



CATALYTIC PYROLYSIS OF WASTE PLASTICS INTO LIQUID HYDROCARBON USING MESOPOROUS KAOLIN CLAY

MAHMUDUR RAHMAN^{1*}, SUBRATA CHANDRA ROY¹, MD-MIZANUL HASSAN², BIJOY KUMAR MONDAL³, MUHAMMAD OMAR FARUK², MD. ARIFUR RAHMAN¹, MUHAMMAD ZAHIDUZZAMAN¹, AYESHA SHARMIN², MD. JUWEL HOSEN⁴, MIROLA AFROZE⁴, MALA KHAN⁴, ZINIA NASREEN³, MD. ABDUL MATIN⁵

¹Department of Chemistry, Jagannath University, Dhaka 1100, Bangladesh

ABSTRACT

Catalytic pyrolysis of waste plastics into liquid hydrocarbon was conducted in a locally-made stainless steel reactor. Mesoporous kaolin clay treated with sulfuric acid in the concentration range of 3-7 M was used as a catalyst and waste polyethylene was the plastic feed. The X-ray powder diffraction (XRPD) pattern showed that the raw kaolin clay is crystalline. However, XRPD patterns of H₂SO₄ acid treated kaolin and Ni and Ru metal impregnated H₂SO₄ treated kaolin did not exhibit any characteristic diffraction peaks of kaolin. The acid treatment of kaolin causes leaching of Al³⁺ and results in disintegration of layered structure of kaolin, leading to the formation of Al₂(SO₄)₃, SiO₂, and amorphous phase. After 5 M H₂SO₄ acid treatment, the content of Al₂O₃ decreased significantly to 18.62%. The Si/Al ratio and specific surface area were found to increase after 5 M sulfuric acid treatment from 1.79 to 3.48 and 6.85 m²/g to 17.92 m²/g, respectively. The nitrogen adsorption-desorption isotherms of the 5 M H₂SO₄ acid treated kaolin clay showed the isotherm to be of type IV typical for mesoporous structure. Among 3, 5, and 7 M H₂SO₄ treated kaolin catalysts, the 3 M H₂SO₄ treated kaolin (at a catalyst to plastic feed ratio of 1:5) exhibited the highest activity with the yield of 83% liquid hydrocarbon. The Ru- and Ni-impregnated 5 M H₂SO₄ treated kaolin catalyst provided 76% and 79% yield, respectively of liquid hydrocarbon at a catalyst to plastic ratio of 1:5. The gas chromatography-mass spectrometry (GC-MS), ¹H NMR, and FTIR spectral analysis confirmed the presence of linear and branched alkanes and alkenes (C₉-C₂₀) in the end product obtained with 5 M H₂SO₄ treated kaolin catalyst. The produced liquid hydrocarbon was found to be free from aromatic compounds importantly polycyclic aromatic hydrocarbons which are potent mutagenic and carcinogenic.

Keywords: H₂SO₄ treated kaolin, metal-impregnated kaolin, polyethylene, liquid hydrocarbon, catalyst.

INTRODUCTION

Plastics have become integral part of our modern life. Plastics are used in numerous applications such as packaging, electronics, construction, medical, automotive, aerospace, food and many more. The global demand of plastics is increasing by 4% per year (Yan *et al.* 2015 and Al-Salem *et al.* 2017). Plastics do not degrade and stay for decades in soil due to their non-biodegradability. For this reason, plastic wastes have become a major environmental concern in many countries.

Common methods for disposal of waste plastics are landfill, incineration (energy recovery), mechanical (similar recycled product) and chemical recycling (Al-Salem *et al.* 2017). More prominently, plastic waste is more voluminous than the organic waste and thus takes up a huge amount of landfill space. Moreover, land filling is becoming more expensive and undesirable in environmental aspect. Mechanical recycling means processing of used plastics to make similar or low grade products. The recycled plastic materials show inferior mechanical

*Corresponding author: <mm_rahman1978@yahoo.co.uk>

²Department of Chemistry, Bangladesh University of Engineering and Technology, Dhaka 1000, Bangladesh

³Department of Chemistry, Dhaka University of Engineering and Technology, Dhaka-1000, Bangladesh

⁴Designated Reference Institute for Chemical Measurements, Bangladesh Council of Scientific and Industrial Research, Dhaka 1205, Bangladesh

⁵Department of Glass and Ceramic Engineering, Bangladesh University of Engineering and Technology, Dhaka 1000, Bangladesh

quality and lack of durability than those made from virgin polymers. Incineration to recover energy is also not a suitable option as it produces toxic gases like dioxins and furans (Serrano *et al.* 2012). The only sustainable solution could be converting the waste plastics to high value liquid fuel and this can be achieved by thermal and catalytic pyrolysis process (Aguado *et al.* 2008). Drawback of thermal process is that the plastic wastes are degraded only at high temperature (400-800 °C). Moreover, a broad range of hydrocarbons is produced which needs further processing for application as gasoline fuel (C₅-C₁₂). In this respect, catalytic degradation of waste plastic is more promising (Serrano *et al.* 2012 and Aguado *et al.* 2008). Catalysts developed for cracking of waste plastics are zeolite (ZSM-5 and zeolite-Y), silica-alumina, spent FCC catalysts, and MCM-41 (Chandrasekaran *et al.* 2015, Aguado *et al.* 1997, Ratnasari *et al.* 2017). Acidity, porosity and surface area are attributed for the catalytic activity in those catalysts. The clay-based catalysts have weaker acidity and they are cheap and abundant. The kaolin clay is a hydrated alumino-silicate as major quantities and trace amount of oxides of magnesium, calcium, potassium, zinc and titanium. It is a 1:1 clay having one (SiO₄) tetrahedral layer and one (AlO₆) octahedral layer.

Manons *et al.* (2001) reported catalytic cracking of polyethylene using two types of smectites: a saponite and a montmorillonite clay. In smectites (2:1 clay) an octahedral sheet is sandwiched between two tetrahedral sheets. Catalytic pyrolysis of waste high-density polyethylene (HDPE) using 3 M nitric acid treated kaolin clay catalyst produces oil of alkanes and alkenes with carbon C₁₀-C₂₅ (Kumar *et al.* 2013). Uzair *et al.* (2016) reported degradation of polypropylene at 470 °C using 1, 3 and 5 M HCl activated kaolin clay. The 3 M HCl activated kaolin clay catalyst produces hydrocarbon oil containing alkanes and alkenes

with carbon C₆-C₁₂. The products are branched and mostly alkenes. Panda *et al.* (2010) reported only the effect of 1, 3, 5, and 10 M sulfuric acid treated kaolin clay on its structural and chemical properties. They found that kaolin clay becomes amorphous with treatment of 5 and 10 M H₂SO₄. Leaching of Al³⁺ increases with increasing the concentration of sulfuric acid (Makó *et al.* 2006). However, pyrolysis of waste plastics with sulfuric acid treated kaolin has not been explored yet. Hakeem *et al.* (2018) reported the use of raw Ahoko kaolin from Nigeria without performing any treatment as a catalyst for pyrolysis of polypropylene. They found that the produced liquid oil contains hydrocarbons with different functional groups such as aromatics, olefins, carbonyl, amines and hydroxyl. Here we report catalytic pyrolysis of waste polyethylene in a locally-made stainless steel batch reactor using different concentrated sulfuric acid treated kaolin clay catalysts. The nickel and ruthenium impregnation on H₂SO₄ treated kaolin clay catalysts have also been explored to improve yield of liquid and also promote hydrogenation of the liquid hydrocarbons.

MATERIALS AND METHODS

Low cost kaolin clay was collected from Rajasthan, India. Sulfuric acid was purchased from Sigma Aldrich. Waste plastics used consisted of colorless polyethylene (PE) shopping bags which were collected from waste bins, near the Jagannath University, Dhaka. Collected waste plastic was thoroughly cleaned with water and then dried and cut into small pieces in 1-2 cm rectangle shape and was made ready to feed into the reactor as starting material for catalytic pyrolysis. Assuming the formula of polyethylene to be (□CH₂ □)_n with n = 20000, its carbon and hydrogen contents are 85.63, and 14.37%, respectively.

*Preparation of catalysts***3, 5 and 7 M sulfuric acid treatment of kaolin:**

Kaolin (40 g) was added to 3 M sulfuric acid (400 mL) solution in a 1000 mL round-bottom flask. It was refluxed for 4 hours at 120 °C. The resulting suspension was filtered and excess acid and accompanying soluble metal salt was washed away with distilled water. The final catalyst was prepared by drying it at 120 °C for 12 h and was calcined at 550 °C for 14 h in a muffle furnace. The amount of final catalyst was 30 g. Similarly, 5 and 7 M sulfuric acid treated kaolin catalysts were prepared and the final amount of catalyst was 28 g and 26 g, respectively.

Ruthenium and nickel impregnated 5 M sulfuric acid treated kaolin:

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and 5 M sulfuric acid treated kaolin were taken in the mass ratio of $m(\text{Ni})/m(\text{kaolin}) \approx 0.05$, i.e. 5 g Ru metal in 100 g kaolin. 100 mL of deionized water was added to 2.8 g of 5 M sulfuric acid treated kaolin. The kaolin suspension was heated at 120 °C with stirring. After 30 minutes, the ruthenium chloride solution (dissolving 0.34 g $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in 30 mL deionized water) was added drop wise to the kaolin suspension and kept heating at 120 °C with continuous stirring. The slurry was dried at 100 °C for 12 h and then calcined at 400 °C for 4 h. Ni-impregnated 5 M sulfuric acid treated kaolin was also prepared accordingly. Here the precursor was 1.24 g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 5 M sulfuric acid treated kaolin was 5.0 g. The obtained catalysts contain nominal 5 wt% of each metal.

Characterization Techniques

The raw and acid treated kaolin catalysts were characterized by X-ray fluorescence (XRF), X-ray powder diffraction (XRPD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and nitrogen adsorption/desorption isotherms. The

product of catalytic pyrolysis was analyzed by GC-MS, FTIR and ^1H NMR spectroscopy.

The XRF analyses of the samples were done using XRF-1800 (Lab Center), Shimadzu, Japan. 1.0 g sample was ground and mixed with 0.25 g boric acid as binder and pressed it into pellets. The sample was excited by primary Rh x-ray source operated at 30 kV, and 140 mA.

The XRPD patterns of the raw and acid treated kaolin clay were taken with a PANalytical Empyrean diffractometer. The operating conditions of the diffractometer were 40 kV, 40 mA, $\text{Cu-K}\alpha_1$ radiation ($\lambda = 1.54051 \text{ \AA}$), exposure time 3 deg/minute.

FTIR spectra were recorded on Shimadzu 8400S, Japan using KBr pellets in the range of 400-4000 cm^{-1} . Both the catalyst and KBr were dried at 100 °C for one day prior to the analysis. The specific surface area and pore volume were determined by measuring nitrogen adsorption-desorption isotherms at liquid N_2 temperature (-196 °C) with a BELSORP MINI-11 (BEL Japan) apparatus. Belsorp Adsorption/Desorption Data Analysis Software-Ver.6.1.0.8 was used for data analysis and evaluation of BET surface area and pore size distribution. Before each measurement, the samples were pretreated at 165 °C for 1.5 hours, under N_2 gas flow. SEM images were recorded on a JEOL-SEM, VERSION 3, 7600F, equipped with an energy dispersive X-ray spectrometry detector at 5 kV. The clay was placed on a sample holder with an adhesive carbon foil and sputtered with gold before analysis.

Liquid hydrocarbon obtained by 5 M H_2SO_4 treated kaolin catalyst was analyzed by GC-MS (Agilent Technologies 7890A /5975C) with a capillary column HP-5MS (30 m length \times 0.250

mm id). Sample (0.5 μL) was injected in splitless mode where the inlet temperature was set at 250 $^{\circ}\text{C}$ and oven temperature was programmed as 40 $^{\circ}\text{C}$ for 1 min. Then it was increased at the rate of 2 $^{\circ}\text{C}/\text{min}$ up to 150 $^{\circ}\text{C}$. Column flow rate was 1 mL/min and total run time was 57 min. MS detection was conducted with electron impact ionization conditions in full scan mode from 50-550 m/z. The quadrupole mass analyzer was used as mass analyzer in GC-MS analysis. The individual hydrocarbons were identified by computer-assisted mass spectral search by NIST-MS library 2009.

^1H NMR spectrum was recorded at room temperature on a Bruker (model AVANCE III HD, 400 MHz) and the chemical shifts were reported relative to SiMe_4 ($\delta = 0$).

Catalytic pyrolysis experiment

The catalytic degradation of waste polyethylene was carried out in a locally-made stainless steel batch reactor as shown in Fig. 1. The reactor was washed well with acetone, dried and purged with N_2 gas. The catalyst and waste polyethylene

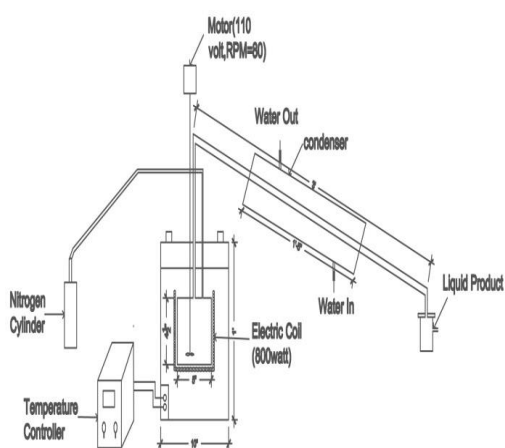


Fig. 1. Locally-made stainless steel batch reactor for catalytic cracking of waste plastics.

pieces were fed into the reactor at different catalyst to plastic ratio. N_2 gas was purged again. The reactor temperature was set to 450 $^{\circ}\text{C}$ and at particular range of temperature liquid hydrocarbon started to appear in the collection chamber. Each pyrolysis experiment was carried out for 40 minutes. The yield of liquid oil product was calculated as follows:

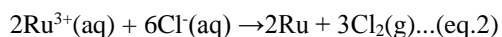
$$\text{Yield}(\text{wt}\%) = \frac{\text{mass of product}}{\text{mass of starting material}} \times 100\% \dots (\text{eq. 1})$$

RESULTS AND DISCUSSION

Catalyst characterization

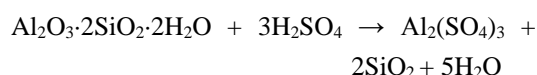
The XRPD was used to analyze the structural changes that occur in the kaolin clay due to sulfuric acid treatment (Fig. 2). The parent clay is crystalline and shows characteristic peaks at 2θ (hkl) values of 12.30 $^{\circ}$ (001) and 24.90 (002) (Hanawalt *et al.* 1938). However, H_2SO_4 treatment alters the crystal structure of kaolin. The XRPD patterns of 3, 5, 7 M H_2SO_4 treated kaolin and even Ru and Ni metal impregnation on H_2SO_4 treated kaolin do not show any characteristic diffraction peaks of kaolin (Fig. 2). Treatment of parent kaolin with H_2SO_4 (3, 5, 7 M), causes leaching of Al^{3+} and results in disintegration of the layered structure of kaolin, leading to the formation of $\text{Al}_2(\text{SO}_4)_3$, SiO_2 , and amorphous phase. Characteristics XRPD peaks of $\text{Al}_2(\text{SO}_4)_3$ are found at 2θ (hkl) values of 15.20 $^{\circ}$ (012), 21.00 $^{\circ}$ (104), 25.53 $^{\circ}$ (113), 30.65 $^{\circ}$ (024), 33.60 $^{\circ}$ (116) (Hubbard and Carmel 1978) and SiO_2 are found at 2θ (hkl) values of 21.00 $^{\circ}$ (100) and 26.60 $^{\circ}$ (101) (Liu *et al.* 1994). Humps at the XRPD patterns are indicative of amorphous phase. On the other hand, XRPD patterns of Ru- and Ni-impregnation on 5 M

H₂SO₄ treated kaolin show mostly amorphous phase indicated by huge hump. Formation of noble Ru⁰ metal at 2θ (hkl) values of 44.60° (101) (Hanawalt *et al.* 1938) can be attributed to the redox reaction between Ru³⁺ and Cl⁻ (eq. 2).



The chemical composition of the raw and 5 M H₂SO₄ treated kaolin clay was obtained by XRF analysis as shown in Table 1. The main components of raw kaolin clay contain 30.72 % Al₂O₃ and 62.56 % SiO₂. The Si/Al ratio

reported the increase of Si/Al ratio after acid treatment and the increase became higher as the concentration of the acid was increased. The reaction between kaolin clay and sulfuric acid is as follows (Makó *et al.* 2006 and Panda *et al.* 2010):



The formation of Al₂(SO₄)₃ and SiO₂ after sulfuric acid treatment was also confirmed by the XRPD patterns (Fig. 2). Although Al₂(SO₄)₃ is soluble in water, after several times washing with distilled water some Al₂(SO₄)₃ was found to be left over in acid treated catalyst material. After 5 M H₂SO₄ acid treatment of kaolin, the amount of TiO₂ remains unchanged and SO₃ increases. SO₃ forms from sulfuric acid which is used for acidification of kaolin clay. Similar observation was reported by Temuujin *et al.* (2001). SO₃ may also come from the decomposition of aluminum sulfate (Truex *et al.* 1997). On the other hand, Okada *et al.* (1998) found a different observation. They found that TiO₂ content increases after H₂SO₄ treatment of kaolin (Okada *et al.* 1998). Temuujin *et al.* (2001) reported that the content of K₂O significantly reduced after 2.5 M H₂SO₄ acid treatment. However, in our experiment we found that K₂O content remain unchanged after H₂SO₄ treatment. It is worthwhile to note that the sensitivity of XRF for light element like K, Na detection is low (Declercq *et al.* 2019). Moreover, Önal and Sarikaya (2007) investigated sulfuric acid treated bentonite clay and found that K₂O content did not change much even at higher concentrations of sulfuric acid. The yield of liquid hydrocarbon significantly

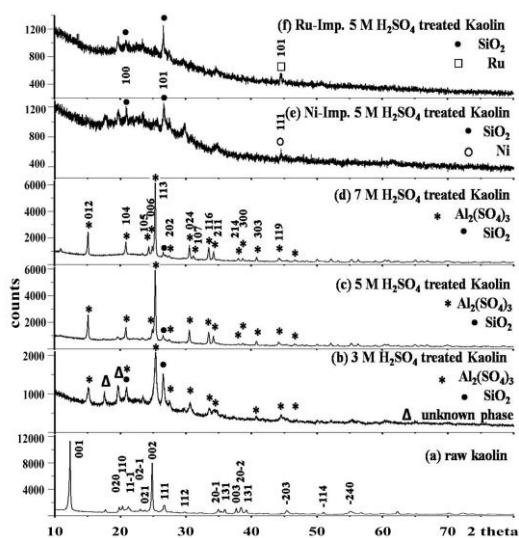


Fig. 2. X-ray powder diffraction patterns of parent kaolin (a), 3, 5, 7 M H₂SO₄ treated kaolin (b, c, d) respectively, and metal impregnated kaolin treated with 5 M H₂SO₄ (e, f).

obtained is 1.73 which is very close to the value observed by Hakeem *et al.* (2018) in Ahoko kaolin of Nigeria. This ratio changed considerably after acid treatment due to leaching of Al₂O₃. In this sample, the Al₂O₃ content decreased to 18.62 % and the Si/Al ratio increased from 1.79 to 3.48. Panda *et al.* (2010)

increased (from 33 to 83%, Table 2) due to acid activation of kaolin compared to parent kaolin.

The BET experiment showed that the specific surface area and pore volume increased due to acid treatment.

Table 1. Chemical composition of parent and 5 M sulfuric acid treated kaolin (obtained by XRF), compared with Ahoko kaolin from Nigeria (Hakeem *et al.* 2018).

Types of kaolin	SiO ₂	Al ₂ O ₃	K ₂ O	Fe ₂ O ₃	MgO	P ₂ O ₅	TiO ₂	Na ₂ O	CaO	SO ₃	Rb ₂ O	Cr ₂ O ₃	MnO	SrO	ZrO ₂	Si/Al
Raw kaolin (%)	62.56	30.72	4.35	1.23	0.46	0.13	0.11	0.09	0.09	0.06	0.05	0.03	0.02	0.01	0.009	1.79
5 M H ₂ SO ₄ treated kaolin (%)	73.53	18.62	4.33	0.84	0.35	0.03	0.10	0.06	0.04	1.98	0.04	-	0.02	-	-	3.48
Ahoko kaolin (%)	72.26	18.96	0.43	1.05	0.13	-	1.485	0.021	-	-	-	-	0.004	-	-	1.90

The N₂ adsorption/desorption isotherms of parent and 5 M sulfuric acid treated kaolin clay are shown in Fig. 3. The isotherm is type IV. This type of isotherm is found in mesoporous material (Panda *et al.* 2010 and Sing *et al.* 1985). The hysteresis loops of both untreated and acid treated clay are similar to type H3 which are typical of agglomerates of plate like particles containing slit-shaped pores. The catalyst is mostly mesoporous.

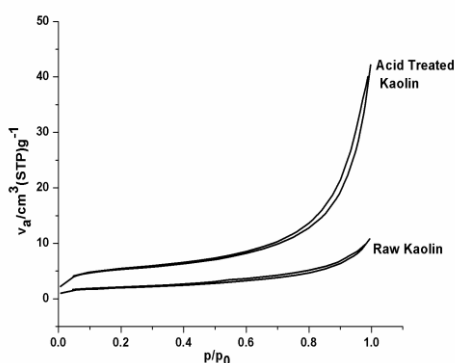


Fig. 3. N₂ adsorption/desorption isotherms of parent and 5 M H₂SO₄ treated kaolin clay.

The increase in specific surface area and pore volume is due to de-alumination leading to the change of microstructure and formation of amorphous phase. The Si/Al ratio and specific surface area were found to increase after 5 M sulfuric acid treatment from 1.79 to 3.48 and 6.85 m²/g to 17.92 m²/g, respectively.

The BJH pore size distribution (Fig. 4) of parent clay shows the presence of well-defined pores with 2.1 nm diameter. On the other hand, 5 M H₂SO₄ treated kaolin clay exhibits a very wide distribution of pore sizes.

In fact, this material presents pores with sizes in the whole range between 1.2 and 100 nm with many maxima denoting the irregularity of its pore structure. The increased surface area and mesoporosity is due to breakdown of the crystal structure of kaolin and leaching out of Al₂O₃ by the acid.

The leaching out of Al₂O₃ from kaolinite in acids varies with the nature and concentration of the acid, the acid-to-kaolinite ratio, the temperature, and the duration of treatment (Okada *et al.* 1986, Temujin *et al.* 2001). More

disintegration of kaolinite occurs with sulfuric acid compared to hydrochloric acid (Mako *et al.* 2006). After H_2SO_4 treatment, no x-ray diffraction peak of kaolin was observed (Fig. 2).

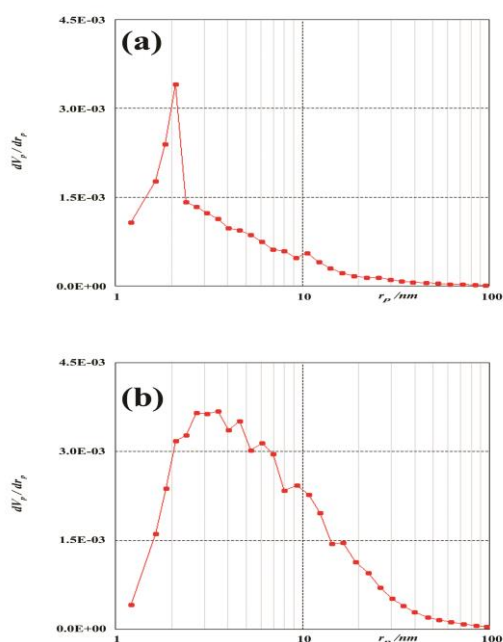


Fig. 4. BJH pore size distribution of parent (a), and 5 M H_2SO_4 treated kaolin clay (b).

H_2SO_4 treatment leads to the collapse of the silica-oxygen network which covers the Al^{3+} ions and the Al-O-Si bonds and hence to severe leaching of Al^{3+} , and other ions destroying the kaolin structure (Panda *et al.* 2010). Severe leaching of cations from kaolin results in mesoporosity, amorphization, and increased surface area of kaolin. However, upon treatment with 5 M HCl, only the intensities of the x-ray diffraction peaks of kaolin decreased compared to raw kaolin which indicate low disintegration of kaolin by HCl (Uzair *et al.* 2016).

The SEM images of raw and 5 M H_2SO_4 treated kaolin are shown in Fig. 5. The SEM image of

untreated kaolin shows layered-type particles and it is crystalline. However, after acid treatment, there are no more layered-type structures presumably due to breakdown of the crystal structure of kaolin.

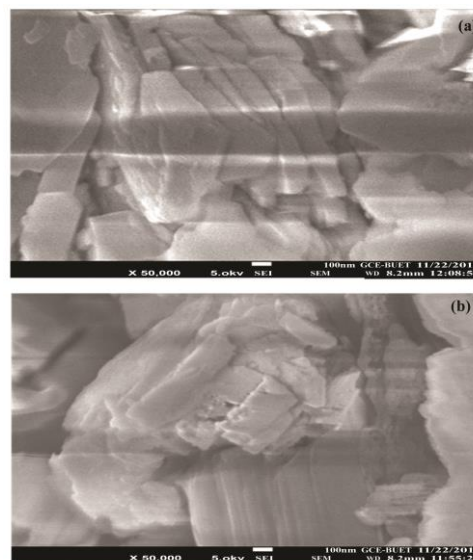


Fig. 5. SEM micrographs of raw kaolin (a) and 5 M H_2SO_4 treated kaolin clay (b).

The thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) of untreated raw clay and 5 M H_2SO_4 treated kaolin clay are shown in Fig. 6 (I) and (II), respectively. The TGA and DTG of raw kaolin show that physisorbed water loss occurs at 100-130 °C, dehydroxylation of coordinated and structural water loss occurs at 535 °C. The structural hydroxyl groups condense and dehydrate at 735 °C. On the contrary, no mass loss occurred until 435 °C in 5 M H_2SO_4 treated kaolin.

Above 435 °C, dehydroxylation of coordinated and structural water loss occurs which is complete at 600 °C. Thermal degradation behavior of polyethylene was reported by Panda *et al.* (2019) and it was stated that 50% weight loss, (T_{50}) of polyethylene occurs in the range of temperature 400-500 °C. Hence, all the catalytic

pyrolysis experiments with acid treated kaolin were performed in the range of 380-420 °C (i.e. below 435 °C).

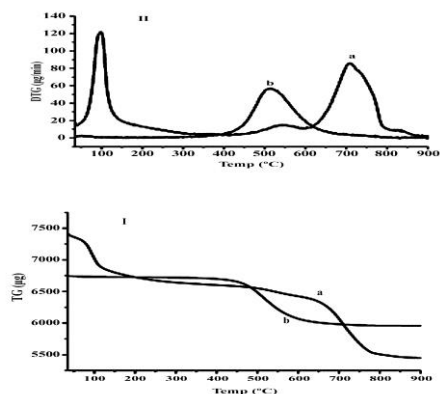


Fig. 6. Thermo-gravimetric analysis (I) and derivative thermo-gravimetric (II) analysis of untreated (a) and 5 M H₂SO₄ treated kaolin clay (b).

Catalytic pyrolysis of waste plastics

A range of kaolin based catalysts were explored for catalytic pyrolysis of waste polyethylene. The results of these experiments are shown in Table 2.

Table 2. Details of catalytic pyrolysis experiments of waste polyethylene with raw, different concentrated sulfuric acid (3, 5, 7 M) treated kaolin, and Ru- and Ni-impregnated 5 M sulfuric acid treated kaolin.

Kaolin		Waste plastics, g	Catalyst to plastic feed ratio	Pyrolysis temperature, °C	Final product		Color of the product	Yield, %
H ₂ SO ₄ treatment	Amount, g				mL	g		
-	-	50.0	-	480	30	23.8	Black ^a	47
Raw	5.0	50.0	1:10	450	21	16.7	Black ^a	33
3 M	5.0	25.0	1:5	350-420	26	20.7	Pale yellow ^b	83
5 M	5.0	50.0	1:10	350-420	34	27.0	Pale yellow ^b	54
5 M	5.0	35.0	1:7	350-420	12	9.5	Pale yellow ^b	27
5 M	5.0	25.0	1:5	350-420	25	19.9	Pale yellow ^b	79
7 M	5.0	25.0	1:5	350-420	21	16.7	Pale yellow ^b	67
5 M, Ru-Imp.	3.4	34.0	1:10	350-420	32	25.5	Pale yellow ^b	75
5 M, Ni-Imp.	2.5	12.5	1:5	350-420	12	9.5	Pale yellow ^b	76

^aliquid oil solidified after few hours, ^b remain in liquid state even after a month, density of liquid hydrocarbon is 0.7953 g/mL.

Among 3, 5 and 7 M H₂SO₄ treated kaolin catalysts, the 3 M H₂SO₄ treated kaolin

catalyst (at a catalyst to plastic ratio of 1:5) exhibited highest activity with the yield of 83% liquid hydrocarbon. The yield was found to be lower with 5 M H₂SO₄ treated kaolin. The density of the obtained liquid hydrocarbon product was found to be 0.7953 g/mL.

Uzair *et al.* (2016) investigated catalytic degradation of polypropylene using kaolin clay activated with different molar concentrations of HCl (1, 3 and 5 M). They observed that with HCl treated kaolin catalysts, the yield of liquid product decreased at HCl concentrations above 3 M, though yield of gaseous products increased and maximum liquid yield (71.9%) was obtained using kaolin clay activated with 3 M HCl (at 470 °C, catalyst to plastic ratio 1:3).

Higher yield of liquid product obtained by H_2SO_4 treated kaolin implies that H_2SO_4 can be more effective than HCl for activation of kaolin. Moreover, 3 M H_2SO_4 treated kaolin provided higher amount of liquid (83%) compared to the liquid obtained (79.85%) from the waste polypropylene pyrolysis using Ahoko kaolin from Nigeria (Hakeem *et al.* 2018).

The 5 M H_2SO_4 treated kaolin catalyst was investigated with three different catalysts to plastic ratio to find out the optimum condition (Table 2). The 5 M H_2SO_4 treated kaolin catalyst at catalyst to plastic ratio of 1:7 provided a viscous liquid with much lower yield of 27%. About 51% yield was observed at 1:10 ratio. A good quantity of liquid was obtained at a catalyst to plastic ratio of 1:5 with the yield of 79%. This shows that 1:5 ratio of catalyst to plastic is the best condition for getting optimum yield of product. The 7 M H_2SO_4 treated kaolin catalyst at a catalyst to plastic ratio of 1:5 provided little bit of viscous liquid with the yield of 67%. Furthermore, pyrolysis of PE with H_2SO_4 treated kaolin catalyst was conducted several times to examine the reproducibility of the experiment. These experiments gave approximately same percentage of yield.

Only sulfuric acid treated kaolin produces a liquid hydrocarbon product which is rich in linear and branched alkenes. In order to improve catalytic activity and promote internal hydrogenation to produce alkanes, ruthenium (Ru) and nickel (Ni) metals were impregnated

on 5 M H_2SO_4 treated kaolin. However, from this study we found that Ni and Ru metals impregnated kaolin catalysts provided lower yield of liquid hydrocarbon. Ru and Ni impregnated 5 M H_2SO_4 treated kaolin catalyst at a ratio of 1:10 and 1:5, respectively provided liquid yield of 75 and 76%. Whereas 5 M H_2SO_4 treated kaolin catalyst produced 79% liquid (catalyst to plastic ratio 1:5). Recently, Akubo *et al.* (2019) reported that addition of the promoter metals (Ni, Fe, Mo, Ga, Ru, and Co) on Y-zeolite has only a small influence on aromatic oil content and it increases hydrogen gas yield from the pyrolysis of HDPE.

The raw kaolin was also investigated for pyrolysis at a catalyst to plastic ratio of 1:10. About 21 mL viscous liquid was obtained from 50 g polyethylene. The produced black liquid solidified within an hour. Moreover, thermal degradation (without using any clay catalyst) of polyethylene was also studied. Thermal degradation of 50 g waste plastics at 480 °C provided a highly viscous 30 mL black liquid which solidified within 30 minutes.

The liquid hydrocarbon mixture obtained using 5 M H_2SO_4 treated kaolin catalyst was analyzed by GC-MS and the results are summarized in Table 3. The GC-MS study indicates the presence of different hydrocarbons mostly alkanes and alkenes ranging from C_9 - C_{20} . The produced liquid hydrocarbon mixture was found to be free from aromatic compounds importantly polycyclic aromatic hydrocarbons (PAHs) which are potent mutagenic and carcinogenic.

Table 3. GC-MS analysis of liquid hydrocarbon obtained by catalytic pyrolysis of waste polyethylene with 5 M H₂SO₄ treated kaolin as catalyst.

Retention time, min	Name of Compound	Chemical Formula
3.008	4,4,5-Trimethyl-2-hexene	C ₉ H ₁₈
3.075	2,3-Dimethyl-2-heptene	C ₉ H ₁₈
3.142	2,4-Dimethyl-1-heptene	C ₉ H ₁₈
3.175	2-Methyl-3-methyleneheptane	C ₉ H ₁₈
3.292	1,3,5-Trimethylcyclohexane	C ₉ H ₁₈
3.533	2,4,6-Trimethyl-3-heptene	C ₁₀ H ₂₀
4.717	3,3-Dimethyloctane	C ₁₀ H ₂₂
4.758	2,5,5-Trimethylheptane	C ₁₀ H ₂₂
5.192	2,4-Dimethyl-2-decene	C ₁₂ H ₂₄
5.283	2,2-Dimethyl-3-decene	C ₁₂ H ₂₄
5.375	4,5-Dimethyl-2-undecene	C ₁₃ H ₂₆
6.975	2,6,10-Trimethyl-dodecane	C ₁₅ H ₃₂
9.342	Eicosane	C ₂₀ H ₄₂

The ¹H NMR spectrum of liquid hydrocarbon obtained by pyrolysis of PE using 5 M H₂SO₄ treated kaolin (Fig. 7) shows peaks only in the range 1-1.9 ppm which correspond to alkyl (methyl), and alkylene (methylene) protons originating from alkane compounds.

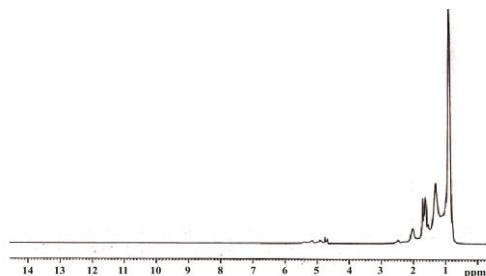


Fig. 7. The ¹H NMR spectrum of the liquid hydrocarbon oil obtained after pyrolysis of waste PE by 5 M H₂SO₄ treated kaolin as a catalyst.

The FTIR spectrum of the product liquid obtained with 5 M H₂SO₄ treated kaolin catalyst (Fig. 8) shows that the liquid product contains linear alkanes, as well as branched alkanes and alkenes. The observed peaks were assigned as follows: 2956 cm⁻¹ C-H stretching of alkane; 1651 cm⁻¹ C=C stretching of alkene; 1458 cm⁻¹ >CH₂ scissoring; 970 cm⁻¹ C-H bending of alkane; 889 and 738 cm⁻¹ C-H rocking from alkane. There was no peak in the range of 400–700 cm⁻¹.

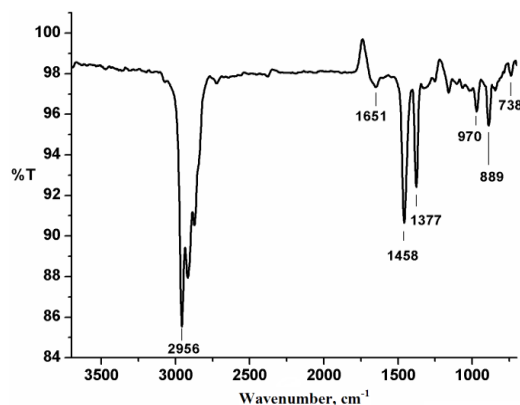


Fig. 8. FTIR spectrum of liquid hydrocarbon obtained after pyrolysis of waste PE using 5 M H₂SO₄ treated kaolin catalyst.

All these absorption bands of liquid hydrocarbon mixture produced using 5 M H₂SO₄ treated kaolin catalyst were also observed in the FTIR spectrum of the liquid hydrocarbon obtained using other concentrated (3, 7 M) H₂SO₄ treated kaolin, Ru- and Ni-impregnated kaolin and untreated kaolin.

Hakeem *et al.* (2018) used Ahoko kaolin from Nigeria and performed catalytic pyrolysis of polypropylene without any acid treatment of the kaolin. They found that the produced liquid oil contains hydrocarbons with different functional groups such as aromatics, olefins, carbonyl, amines and hydroxyl. However, the liquid produced from the current study using H₂SO₄ treated kaolin clay catalyst appeared to be free

from any aromatic, carbonyl or amine compounds, as confirmed by GC-MS, ^1H NMR, and FTIR spectral analysis. The presence of aromatic, carbonyl or amine functional groups in the oil produced by Hakeem *et al.* (2018) may be ascribed to the use of unmodified kaolin which might contain impurities that promote formation of those functional groups.

CONCLUSIONS

Catalytic pyrolysis of waste polyethylene was successfully carried out at a temperature between 350–420 °C under N_2 atmosphere using various concentrated H_2SO_4 treated kaolin and Ni and Ru impregnated H_2SO_4 treated kaolin catalysts. The raw and acid treated kaolin catalysts were characterized by XRPD, XRF, SEM, TG, and DTG. The XRPD measurements indicated that treatment with sulfuric acid leads to breakdown of the kaolinite crystal structure and leaching out of Al_2O_3 resulting in probably a $\text{SiO}_2\text{-Al}_2\text{O}_3$ composite with other metal oxides impregnated in it. A comprehensive analysis of the XRPD data is necessary to understand the effect of acid treatment. Among 3, 5, and 7 M H_2SO_4 treated kaolin catalysts, the 3 M H_2SO_4 treated kaolin catalyst exhibited the highest activity with a yield of 83% liquid hydrocarbon. It is likely that treatment with 3 M sulfuric acid at 120 °C results in a catalyst with an optimum $\text{SiO}_2\text{-Al}_2\text{O}_3$ ratio for pyrolysis of polythene. The 1:5 ratio of catalyst to plastic feed provided a better yield compared to 1:10 and 1:7 ratio. The Ni impregnated 5 M H_2SO_4 treated kaolin catalyst showed 76% yield of liquid hydrocarbon compared with 5 M H_2SO_4 treated kaolin catalyst which produced 79% liquid at catalyst to plastic ratio of 1:5. The Ru impregnated 5 M H_2SO_4 treated kaolin catalyst provided a viscous liquid with a yield of 75%. The GC-MS, ^1H NMR and FTIR spectral analysis confirmed linear and branched alkanes and alkenes ($\text{C}_9\text{-C}_{20}$)

in the liquid hydrocarbon obtained using 5 M H_2SO_4 treated kaolin catalyst. The produced liquid hydrocarbon was free from PAHs which are potent mutagenic and carcinogenic.

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