. Meanwhile, living near landfills also increases the likelihood of problems with health like low birth weight, birth defects, and certain types of cancers [1]. Municipal solid waste (MSW) contains a large percentage of plastic waste with a typical composition of polyethylene terephthalate (PET) at 10%, high-density polyethylene (HDPE) at 19%,

polyvinyl chloride (PVC) at 6%, low-density polyethylene (LDPE) at 23%, polypropylene (PP) at 14%, and polystyrene (PS) at 9% [3]. The disposal and decomposition of plastics have been an issue, and research is ongoing for appropriate solutions. Currently, the disposal methods employed are land filling, biological degradation, and thermal/chemical recycling [4].

In pyrolysis, long-chain polymer molecules are degraded into smaller, less complex molecules through heat and pressure, resulting in liquid oil, char, and gases [5, 6]. The process requires intense heat with a shorter duration and an absence of oxygen. Pyrolysis has been chosen by many researchers since the process is able to produce a high amount of liquid oil, up to 80 wt%, at a temperature of around 500°C. The pyrolysis of plastic waste produces a whole spectrum of hydrocarbons including paraffins, olefins, isoalkanes, and aromatics. Petroleum-based plastic pyrolysis oil contains unsaturated compounds, and the presence of these compounds makes the produced fuel unsuitable for combustion in diesel engines. Hydrogenation of pyrolysis oil is performed to convert unsaturated compounds to saturated compounds. The physicochemical properties of HPPO have been found to match the EN590 standards for diesel [7].

Pyrolysis product yield and quality heavily depend on a number of operating parameters, namely, temperature, feedstock composition, type of reactor, residence time, pressure, heating rate, choice of catalyst, particle size, and type of fluidizing gas with its flow rate. Thermal pyrolysis in general produces more heavy oil with a lower octane number and a higher quantity of char, whereas catalytic pyrolysis produces less liquid with a higher octane number gasoline range compounds and lesser char [8].

Temperature is the most important factor as it affects the cracking reactions that alter the yield of gases and liquid oil, with little effect on the amount of produced char. At low temperature, long-chain hydrocarbons are produced, while an increase in temperature results in short-carbon-chain compounds due to the cracking of C-C bonds. Aromatic compounds are produced at higher temperatures due to the triggering of secondary process reactions [9].

Retention time has shown little effect on the quality of pyrolysis [9, 10]. The feedstock composition affects the yield of pyrolysis products. PE and PP types of plastics require higher temperatures for their complete degradation as compared to PS plastic, due to their complex structures [11]. Conventional copyrolysis of seaweeds with waste plastic, microwave vacuum copyrolysis of waste plastic and seaweeds, and copyrolysis of different biomasses and waste plastics are some of the recent studies on plastic pyrolysis and copyrolysis as cost-effective methods. The major drawback of biofuel production using microalgae is its high cost of harvesting, owing to its low biomass concentration and small cell size [12]. The oil produced by the pyrolysis of biomass needs to be upgraded since it contains high levels of oxygen, which causes low calorific value, corrosion problems, and instability [13]. Catalyst improves the quality of pyrolysis products, reduce the process temperature, increase the reaction rate, and decrease the overall process energy

inputs [14], and the choice of catalyst affects the product (gas, gasoline fraction, heavy oil fraction, and residue) yields [15]. Among the core reasons for the utilisation of catalysts is the reduction of the length of carbon chains in pyrolysis products, which allows a decrease in the boiling point of the products [16]. A number of catalysts have been used such as  $\text{Fe}_2\text{O}_3$  [17],  $\text{Ca}(\text{OH})_2$  [18], FCC [19], natural zeolite [20], synthetic zeolite [9], red mud [14], ZSM-5 [14], HZSM-5 [21], and Y-zeolite [22]. Clays generally constitute hydrous silicates of aluminium and/or magnesium with significant amounts of iron, nickel, chromium, and other cations, and the peculiar crystalline structure of some clay minerals generates a capacity for reversible exchange with organic or inorganic cations and metal-organic cations [23]. The exchange of specific cations generates active centers in the clay minerals, making them suitable catalysts. The classes of clay minerals include smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pyrophyllite (talc), vermiculite, and sepiolite. Clays have adsorption capabilities which result from a net negative charge on the structure of minerals and sorption properties attributed to their high surface area and high porosity [24]. The research gap in this study was based on the use of Kenyan clay from the River Oren in Awasi Town, Kisumu County, as a catalyst for waste plastic pyrolysis. The main aim of this study was the optimization of liquid fuel from different types of plastic wastes using indigenous clay as a catalyst through catalytic pyrolysis.

Clay from the River Oren in Awasi Town (Kisumu County) in Kenya was used as a catalyst in this study. Major elements present in these clays are silica ( $\text{SiO}_2$ ), alumina ( $\text{Al}_2\text{O}_3$ ), iron oxide ( $\text{Fe}_2\text{O}_3$ ), and water. The other elements present are potassium oxide ( $\text{K}_2\text{O}$ ), sodium oxide ( $\text{Na}_2\text{O}$ ), titanium oxide ( $\text{TiO}_2$ ), and calcium oxide ( $\text{CaO}$ ), with traces of magnesium oxide ( $\text{MgO}$ ) and manganese oxide ( $\text{MnO}$ ). The clay has a high percentage of silica (50-56%) [25].

## 2. Materials and Methods

*2.1. Equipment and Materials.* Specifications of apparatus and instruments include a pulverizer (Retsch model no. Rs 200 at 1200 rpm), an electronic weighing balance (Kernpu), an atomic absorption spectrophotometer (Shimadzu model no. AA 7000), an X-ray diffractometer (Rigaku MiniFlex 11), and an X-ray fluorescence (Rigaku model no. ZSX primus 11). The current and voltage settings for the analysis of the elements are done automatically by the ZSX software upon selection of the sample. Other equipments are the pelleting machine, bomb calorimeter (Coshwania), gas chromatography mass spectrometer (GCMS QP 2010 SE), centrifuge (Hettich Zentrifugen at 2000 rpm), round-bottomed flasks, Liebig condenser, oil collection flasks, electric brick furnace with a thermocouple for temperature control, rubber tubing, stands, rubber corks, density bottle, thermometer, and viscometer.

The plastics were collected locally from the Nandi Hills town dumpsite as used detergent bottles (high-density polyethylene), used yoghurt cups (polypropylene), and used packaging materials (polystyrene). Manufacturers place an SPI code, or number, on each plastic product, usually

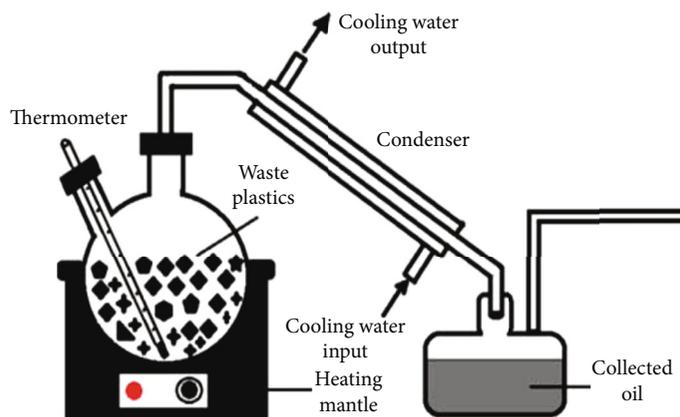


FIGURE 1: Experimental setup for liquid oil production.

TABLE 1: Independent variables and their levels in CCD.

Independent variables	Codes	Variable levels				
		$-\alpha = -1.414$	-1	0	1	$+\alpha = 1.414$
Temperature, °C	X1	158.6	200	300	400	441.4
Catalyst conc, mass %	X2	2.93	5	10	15	17.07

moulded into the bottom. This guide provided the basic outline for the different types of plastics associated with each code number.

Catalyst clay was collected from the River Oren near Awasi Town in Kisumu County.

**2.2. Characterization of Clay Soil.** The clay sample was transferred into clean glass beakers, dried in the oven at 120°C for 3 hours, and then cooled in a desiccator. A dried clay sample was fed into a container and put inside the pulverizer for 2 minutes for grinding. Clay was ground into a fine powder of size 400  $\mu\text{m}$  suitable for use in the XRD and XRF laboratory analyses (Norton, 1974, Richerson, 1992).

XRF analysis was used to determine the percentage composition of the elements in oxide form. Oven-dried clay powder was accurately weighed in an electronic weighing balance and transferred into a clean, dry porcelain crucible. Starch powder weighing 2 g was added to the sample. The mixture was then ground, uniformly mixed into a fine powder using the pulverizer, and then transferred into the pellet binder. The clay-starch mixture was placed into a compressor and compressed to 175 KN to form clay pellets which were labelled and analyzed for mineral composition.

For the XRD analysis, dried clay powder was fed into a glass sample holder having a capacity of about 0.35 g of sample. A glass sample holder was mounted onto the diffractometer and then set to rotate the sample holder through angle  $\theta$ , while the detector rotates through  $2\theta$ . X-rays of Cu  $k\alpha$  wavelength  $1.54056 \times 10^{-10}$  m were selected and used to scan the samples. The scans were taken between  $2\theta$  of 10° and 45°.

**2.3. Experimental Setup.** Waste plastics were washed with tap water to remove dirt that was on the surface of the plastics. They were then sun-dried to remove moisture that

TABLE 2: X-ray fluorescence analysis result.

Component	Composition (mass %)
Na <sub>2</sub> O	1.9592
MgO	0.5597
Al <sub>2</sub> O <sub>3</sub>	16.3294
SiO <sub>2</sub>	64.4654
P <sub>2</sub> O <sub>5</sub>	0.0721
SO <sub>3</sub>	0.1052
Cl	0.0775
K <sub>2</sub> O	4.3336
CaO	1.1729
TiO <sub>2</sub>	0.7714
MnO	0.4677
Fe <sub>2</sub> O <sub>3</sub>	9.2879
ZnO	0.0304
Ga <sub>2</sub> O <sub>3</sub>	0.0068
As <sub>2</sub> O <sub>3</sub>	0.0023
Rb <sub>2</sub> O	0.0205
SrO	0.0167
Y <sub>2</sub> O <sub>3</sub>	0.0123
ZrO <sub>2</sub>	0.1526
Nb <sub>2</sub> O <sub>5</sub>	0.0508
BaO	0.0674
CeO <sub>2</sub>	0.0382

could interfere with the pyrolysis process. The plastics were then chopped by a knife to the required particle size range of 5-8 mm; this is the average size for higher production of

TABLE 3: Peak list (anorthoclase).

No.	2-theta (deg)	D (ang.)	Height (cps)	FWHM (deg)	Int. I (cps deg)	Int. W (deg)	Asym. factor
1	13.6253	6.49353	18.634	0.709403	26.807	1.438610	1.28816
2	23.66 (5)	3.758 (8)	53 (9)	1.5 (3)	165 (14)	3.1 (8)	5 (5)
3	26.6436	3.34295	40.8965	0.709403	58.8341	1.438610	1.28816
4	27.41 (2)	3.251 (3)	111 (14)	0.71 (7)	130 (9)	1.2 (2)	1.2 (4)
5	34.92 (7)	2.567 (5)	47 (9)	0.60 (10)	43 (7)	0.9 (3)	1.3 (6)

TABLE 4: Peak list (albite).

No.	2-theta (deg)	D (ang.)	Height (cps)	FWHM (deg)	Int. I (cps deg)	Int. W (deg)	Asym. factor
1	8.93483	9.88908	17.2301	0.1	4.05162	0.235148	1
2	20.1344	4.40656	30.8578	0.1	7.25615	0.235148	1
3	24.0591	3.69589	54.3549	0.1	12.7815	0.235148	1
4	27.7923	3.20733	132.652	0.1	31.1929	0.235148	1
5	37.4603	2.3988	25.5316	0.1	6.00372	0.235148	1
6	42.055	2.14673	22.454	0.1	5.28002	0.235148	1
7	47.0326	1.93048	13.2361	0.1	3.11245	0.235148	1

TABLE 5: Peak list (quartz).

No.	2-theta (deg)	D (ang.)	Height (cps)	FWHM (deg)	Int. I (cps deg)	Int. W (deg)	Asym. factor
1	20.1 (2)	4.41 (5)	38 (8)	1.5 (3)	74 (12)	2.0 (7)	0.5 (4)
2	23.68 (6)	3.754 (9)	88 (12)	0.23 (7)	33 (4)	0.38 (10)	0.8 (9)
3	26.684 (3)	3.3379 (4)	3075 (72)	0.098 (3)	374 (5)	0.122 (5)	0.99 (11)
4	27.61 (2)	3.229 (2)	156 (16)	0.60 (4)	117 (5)	0.75 (11)	0.99 (11)

TABLE 6: CCD matrix with experimental and predicted liquid oil yield for HDPE waste plastics.

Runs	Temp (°C)	Catalyst amount (wt%)	Liquid yield (mass %)	Predicted yield	Char (mass %)	Gas (mass %)
1	300	2.93	47.56	47.73	16.55	35.89
2	200	5	19.23	19.19	61.20	19.57
3	300	17.07	50.12	50.14	10.23	39.65
4	441.42	10	21.48	21.73	8.84	69.68
5	300	10	87.01	87.13	11.28	1.71
6	300	10	87.27	87.13	11.27	1.45
7	400	5	38.06	37.81	9.37	52.57
8	300	10	87.09	87.13	11.30	1.61
9	200	15	22.54	22.61	55.45	22.01
10	158.58	10	0	-2.18	98.54	1.46
11	400	15	37.96	37.81	10.02	52.02
12	300	10	87.27	87.13	11.26	1.47
13	300	10	87.02	87.13	11.40	1.58

liquid oil. A smaller particle size results in a higher gas yield. The feedstock was then ready for pyrolysis. The clay soil was dried in an oven at 105°C for 1 hour. The dried clay catalyst was crushed using a pulverizer. Powdered clay was sieved using a 400  $\mu\text{m}$  sieve to get a homogeneous fine powder.

The pyrolysis set-up consisted of an electric coil furnace, an electric sensor connected to a temperature control box, a round-bottomed glass flask with an arm, a Liebig condenser, water, and a sample collection flask. Chopped plastics were mixed with the catalyst and put into the round-bottomed

TABLE 7: ANOVA for quadratic model.

Source	Sum of squares	Df	Mean square	F value	p value	
Model	12385.67	5	2477.13	68199.92	<0.0001	Significant
A-temperature	571.65	1	571.65	15738.55	<0.0001	
B-catalyst amount	5.83	1	5.83	160.56	<0.0001	
AB	2.91	1	2.91	80.04	<0.0001	
A <sup>2</sup>	10407.48	1	10407.48	2.865E + 05	<0.0001	
B <sup>2</sup>	2537.58	1	2537.58	69864.01	<0.0001	
Residual	0.2543	7	0.0363			
Lack of fit	0.1870	3	0.0623	3.71	0.1191	Not significant
Pure error	0.0673	4	0.0168			
Cor total	12385.92	12				

flask for catalytic pyrolysis. In each experiment, 50 g of the HDPE feedstock was mixed with varying concentrations of catalysts (2.93 wt%-17.07 wt%) and heated by an electric coil furnace in a reaction flask to a specific temperature (range of 158.58°C-441.42°C). Pyrolysis products were separated through condensation, whereby the Liebig condenser was used to cool and condense the gases from the glass reactor; the vapors coming out after melting of the waste were passed through the Liebig condenser, and the liquid oil obtained was collected in a sample collection flask. The condensable gases produced liquid oil upon cooling, while the uncondensed gases produced during the experiment were left to escape into the atmosphere. The solid residue remained in the round-bottomed flask. At the end of each experiment, the mass of gas (noncondensable) was obtained by subtracting the mass of liquid oil and char from the total mass.

$$m_g = m_t - m_l - m_c, \quad (1)$$

where  $m_g$  is the mass of gas (g),  $m_t$  is the total mass of plastic feedstock and catalyst (g),  $m_l$  is the mass of liquid oil (g), and  $m_c$  is the mass of char (g).

The procedure was repeated for the other plastic types PP and PS at different temperature levels (158.58°C-441.42°C) and amounts of catalysts (2.93 wt%-17.07 wt%). Figure 1 shows the experimental setup of the experiment. A batch reactor was used in the pyrolysis process because the reactor is better for producing small amounts of products while still in the testing phase.

**2.4. Design of Experiment for Optimization Studies.** A 2-factor central composite design (CCD) and response surface methodology (RSM) in design expert software were used to study the effect of pyrolysis operating variables on the liquid fuel yield and also to identify conditions for optimal yield. A total of 13 experiments, including 5 replications at the center point, were conducted. Variables were reaction temperature and catalyst concentration with, 5 levels as given in Table 1. A full quadratic model for liquid fuel yield was tested, and a design-expert 13 was used for ANOVA and regression analyses.

### 3. Results and Discussion

**3.1. Characterization of Clay.** Elemental analysis of clay was performed using XRF. The results were given in Table 2.

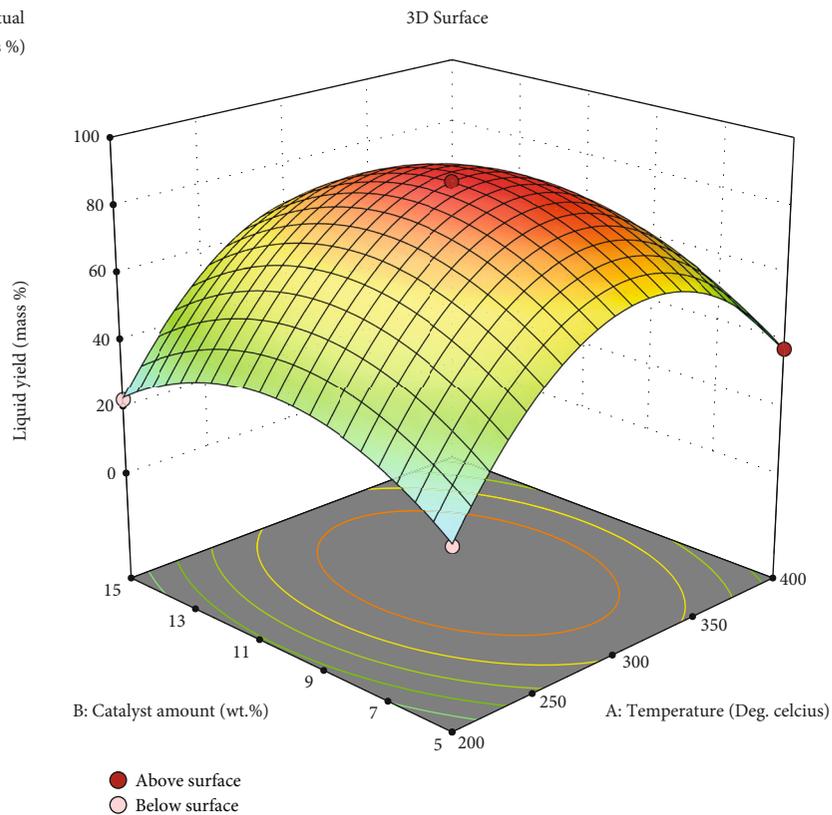
Results indicated that the clay from the River Oren, Kisumu County, had silica (64.5%), alumina (16.3%), and iron(II) oxide (9.3%) as the major elements. Other elements present were potassium oxide, sodium oxide, titanium oxide, calcium oxide, magnesium oxide, and manganese oxide. From the results, it was established that the clay had a high composition of silica and alumina (64.5 wt% and 16.3 wt%, respectively) and a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 3.96, being requirements for a good pyrolysis catalyst. Comparison was attributed to the analysis of clay from the Kano plains done by Oswago (SiO<sub>2</sub> 64.70 ± 0.10, Al<sub>2</sub>O<sub>3</sub> 13.65 ± 0.08, Fe<sub>2</sub>O<sub>3</sub> 3.74 ± 0.08, K<sub>2</sub>O 2.40 ± 0.05, Na<sub>2</sub>O 1.16 ± 0.02, TiO<sub>2</sub> 0.92 ± 0.02, CaO 0.56 ± 0.02, MgO 0.44 ± 0.0, MnO 0.02 ± 0.01). The acidity of the catalysts was determined by using the mole ratio of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. A low ratio of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> indicates the high acidity of the catalyst. The acidity of the catalysts affects the clay's reactivity, production yield, and composition of liquid oil from the pyrolysis of plastics (Uddin, 1997).

The mineral analysis of clay was done using XRD. The major minerals are anorthoclase KAlSi<sub>3</sub>O<sub>8</sub>, albite Na(AlSi<sub>3</sub>O<sub>8</sub>), quartz SiO<sub>2</sub>, and mordenite (Ca, Na<sub>2</sub>, K<sub>2</sub>)Al<sub>2</sub>Si<sub>10</sub>O<sub>24</sub>·7H<sub>2</sub>O. Tables 3-5 give the XRD peak list of the minerals contained in the clay. The silica-tetrahedron and alumina-octahedron layers are combined differently in each clay mineral, and this forms the basis of their identification and differentiation by X-ray diffraction. The results establish that the clay mineral is composed of tetrahedra of silica and alumina as structural components and is linked through oxygen atoms. Each oxygen atom is shared by two silicon or aluminium atoms, thus giving rise to a three-dimensional microporous structure.

**3.2. Process Optimization.** This involved the study of the pyrolysis operating variables, that is, the catalyst concentration and reaction temperature on liquid oil yield. Optimization studies involved analyzing the process variables for the maximum yield. Experimental data were fitted into the correlation, which was then plotted in surface and contour plots that depict the optimal conditions. The waste plastics used

Factor coding: Actual  
 Liquid yield (mass %)  
 Design points:

0  87.27  
 X1 = A  
 X2 = B



Factor coding: Actual  
 Liquid yield (mass %)  
 Design points:

-4.85  60.72  
 X1 = A  
 X2 = B

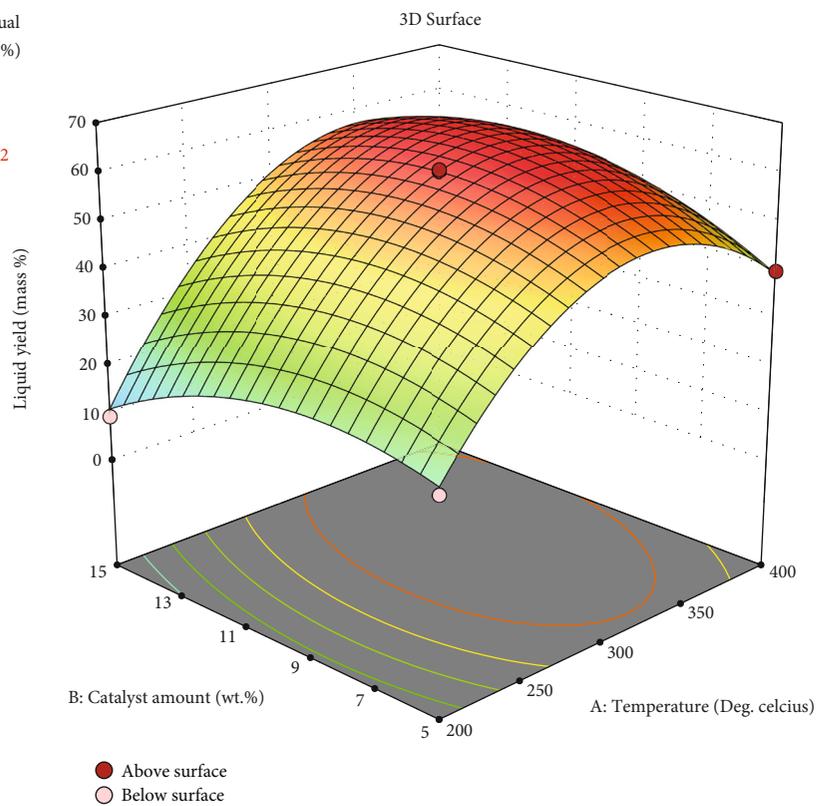


FIGURE 2: Continued.

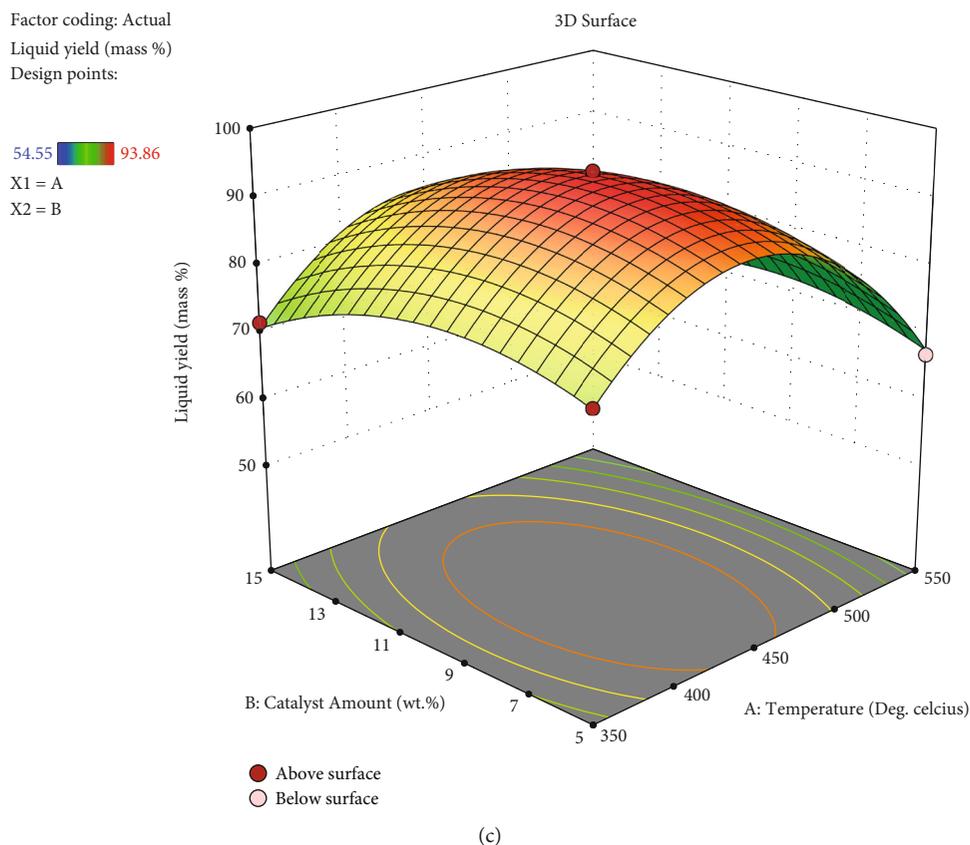


FIGURE 2: (a–c) RSM plot for the effect of the catalyst concentration and temperature on yield for HDPE, PP, and PS liquid oil.

TABLE 8: CCD matrix with experimental and predicted liquid oil yield from PP waste plastics.

Runs	Temp (°C)	Catalyst amount (wt%)	Liquid yield (mass %)	Predicted yield	Char (mass %)	Gas (mass %)
1	300	10	60.40	60.36	14.68	24.92
2	200	15	9.36	9.53	69.30	21.34
3	300	10	60.14	60.36	15.20	24.66
4	300	10	60.18	60.36	15.25	24.57
5	300	10	60.36	60.36	14.91	24.73
6	400	5	40.10	39.75	7.27	52.63
7	158.58	10	0	-5.05	98.72	1.28
8	300	10	60.72	60.36	14.34	24.94
9	300	2.93	43.82	43.99	6.18	50.00
10	441.42	10	38.01	38.38	10.18	51.81
11	200	5	20.71	20.77	55.75	23.54
12	300	17.07	44.68	44.69	16.36	38.96
13	400	15	52.20	51.97	18.55	29.25

for the optimization study were high-density polyethylene, polypropylene, and polystyrene.

**3.2.1. High-Density Polyethylene Waste Plastics.** The central composite design matrix for RSM is given in Table 6.

From Table 6, for HDPE, the highest oil yield (87.23 wt%) corresponds to a pyrolysis temperature of

300°C and 10% catalyst. At temperatures below 200°C, there was no degradation of the waste plastic, but as the temperature increased, the liquid oil yield increased in quantity. The gaseous product was high at temperatures above 400°C, and the liquid oil yield decreased; this was mainly because the process had passed the maximum thermal degradation point. HDPE consists of a long chain and

TABLE 9: ANOVA for response surface quadratic model.

Source	Sum of squares	Df	Mean square	F value	p value	
Model	5532.65	5	1106.53	12315.48	<0.0001	Significant
A-temperature	1886.31	1	1886.31	20994.25	<0.0001	
B-catalyst amount	0.4833	1	0.4833	5.38	0.0535	
AB	137.48	1	137.48	1530.08	<0.0001	
A <sup>2</sup>	3319.87	1	3319.87	36949.55	<0.0001	
B <sup>2</sup>	446.40	1	446.40	4968.36	<0.0001	
Residual	0.6289	7	0.0898			
Lack of fit	0.4169	3	0.1390	2.62	0.1873	Not significant
Pure error	0.2120	4	0.0530			
Cor Total	5533.28	12				

TABLE 10: CCD matrix with experimental and predicted liquid oil yield from PS waste plastics.

Std	Run	Temp °C	Catalyst amount (wt%)	Liquid yield (mass %)	Predicted yield	Char (mass %)	Gas (mass %)
11	1	450	17.07	77.47	78.05	16.23	6.30
5	2	308.58	10	64.02	64.68	28.18	7.80
13	3	450	10	93.86	93.30	3.60	2.54
3	4	350	5	77.14	77.01	12.38	10.48
2	5	350	15	71.79	70.95	14.78	13.43
1	6	550	5	67.01	67.71	7.62	25.37
8	7	450	10	93.45	93.30	4.55	2.00
10	8	450	10	92.73	93.30	2.73	4.54
12	9	450	10	93.27	93.30	3.64	3.09
9	10	591.42	10	54.55	54.04	11.34	34.11
4	11	450	10	93.18	93.30	4.55	2.27
7	12	550	15	65.22	65.20	14.78	20.00
6	13	450	2.93	84.54	84.11	11.67	3.79

follows the random chain scission mechanism during its thermal degradation; this requires a relatively higher temperature [11].

(1) *ANOVA for Quadratic Model.* Table 7 shows the ANOVA for the quadratic model.

The model  $F$  value of 68199.92 implies that the model was significant. There was only a 0.01% chance that an  $F$  value this large could occur due to noise.  $p$  values less than 0.0500 indicate that model terms are significant. In this case, A, B, AB, A<sup>2</sup>, and B<sup>2</sup> were significant model terms. Values greater than 0.1000 indicate that the model terms were not significant. The lack of fit  $F$  value of 3.71 implies that the lack of fit was not significant relative to the pure error. There was an 11.91% chance that a lack of fit  $F$  value this large could occur due to noise. The lack of fit was insignificant; hence, the model did fit. The predicted  $R^2$  of 0.9999 was in reasonable agreement with the adjusted  $R^2$  of 1.0000, i.e., the difference is less than 0.2. Adequate precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio of 689.806 indi-

cates an adequate signal. This model can be used to predict yield as a function of variables A and B. The model that predicts the yield of pyrolytic liquid oil in terms of coded factors is given by

$$\text{Yield (Y)} = 87.13 + 8.45A + 0.8538B - 0.8525AB - 39.68A^2 - 19.10B^2, \quad (2)$$

where A refers to temperature and B is the actual catalyst concentration as a percentage of waste plastics. Equation (2) was used to plot the response surface and contours of pyrolytic oil yield. The optima lie close to a temperature of 300°C and a catalyst concentration of 10 wt%. Figure 2 shows the RSM plot for the effect of the catalyst concentration and temperature on yield for HDPE liquid oil.

*3.2.2. Polypropylene Waste Plastics.* The thermal degradation of polypropylene waste plastics started at around 240°C. The increase in temperature to 400°C reduced the product conversion and increased the gaseous product. From this study, it was found that the highest total conversion happened at 300°C, with liquid oil being the dominant product yield

TABLE 11: ANOVA for quadratic model.

Source	Sum of squares	Df	Mean square	F value	p value	
Model	2263.94	5	452.79	1020.10	<0.0001	Significant
A-temperature	113.20	1	113.20	255.02	<0.0001	
B-catalyst amount	36.72	1	36.72	82.72	<0.0001	
AB	3.17	1	3.17	7.14	0.0319	
A <sup>2</sup>	2003.40	1	2003.40	4513.54	<0.0001	
B <sup>2</sup>	259.72	1	259.72	585.14	<0.0001	
Residual	3.11	7	0.4439			
Lack of fit	2.43	3	0.8103	4.79	0.0821	Not significant
Pure error	0.6763	4	0.1691			
Cor total	2267.05	12				

(60.36 wt%). Ahmad et al. [26] on PP catalytic pyrolysis summarized that the highest liquid oil was achieved at a temperature of 300°C at around 69.82 wt% which is comparable to this study. Kim et al. [27] explained that the natural zeolite with its low BET surface area, microporous structure, and low acidity supports the initial degradation of PP that may increase gas production as observed. Table 8 shows the CCD matrix with experimental and predicted liquid oil yields for polypropylene plastics.

(1) *ANOVA for Response Surface Quadratic Model.* Table 9 shows the ANOVA for the response surface quadratic model.

The model  $F$  value of 12315.48 implied that the model was significant. There was only a 0.01% chance that an  $F$  value this large could occur due to noise.  $p$  values less than 0.0500 indicate that the model terms were significant. In this case, A, AB, A<sup>2</sup>, and B<sup>2</sup> are significant model terms. Values greater than 0.1000 indicated that the model terms were not significant. The lack of fit  $F$  value of 2.62 implies that the lack of fit was not significant relative to the pure error. There was an 18.73% chance that a lack of fit  $F$ -value this large could occur due to noise. A nonsignificant lack of fit was good.

The predicted  $R^2$  of 0.9994 was in reasonable agreement with the adjusted  $R^2$  of 0.9998, i.e., the difference was less than 0.2. Adequate precision measured the signal-to-noise ratio. A ratio greater than 4 was desirable. The ratio of 321.192 indicated an adequate signal. This model can be used to predict the yield as a function of the variables A and B. The model that predicts the yield of pyrolytic liquid oil in terms of coded factors was given by

$$\text{Yield, } Y = 60.36 + 15.36A + 0.2458B + 5.86AB - 21.85A^2 - 8.01B^2, \quad (3)$$

where  $A$  refers to temperature and  $B$  is the actual catalyst concentration as a percentage of waste plastics. Equation (3) was used to plot the response surface and contours of pyrolytic oil yield. The optima lie close to a temperature of 300°C and a catalyst concentration of 10 wt%. Figure 2(b)

shows the RSM plot for the effect of the catalyst concentration and temperature on yield for PP liquid oil.

3.2.3. *Polystyrene Waste Plastics.* From the experiment, it was found that the highest total conversion happened at 450°C, with liquid oil being the dominant product yield (93.20 wt%). Increasing the temperature further reduced the production of liquid oil and increased the gaseous product. PS plastic waste produced the highest amounts of liquid oil as compared to all other types of plastic waste in this study. Polystyrene degradation follows both end-chain and random-chain scission mechanisms which enhance its degradation process.

The optimal temperature obtained is comparable to Onwudili et al. [28], who investigated the pyrolysis of PS and found that a very high liquid oil yield of around 97.0 wt% was reached at an optimum temperature of 430°C. The high yield of liquid oil product was also supported by Liu et al. [29]; the amount of liquid oil produced was around 97.6 wt% at a temperature of 450°C. Lee et al. [30] reported a higher liquid oil yield from the catalytic pyrolysis of PS with natural zeolite, correlating it with the low BET surface area, acidity, and microporous structure of the natural zeolite. Based on the study done by Alkan, the liquid oil was reduced to 89.5 wt% when the PS pyrolysis was running at 581°C in a batch reactor. Table 10 shows the CCD matrix with experimental and predicted liquid oil yields for polypropylene plastics.

(1) *ANOVA for Response Surface Quadratic Model.* Table 11 shows the ANOVA for the quadratic model.

The model  $F$  value of 1020.10 implies that the model was significant. There was only a 0.01% chance that an  $F$  value this large could occur due to noise.  $p$  values less than 0.0500 indicated that the model terms were significant. In this case, A, B, AB, A<sup>2</sup>, and B<sup>2</sup> were significant model terms. Values greater than 0.1000 indicated that the model terms were not significant. The lack of fit  $F$  value of 4.79 implies that there was an 8.21% chance that a lack of fit  $F$  value this large could occur due to noise. The predicted  $R^2$  of 0.9919 was in reasonable agreement with the adjusted  $R^2$  of 0.9977, i.e., the difference is less than 0.2. Adequate precision

measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio of 86.741 indicated an adequate signal. This model can be used to predict yield as a function of variables  $A$  and  $B$ . The model that predicts the yield of pyrolytic liquid oil in terms of coded factors is given by

$$\text{Yield, } Y = 93.30 - 3.76A - 2.14B + 0.89AB - 16.97A^2 - 6.11B^2, \quad (4)$$

where  $A$  refers to temperature and  $B$  is the actual catalyst concentration as a percentage of waste plastics. Equation (4) was used to plot the response surface and contours of pyrolytic oil yield. The optima lie close to a temperature of 450°C and a catalyst concentration of 10 wt%. Figure 2(c) shows the RSM plot for the effect of the catalyst concentration and temperature on yield for PS liquid oil.

#### 4. Conclusions

A petroleum-based fuel was produced using three types of waste plastics through catalytic pyrolysis, namely, high-density polyethylene, polypropylene, and polystyrene. Indigenous clay was found to have the potential to be used for the pyrolysis of plastic wastes since high yields of liquid fuel were obtained at lower reaction temperatures of 300–450°C, as compared to the 600°C required for thermal pyrolysis. In addition, the clay has a high composition of silica and alumina at 64.5 wt% and 16.3 wt%, respectively, and an  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 3.96, being required for a good pyrolysis catalyst. This will reduce the energy requirement considerably, improve overall process optimization, and improve fuel quality. The optimum conditions for the plastic waste were found based on the liquid oil yield. The liquid oil from catalytic pyrolysis is of good quality and can be used in several energy related applications such as electricity generation, transport fuel, and heating source. The gaseous products can be used to reheat the raw material to reduce the cost of production. Further studies on the modification of the surface and structure of clay are suggested to enhance its catalytic performance in the pyrolysis process for a better fuel yield.

#### Data Availability

The article contains all the relevant data. The corresponding author would provide any additional data upon request.

#### Disclosure

This manuscript is part of the thesis that was presented in “<http://ir.mu.ac.ke:8080/jspui/bitstream/123456789/5491/1/ZEDDY%20C%20MIBEI%202021.pdf>” at Moi University on 7th October 2021.

#### Conflicts of Interest

The authors declare that they have no conflict of interest.

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