

Acidic Influence in Conversion of Hospital Plastic Waste into Liquid Fuel using Kaolin **Base-supported Catalysts**

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ABSTRACT: Assessing acidic influence in conversion of hospital plastic waste into liquid fuel with kaolin base supported catalysts was carried out using samples collected from a tertiary University teaching Hospital Sokoto, which encompassed Drip bags (Linear low density polyethylene LLDPE), Hand gloves (Polyethylene terephthalate PET) and Urine bags (Polyureathane PU). Uncatalyzed pyrolysis was first carried out using thermal cracking only at 300, 350, and 400°C. Catalyzed pyrolysis was also carried out using three different active catalyst mounted on same support and equal catalytic ratio of active catalyst to support. CuO/Kaolin-SO4, FeO/Kaolin-SO4 and CaO/Kaolin-SO4. The liquid fuel obtained from uncanalyzed and catalyzed pyrolysis of the sample were all subjected to GCMS and FTIR analysis. Uncatalyzed pyrolysis was first carried out using thermal cracking only at 300, 350, and 4000C. Catalyzed pyrolysis was also conducted using three different active catalyst mounted on same support and equal catalytic ratio of active catalyst to support. Fe₂O₃/Kaolin-SO₄ (CAT.D), CuO/Kaolin-SO₄ (CAT.E), and CaO/Kaolin-SO₄ (CAT.F). The catalytic activities of all the three synthesized catalysts were successfully tested in the conversion of hospital plastic waste in to liquid fuel. However the conversion using (CAT.D) was found to be more promising and selective to liquid fraction then followed by CAT. E and F. Therefore, the results shows that CAT.D has lower cocking tendency that result to high liquid than the other catalysts. The FTIR and GC/MS analysis revealed that the chemical composition and carbon number distribution of the liquid fraction which indicate the presence of paraffinic, naphthenic and olefins hydrocarbons as the dominant component in the liquid fraction obtained, and high amount of lower hydrocarbon range was also obtained using CAT.D. Thus, sulphated kaolin catalyst (CAT.D) was found to be better in modifying the product than CAT.E and F.

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Plastics provide a fundamental contribution to all main daily activities, the invention of plastics is a major milestone that led to improvement in the quality of the lives of human beings (Gautam, 2013; Demirbas et al., 2004). Since its first synthesis in early 1900s, plastics

have substituted many types of materials such as wood, metals and ceramics in production of consumer products, as they are light, durable, resistant to corrosion by most chemicals, diversity of applications, ease to processing and low-cost (Kaminsky et al.,

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2004; Dilih et al., 2011). In transportation for instance, the use of plastic in manufacturing vehicles components and accessories reduces the weight, hence the fuel consumption of vehicles (Mudgal et al., 2011, Kaminsky et al., 2004). In spite of the aforementioned benefits derived from plastics, environmental problems arise due to accumulation of plastic waste from the onset of their invention. As plastic waste virtually does not degrade, it occupies the landfill space for hundreds of years after their disposal. According to World Bank, plastic waste accounted for 8-12% of total municipal solid waste generated in different countries all over the world (Miscolczi et al., 2009; Angaval et al., 2007). The actual percentage varies according to the income level of the people in the country. It was also estimated that global plastic waste generation by 2025 will increase to 13% of total municipal solid waste, which again varies according to country (Sannita et al., 2012). The rapid increase in the population results in a lot of disposal problems, which will be a great challenge to many countries in the near future (Sannita et al., 2012; Luitel and Khanal, 2010). Generally, wastes are categorized into Hospital, industrial, municipal, and agricultural waste. Hospital plastic waste are chosen for the purpose of this study. and this type of waste are generally incinerated for fear of infection, which in turn increases the emission of harmful greenhouse gases that causes birth defect and several kinds of cancer (Luitel and Khanal, 2010; Kaminsky et al 1997). However this work proposed disinfection of the waste and its conversion to fuel to mitigate the environmental problems of incineration. In Hospital most of the commodity use in medical diagnosis and treatment procedures constitute group of plastics such as linear low density polyethylene (LLDPE) that is use for packaging crystalloid fluid or drip such as normal saline, dextrose saline etc. polyethylene terephthalate (PET) that is use in production of medical glove which gives protection against infection, Polyurethanes (PU) which is use in the production of urine bag, Cyclo olefin polymer (COP) or rather called Copolymer use in the production of different types of syringes for injection (Bhaskar et al., 2003). Thus, various catalysts were reported for conversion of these wastes which include ZSM-5 (Park et al., 1999; Miskolczi et al., 2009), silica alumina (Shah et al., 2010), basic catalysts, such as BaCO₃ (Jan et al., 2010), Bimetallic catalyst, Al-Zn composite (Jan et al., 2003), Fluid catalytic cracking catalyst (Miskoloczi et al., 2006; Huang et al., 2010), and mesoporous catalysts, such as Al-MCM-41 (Saha et al., 2008). So all these reported catalyst including the Zeolite works effectively in terms of high conversion of plastic wastes at lower temperature. However, these catalysts are associated with the problems of higher gaseous products, higher aromatic

content in the liquid product, and higher expensive with long resident time, Thus, the cost of production involving these catalysts may be generally prohibitive (Saha et al., 2008) cited in Almustapha and Andresen (2012). Hence, the objective of this work was to evaluate the acidic Influence during the conversion of hospital plastic waste (drip bags, hand gloves and urine bags) from a tertiary institution teaching hospital Sokoto, Nigeria into liquid fuel with kaolin base supported catalysts.

MATERIAL AND METHODS

The chemicals and solvents used were procured from a local vendor, which include Iron nitrate (71 %, Mark), copper nitrate (71 %, Mark), Calcium nitrate (82 %, Sigma Aldrich) sulfuric acid (99.5 %, Sigma Aldrich), n-hexane (99.5 %, Sigma Aldrich), Dichloromethane (99 %, Sigma Aldrich) etc.

Collection and treatment of sample: The sample feed of hospital plastic waste, consisting of drip bag, urine bag, and hand glove were collected from Usmanu Danfodiyo University Teaching Hospital, Sokoto. The plastic samples were sterilized using Hospital autoclave followed by washing with disinfectant (Jik), and then treated with formaldehyde to completely disinfect the sample (William and David 2016). The sample was then rinsed with distill water and then cut into small size and dried, then 100g of each sample feed were measured and mix together. Then, the sample mixture were kept for the next stage of analysis.

Preparation of catalyst support (kaolin): Natural kaolin was collected from kankara local government area of katsina state, it was grounded and sieved to powder (40 mesh), sixty grams (60g) of kaolin powder was weighed and soaked into of distilled water (500 cm³) contained in a beaker (1000 cm³) and stirred vigorously. The suspended impurities were discarded, after which micro sieve was used to filter the clay suspension. The washed kaolin powder was dried at 105°C in an oven for eight hours (Edomwonyi, et al., 2013; Seung et al., 2004). The entire process was repeated to obtain 120g of clean kaolin.

Preparation of Reagents:

50wt % of $\{Fe(NO_3)_3.9H_2O\}$: A catalyst precursor (Fe (NO₃)₃.9H₂O) of (20.25 g) was accurately weighed and dissolved into a glass beaker (250 cm³) containing distilled water (50 cm³). This is equivalent to (10g of Fe₂O₃), the mixture was stirred until the salt was completely dissolved. The salt solution was transferred into a volumetric flask (250 cm³) the beaker was washed three times with distilled water and the washings was transferred into the volumetric flask

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containing the salt solution and the volume of the salt solution was adjusted to the mark (250 cm³) using distilled water (Edomwonyi, *et. al.*, 2013; Huang, 2001).

50wt % of {Cu(NO3)2.6H2O}: To obtained ten gram (10g) of CuO of the catalyst material, (37g) of the catalyst precursor { $(Cu(NO_3)2.6H_2O)$ } was dissolved into a glass beaker (250 cm³) containing distilled water (50 cm³). The mixture was stirred until the salt was completely dissolved. The salt solution was transferred into a volumetric flask (250 cm³) the beaker was washed three times with distilled water and the washings was transferred into the volumetric flask containing the salt solution and the volume of the salt solution was adjusted to the mark (250 cm³) using distilled water (Edomwonyi *et. al.*, 2013).

50wt % of {Ca(NO3)2.4H2O}: A catalyst precursor {Ca(NO₃)_{2.4}H₂O}of (42.14g) was accurately weighed and dissolved into a glass beaker (250 cm³) containing distilled water (50 cm³). This is equivalent to (10g of CaO), the mixture was stirred until the salt was completely dissolved. The salt solution was transferred into a volumetric flask (250 cm³) the beaker was washed three times with distilled water and the washings was transferred into the volumetric flask containing the salt solution and the volume of the salt solution was adjusted to the mark (250 cm³) using distilled water (Edomwonyi *et. al.*, 2013; Huang, 2001).

Catalysts Synthesis and Screening Processes (*sulphated*): The catalyst combination consist of active catalysts material such as calcium oxide, copper oxide and iron oxide each one mounted on sulphated kaolin as supportive catalyst. The sulphated kaolin base catalyst, may include; Fe₂O₃/ Kaolin-SO₄, CuO/ Kaolin-SO₄ and CaO/ Kaolin-SO₄.

Preparation of $0.2M H_2SO_4$: In to a volumetric flask (1000 cm³) containing distilled water (200 cm³), the concentrated H₂SO₄ acid (19.62 cm³) was transferred. The mixture was stirred and allowed to cool for a moment. After which the volume of the solution was adjusted to the mark (1000 cm³) using distilled water (Angayal *et al.*, 2007)

Preparation of Sulphated Kaolin-base Catalyst: The kaolin (100 g) was transferred into a beaker (500 cm³) and already prepared 0.2 MH₂SO₄ (50 cm³) was added to it gently and stirred the mixture until homogeneity was achieved. The mixture was ultra-sonicated for 5 minutes at 80° C after which it was allowed to stand for 24 hours and then heated on a hot plate at 40° C until the excess solvent evaporates. The mixture was dried

in an oven at 105^{0} C for 3 hours and the dried mass was pulverized (Bagri and William 2002). The successful acidification of Kaolin support was confirmed using FTIR analysis in which the chromatogram peak at 1035.9 and 1171.1 cm⁻¹ correspond to SO₄ vibrational band.

Impregnation of 50wt % Fe₂O₃/ Kaolin-SO₄: The sulphated kaolin Ten gram (10g) was transferred into a beaker (500 cm³). And 250 cm³ of the already prepared solution containing 20.25g of Fe (NO₃)3.9H₂O was added to it gently to form homogeneous The mixture. mixture was ultrasonicated for 5 minutes at 80 °C after which it was allowed to age for 24 hours. After aging, the mixture was placed on a hot plate to evaporate the excess solvent after which the dried mass was further oven dried at 105 °C for 3 hours and pulverized. The pulverized mass was calcined at 600 °C for 3 hours in a muffle furnace and the mass of the calcined sample was taken and the difference were obtained. The decomposition of Fe(NO₃)₃ during calcination was given by Eq. 1 and 2.

 $\begin{array}{c} Fe(NO_3)_3 \ .9H_2O \ \vec{\Delta} \quad Fe(NO_3)_3 + 9H_2O \ _{(1)} \quad1 \\ 4Fe(NO_3)_3 \ \vec{\Delta} \ 2Fe_2O_{3} \ _{(s)} + 12NO_{2} \ _{(g)} + 3O_{2} \ _{(g)} \ldots 2 \end{array}$

Impregnation of 50wt % CuO/ Kaolin-SO₄: Ten gram (10 g) of sulphated kaolin was transferred into a 500 Cm³ beaker. And 250 cm³of the already prepared solution containing 37 g of Cu(NO₃)₂.6H₂O was added to it gently to form homogeneous mixture. The mixture was ultrasonicated for 5 minutes at 80 $^{\circ}$ C after which it was allowed to age for 24 hours. It was then placed on a hot plate to evaporate the excess solvent and further oven dried at 105 $^{\circ}$ C for 3 hours and the then pulverized. The pulverized mass was calcined at 600 $^{\circ}$ C in a muffle furnace for 3 hours and the mass of the calcined sample were taken and the difference also obtained. The decomposition of Cu(NO₃)₂ during calcination was given by Eq.3 and 4.

 $\begin{array}{cccc} Cu(NO_3)_2 \ .6H_2O \xrightarrow{\Delta} \ Cu(NO_3)_2 + 6H_2O \ _{(1)} & \dots \dots .3\\ 2Cu(NO_3)_2 \ \xrightarrow{\Delta} \ 2CuO_3 \ _{(s)} + 4NO \ _{(g)} + O_2 \ _{(g)} \dots \dots .4 \end{array}$

Impregnation of 50wt % CaO/Kaolin-SO₄: The ten grame (10g) of sulphated kaolin was transferred into a 500 Cm³ beaker. And 250 cm³ of the already prepared solution containing 42.14g of Ca (NO₃)₂.4H₂O was added to it gently to form homogeneous mixture. The mixture was then ultrasonicated for 5 minutes at 80^oC after which it was allowed to age for 24 hours. After aging, the mixture was placed on a hot plate to evaporate the excess solvent. It was then oven dried at 105 ^oC for 3 hours and the dried mass was pulverized.

The pulverized mass was calcined at 600° C for 3 hours in a muffle furnace and the mass of the calcined sample was recorded and difference were also obtained. The decomposition of Ca(NO₃)₂4H₂O during calcination was given by Eq. 5 and 6.

| $Ca(NO_3)_2$.4H | $_{2}O \Delta Ca(NO_{3})_{2} + 4H_{2}O_{(1)} \dots 5$ | |
|----------------------------|---|--|
| $4Ca(NO_3)_2 \vec{\Delta}$ | $4CaO_{(s)} + 8NO_{2(g)} + 2O_{2(g)} \dots 6$ | |

GC-MS Analysis of the liquid fraction: The liquid fraction was subjected to GC-MS analysis which was carried out on Agilent GC 7890B couple to an Agilent 5977A MSD equipped with 30m long fused capillary column with a 250 μ m internal diameter and 0.25 μ m film thickness. The temperature was held at 50 °C for 5 minutes then increased to 300 °C at the rate of 7 ⁰C/min. 1 µl of each fraction was injected using a 10 µl syringes. The carrier gas was helium with flow rate of 1.2 /min. The mass spectrometer was operated at electron energy of 70 eV, an ion source temperature of 230 °C and MSD transfer line temperature of 150 ⁰C. System control and data acquisition were achieved with ChemStation software. Total ion count (TIC) was used for evaluation for compound identification and quantification. The spectrum of the separated compound was compared with the data base of the spectrum of known compound saved in NIST05 reference library.

FT-IR Analysis of the liquid fraction: Fourier Transform Infrared Spectroscopy (FTIR), The FT-IR Analysis was carried out using Agilent Cary 630 FT-IR spectrometer with a base system of a high infrared

radiation emission. The base system is used in conjunction with a 5 bounce diamond ATR sampling accessories of internal reflection element (IRE) crystal. The analysis was in the transmittance mode and the signal collected within the range 4000-650 Cm^{-1} wavenumber. The sample scan was 32 while background scan was 64 and the resolution was 4. The generation of the sample spectra was achieved through Microlab software.

Design of experiment: The experiment was design using MINITAB 17 statistical software, and it was based on central composite response surface methodology, two (2) independent variables were studied each at three levels, and the data collected from the experiment were analyzed using same software at α =0.05 at 95% confidence level, (Muhammad *et al.*, 2016).

Description of the experimental procedure: In both catalyzed and non-catalyzed plastic waste pyrolysis, the prepared plastic sample mixture (5 g) was transfer into the tubular glass reactor followed by the addition of (1 g) of catalyst in case of catalyze pyrolysis. The reactor tube was mounted in to the reactor chamber of the furnace and connected appropriately to condenser, nitrogen gas was used in purging the system to ensure that the sample was under inert atmosphere and only reacting to temperature during thermal decomposition. A programmable temperature controller unit was used to provide a uniform heat transfer along the reactor.

Table 1. The reaction variables investigated and their respective levels Variables Symbols Lower level Middle level Upper level S/N0 Temperature (°C) (θ) 300 350 400 Catalyst Type Fe2O3/Kaolin-SO4 CuO/Kaolin-SO₄ CaO/Kaolin-SO₄ (T) Time (mins) (m) 60 60 60

| Table 2: Su | immary of | material balance obtain | ed for uncatalyzed Pyrol | ysis of hospital pla | stic waste (HPW) | Conducted at different t | emperatures |
|-------------|-----------|-------------------------------|--------------------------|----------------------|------------------|--------------------------|-------------|
| | S/No | Temperature (⁰ C) | Gaseous (%) | Liquid (%) | Residue (%) | Conversion (%) | |
| | | 300 | 08.30±0.126 | 65.36±0.045 | 26.34±0.005 | 73.66 | |
| | | 350 | 10.49±0.098 | 74.83±0.050 | 14.74±0.081 | 85.32 | |
| | | 400 | 11.82±0.052 | 75.86±0.049 | 12.18±0.012 | 87.68 | |

Values in table 2 are mean ± SD of replicate measurement, one-way ANOVA confirmed the significance difference between the results run under different condition.

Table 3: Summary of material balance for sulphated catalyzed Pyrolysis of obtained at difference temperatures and constant catalyst loading (50 wt.

| | | | <i>~</i> 0). | | | |
|------|-------------------|--|--------------|-------------|-------------|------------|
| S/No | Temperature | Catalyst Type | Gases (%) | Liquid | Residue | Conversion |
| | (⁰ c) | (%) | | (%) | (%) | (%) |
| | 300 | Fe ₂ O ₃ /Kaolin-SO ₄ | 07.79±0.035 | 65.89±0.046 | 21.32±0.034 | 73.68 |
| | 350 | Fe ₂ O ₃ /Kaolin-SO ₄ | 12.27±0.022 | 74.41±0.043 | 13.32±0.028 | 86.68 |
| | 400 | Fe ₂ O ₃ /Kaolin-SO ₄ | 12.81±0.062 | 77.13±0.032 | 10.06±0.027 | 89.94 |
| | 300 | CuO/Kaolin-SO ₄ | 07.97±0.016 | 64.54±0.015 | 27.84±0.022 | 71.11 |
| | 350 | CuO/Kaolin-SO ₄ | 10.87±0.022 | 74.11±0.043 | 14.32±0.028 | 84.98 |
| | 400 | CuO/Kaolin-SO4 | 11.91±0.062 | 76.14±0.032 | 11.95±0.027 | 88.05 |
| | 300 | CaO/Kaolin-SO ₄ | 08.19±0.035 | 65.89±0.046 | 20.32±0.034 | 73.68 |
| | 350 | CaO/Kaolin-SO ₄ | 08.55±0.132 | 65.84±0.034 | 26.89±0.029 | 73.79 |
| | 400 | CaO/Kaolin-SO | 10 55+0 062 | 75 99+0 032 | 1346+0027 | 86 54 |

Values in table 3 are mean ± SD of replicate measurement, one-way ANOVA confirmed the significance difference between the results run under different condition.

The experimental set up was programmed to heat the reactor at the rate of 10 °C/min from the room temperature to 300 °C for 60 (mins). As the reaction progress emerging vapors were condensed by the icecooled condenser and collected into a liquid collector. The tubular glass reactor, the reactor head and various unit of collection system were weighted before and after the runs to determine the accurate mass balance of the products obtained. At the end of the run, the collected liquid was evacuated into a sample bottles for further analysis, while the solid char was collected and weighed. This procedure was repeated at 350 and 400 °C. A number of runs were repeated in order to check the reproducibility of the results, and the same procedure was repeated for each catalyst. (Nachenius et. al, 2013, Hadi et al., 2017). The yield of liquid product was calculated from equation (7).

$$LY(wt)\% = \frac{Weight of the liquid}{Weight of the sample} \times 100 \dots (7)$$

Where LY = liquid yield

RESULT AND DISCUSSION

Uncatalyzed pyrolysis of hospital plastic waste at varying Temperatures: Table 2: Shows summary of material balance obtained from thermal Pyrolysis of hospital plastic waste conducted at different temperatures. The influence of temperature in the thermal pyrolysis, was considered as the only reaction parameter in respect of the material balance such as the amount of liquid fraction, solid and gaseous product. However for catalyzed pyrolysis both temperature and catalyst were considered as the input variables influencing the reaction process. In reference to material balance Table 2 shows the amount of solid, liquid and gaseous product including the overall conversion obtained during the first pyrolysis experiment. The gaseous product was not collected during the analysis rather its amount was computed by reducing the amount of solid and liquid product from the original mass of the sample. It has been observed from the result, that an increase in the amount of liquid and gaseous product is directly proportional to the corresponding increase in the reaction temperature. Kazansky, (1999), Park, et al., (1999) reported that the temperature influence thermal decomposition of plastic that occurs by a radical mechanism, generating many oligomers by hydrogen transfer from the tertiary carbon atom along the polymer chain. Thus, the heavier components were converted into gas components through secondary cracking reaction at elevated temperatures. The amount of liquid produced at temperature of 300, 350 and 400 °C were 65.36, 74.83 and 75.86%. The result clearly shows that an increase in liquid fraction produced is in accordance with the increase in the reaction temperature, However in terms of residue or char formation reverse is the case in which the amount of the residue were found to be directly decrease with the corresponding increase in degradation temperature. This result was found to be in agreement with the result of Joo-Sik et., al (2010). However this research found to be energy saving than that of Joo-Sik et al., (2010), which operates at a higher temperature of 703, 727 and 746°C.

Catalyzed pyrolysis of hospital plastic waste at varying temperature: Table 3: Shows the summary of material balance obtained for catalyzed pyrolysis of hospital plastic waste at constant catalyst loading, and these were conducted using three different catalyst material each mounted on acidified kaolin as supportive catalyst which involve, Fe₂O₃/Kaolin-SO₄ (CAT.D), CuO/Kaolin-SO₄ (CAT.E) and CaO/Kaolin-SO₄ (CAT.F).

However much emphasis has been giving to the liquid fraction in the material balance, then followed by the type of chemical composition and carbon number distribution in the liquid. The amount of liquid fraction obtained using CAT.D at a temperature of 300, 350 and 400°C were found to be 65.89, 74.41 and 77.13% while for CAT.E is 64.54, 74.11, 76.14% and 64.89, 64.87, 69.84% for CAT.F respectively. The residue formed using CAT.D at same temperatures were found to be 21.32, 13.32, 10.06, for CAT.E 27.84, 26.89, 14.32, 11.95 and 20.32, 26.89, 13.46% for CAT.C.

Table 4: Chemical composition of the liquid product obtained from Hospital plastic waste.

| S/No | Composition | Catalyzed Pyrolysis (%) | | | | |
|------|-------------|-------------------------|--------|--------|--------|--|
| | | UCP | CAT. D | CAT. E | CAT. F | |
| 1 | Naphthenes | 44 | 38 | 40 | 40 | |
| 2 | Paraffins | 25 | 26 | 25 | 26 | |
| 3 | Olefins | 23 | 29 | 28 | 24 | |
| 4 | Others | 8 | 7 | 7 | 10 | |

[Key: CAT.D= Catalyst $\overline{D(Fe_2O_s/Kaolin-SO_4 ratio 1:1)}$, CAT.E= Catalyst $E(CuO/Kaolin-SO_4 ratio 1:1)$, CAT.F = Catalyst $F(CaO/Kaolin-SO_4 ratio 1:1)$, others =Aromatic and hydrocarbon containing hetro atom].



Fig 2: GCMS Chromatogram of catalyzed pyrolysis using FeO/ Kaolin-SO₄ (CAT.D)



However, It was also observed from the catalytic cracking that the amount of the liquid fraction obtained were found to be proportionally increase with the corresponding increase in degradation temperature, while the char formation however reverse is the case, in which the increase in char formation was found to be inversely proportional to the corresponding increase in degradation temperature. The yield to liquid product obtained from catalyzed pyrolysis using CAT.D found to be higher than that of CAT.E and F and the residue obtained were found to be much lower than that of CAT.E and F at same temperature. This results clearly indicates that the CAT.D catalyst has slow coking tendency than CAT. E and F. And this is a behavior of a very good catalyst, because the lower the coking tendency the higher the liquid and gaseous product and vice versa.

Molecular Profile of the Pyrolysis liquid fuel: The GC/MS analysis revealed the presence of compounds such as hexane, cyclopentane, 1,3 Butadiene, 2methylepropyl, 3,4-Hexanediole etc and aromatic hydrocarbon such as Benzene-1,1-(1,3-propanediyl) which are present in small proportion, the compound were *al.*, 2017). Identified using their respective mass spectra in comparison with standard mass spectra in the NISTLE library.

Figure 1-4. compares the chromatograms of the liquid fraction obtained from uncatalyzed and catalyzed pyrolysis of Hospital plastic waste using three different catalysts in which Fe₂O₃/Kaolin-SO₄ is designated as CAT.D, while CuO/Kaolin-SO₄ is designated as CAT.E and CaO/Kaolin-SO₄ is designated as CAT F, that is Catalyst D, E and F.

Fig 3: GCMS Chromatogram of catalyzed pyrolysis using CuO/ Kaolin-SO₄ (CAT.E)

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Fig 4: GCMS Chromatogram of catalyzed pyrolysis using CaO/ Kaolin-SO₄ (CAT.F)

And Figure 1 are chromatograms obtained from uncatalyzed pyrolysis. The analysis also revealed different compositional hydrocarbon of the liquid product obtained from using catalyzed pyrolysis. The percentage yields of naphthenes, paraffins olefins and other heteroatoms observed in Uncatalyzed pyrolysis are 44, 25, 23 and 8% respectively, and this served as control. However the emphasis is to improve the percentage yield of olefins and paraffins hydrocarbon which are industrially more attractive, especially the olefin which served as an intermediaries of many valuable and expensive chemicals in petrochemical industries (Almustapha and John 2012; Buekens and Huang 1998). And also to reduce the proportion of naphthenic and hetroatom in the liquid fraction. The catalyzed pyrolysis were presented in Table 4, the amount of the reaction over CAT.D the percentage yield were found to be 38, 26, 29 and 7%. Over CAT.E are 40, 25, 28 and 7%, then the reaction over CAT.F 40, 26, 24 and 10%. The results shows that the reaction using CAT.D the amount of olefins and paraffinic hydrocarbons were significantly improved to about 6 and 1% while reducing the formation of Naphthenic hydrocarbons and others by 6 and 1% compared to other catalysts. While using CAT.E the amount of naphthenic hydrocarbons was decreased by 4%, and increases the formation of olefins hydrocarbon by 5%. While the reaction over CAT.F the amount of naphthenic hydrocarbons was also decreased by 4% while the olefins and paraffins increased by 1% respectively. Each catalyst has its own effect toward the formation of various hydrocarbon group which should be as a result of different degradation mechanism as reported by Lee and Shin (2007).

| Table 5: Carbon number distribution determined from liquid product obtained. | | | | | | | |
|--|-----------------|-----|-----------|-----------|--------|--|--|
| S/No | Carbon Range | | Catalysed | Pyrolysis | (%) | | |
| | - | UCP | CAT. D | CAT. E | CAT. F | | |
| 1 | C5 C14 | 9 | 18 | 10 | 12 | | |
| 2 | C15 C20 | 20 | 28 | 23 | 24 | | |
| 3 | C21C25 | 22 | 25 | 26 | 22 | | |
| 4 | C26C31 | 27 | 14 | 21 | 22 | | |

| [Key: UCP = Uncatalysed pyrolysis, CAT.D = Catalyst D (Fe ₂ O ₃ /Kaolin-SO ₄ ratio 1:1), |
|---|
| CAT.E = Catalyst E (CuO/Kaolin-SO ₄ ratio 1:1), CAT .F = Catalyst F (CaO/Kaolin-SO ₄ |
| ratio1:1). |

15

20

22

Above C₃₁

The results is in line with the finding of Stefanis *et al.*, (2013) which reported that the appropriate size of the catalyst porosity helps to

produced hydrocarbons in the naphthenic, paraffinic or gasoline range. The result of Carbon number distribution determined from liquid fraction are provided in Table 5, which also indicate that the catalyst under study affected the carbon number distribution of the derived liquid fraction. The percentage of different carbon number distribution derived from uncatalysed pyrolysis (UCP) which served as the control were observed as follows, C5-C14, C15- C20, C21-C25, C26-C31 and Above C₃₁, are 9, 20, 22, 27 and 22. While the reaction over (CAT.D) are 18, 28, 25, 14, and 15%, then the reaction over CAT.E are 10. 23. 26. 21 and 20%, and that of CAT.F are 12, 24, 22, 22 and 20% respectively. It can be seen that CAT.D has improved the amount of lower and middle carbon ranges (C5-C14, C15- C_{20} , and C_{21} - C_{25}) to about but 9, 8 and 3% while decreases formation of high carbon range hydrocarbons $(C_{26}-C_{31}, Above C_{31})$ and by 13 and 7% respectively. While CAT.E also enhanced the yields of the lower and middle range hydrocarbons (C₅-C₁₄ , C₁₅- C₂₀, C₂₁-C₂₅) by 1, 3 and 4%, whereas as also reduced the yield of high carbon range hydrocarbon $(C_{26}-C_{31} \text{ and } above C_{31})$ by 6 and 2%. And CAT.F also improved the yields of the lower range hydrocarbons (C_5 - C_{14} and C_{15} - C_{20}) by 3 and 4%, while living the middle range hydrocarbon at its constant position. and It also slightly decreases the higher range hydrocarbon. It can be observed that almost all the catalysts altered the product distribution of light and medium carbon range by enhancing their amount but did not significantly affect the formation of heavy carbon range products, and this is due to the fact that metal oxide has less acid sites which affect the formation of tertiary carbanion ion yielding more straight chain hydrocarbons in the diesel range (Khowatimy et al., 2014).

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| No Of | Frequencies | Attribution | Functional | Peak Intensity | | | |
|-------|-------------|------------------|------------|----------------|-------|-------|-------|
| Peak | | | Group | UCP | CAT.D | CAT.E | CAT.F |
| 1 | 697 | C-H bend | Aromatic | ND | М | S | S |
| 2 | 766 | C-H bend. | Aromatic | ND | S | W | W |
| 3 | 906 | C-H bend. | Alkenes | W | S | Μ | S |
| 4 | 1100 | C-O bend. | Alkoxy | W | Μ | Μ | W |
| 5 | 1150 | C-O stretching | Alkoxy | W | Μ | Μ | W |
| 6 | 1466 | C≡≡C stretching. | Alkynes | ND | W | S | W |
| 7 | 1596 | C=C stretching | Aromatic | W | W | S | W |
| 8 | 1775 | C=O stretching. | Carbonyl. | ND | S | W | S |
| 9 | 1850 | | | W | S | Μ | S |
| 10 | 2923 | C≡≡C stretching | Alkynes | W | S | S | S |
| 11 | 2957 | C≡≡C stretching | Alkynes | W | S | W | S |

 Table 6: Result for FTIR analysis of the liquid fuel obtained from uncatalysed and catalyzed pyrolysis of hospital plastic waste into liquid fuel at different temperatures.

The Peak Intensity is Reported as follows; S= *Strong, M*= *Medium, W*= *Weak*

FT-IR Analysis of the liquid fraction obtained from the Pyrolysis: Figure 5-8 of are FTIR chromatograms of the Uncatalyzed and catalyzed pyrolysed liquid products. And Table 6. Also shows that there are about 11 peaks which include strong, medium and week intense peak associated with each catalytic cracking, while 7 peaks were observed in uncatalyzed pyrolysis in Figure 5. The Table also revealed the detail of peak intensity and the wave number which attributes different chemical composition and its functional group associated to the liquid fuel obtained from the pyrolysis processes. The spectrum of the liquid oil obtained by the catalyzed pyrolysis over CAT.D (Figure.6) features some strong absorption peaks mostly positioned at 210, 2923 and 2957 cm-1 which can be corresponded to asymmetric stretching of $C \equiv C$, C-H of - CH₃ and = CH₂, respectively. A weak absorption peak at 1525-1596 cm-1 indicates C=C of olefins (Islam et al., 2010), and a medium peak centered at 1456 cm-1 shows CH₂ bending vibrations, (Kumar and Singh, 2011). The results indicate that the liquid fraction contains paraffinic and olefinic hydrocarbons. The spectrum of the catalytically derived liquid oil over CAT. E and F (Figure 7 and 8) shows peaks corresponded to methyl and methylene groups. The peak at 697 and 766 cm⁻¹ ware observed in most of the liquid oils obtained using both catalysts, which corresponds to the high concentration of aromatic compounds that include monosubtituted and disubtituted aromatic hydrocarbond. Two more peaks, which were obvious, and visible around 1466 and 1596 cm⁻¹ correspond to C-C single bond of alkane and C=C double bonds, corresponding to aromatic compounds (Khowatimy et al., 2014)







Kaolin-SO₄ (CAT.F)S Conclusion: In this study, an acidic influence in conversion of Hospital plastic waste into liquid fuel

conversion of Hospital plastic waste into liquid fuel have been evaluated using acidified Kaolin-base supported catalyst. The results shows less gaseous product in the material balance, low aromatic content in the liquid fraction, and with short resident time. And the amount of liquid fraction was improved from 74.94 to 77.13%, compared to non-acidified kaolin in the previous work. The FTIR and GC/MS analysis revealed the presence of paraffinic, naphthenic and olefins hydrocarbons as the dominant component in the liquid fraction obtained.

REFFERENCE

- Abbas-Abadi, M S; Mehdi, N H and Hamid Y (2013). Evaluation of pyrolysis product of virgin higher density polyethylene degradation using different process parameters in a reactor. *Fuel Process. Technol. J.* (109) 90-95
- Adriana, D S; Patrizia, C; Fortunata, G; Elisabetta, B; Agostina, N; and Giorgio, P (2013). Catalytic

pyrolysis of polyethylene: A comparison between pillared and restructured clays. JAAP. 105 (2013).

- Aguado, J; Serrano, D P and Escola, J M (2008). "Catalytic cracking of polyethylene over zeolite mordenite with enhanced textural properties" *Ind. Eng. Chem. Res.* 47, 7982-7992.
- Almustapha, M N; and Andresen, J M (2012). Recovery of Valuable Chemicals from High Density Polyethylene (HDPE) Polymer: a Catalytic Approach for Plastic Waste Recycling; *IJESD*. 3, (3) 265-266
- Angayal, A; Miskolczi, N and Bartha, L (2007). Petrochemical feedstock by thermal cracking of plastic waste. JAAP. 79 409–414.
- Bagri, R and Williams, PT (2002). Fluidised-bed Catalytic Pyrolysis of Polystyrene. J. Energy Inst. 75(505): 117-123
- Bhaskar, T; Uddin, A; Murai, K; Kaneko, J; Hamano, K; Kusaba, T; Muto, A and Sakata, Y (2003). Comparison of thermal degradation products from real municipal wasteplastic and model mixed plastics; JAAP. 70 579–587
- Buekens, AG and Huang, H (1998). Catalytic plastics cracking for recovery of gasoline-range hydrocarbons from municipal plastic wastes. *Resour. Conserv. Recycl. Journal.* 23: 163–181
- Demirbas, A (2004). Pyrolysis of municipal plastic wastes for recovery of gasoline-range hydrocarbons. JAAP. 72, 97–102
- Edomwonyi-Out, LC; Adenowo, A.S. & Aderemi B.O. (2013) Ferric Alum Production from Brown Kankara Kaolin Clay, *PTDF.Journal* 3, (2), 81-87
- Gautam, K. R. (2013). A Novel Process of Converting Polyethylene to Gasoline, Middle Distillate and Heavy Oil through Hydro pyrolysis Route. *Int. J. Energy Environ. Eng.* 3(3) 147-157.
- Hadi B, Abdullahi M S, Mahmud M G, Aminu B M, (2017). Effect of neat kaolin and CuO/Kaolin on the yield and composition of products from pyrolysis of polystyrene waste. *Journal of Energy sources part A*: Recovery, Utilisation and environmental effects 39:2,148-153.
- Huang, X.Y (2001). Sintering of microfilteration membrance of alumina with nanometer aluminum

hydroxide additive new technology and new process. Fuel. 10 35-36.

- Jan, M.R; Shah, J; and Gulab, H.(2010). "Catalytic degradation of waste high-density polyethyleneinto fuel products using BaCO3 as a catalyst". *Fuel Process*. 91:1428-1437.
- Joo-Sik, Kim, Bo-Sung Kang, Min-Hwan Cho, Su-Hwa Jung (2010). Pyrolysis of a fraction of waste polyethylene and and polyethylene for the recovery of BTX aromatics using a fluidized bed reactor. *Fuel Process*. (91) 277-284
- Kaminsky W and Kim JS (1999). Pyrolysis of mixed plastics into aromatics. JAAP. 51 127–134.
- Kaminsky W, Prede M, Sadiki A, (2004). Feedstock recycling of polymers by pyrolysis in a fluidised bed. *Polym. Degrad. Stab.* 85 1045–1050
- Kazansky, V.B (1999) .Adsorbed carbocations as transition states in heterogeneous acid catalyzed transformations of hydrocarbons; *Catal. Today*. 51.419–434.
- Lopez-Urionabarrenechea A, Marco I, Caballero M (2010). Laresgoiti, A. Adrados, Pyrolysis of municipal plastic wastes: Influence of raw material and composition. *Waste Manage*. 30 620–627.
- Luitel K.P., Khanal S.N. (2010) Study of scrap waste in Kathmandu Valley Kathmandu.*University J. Sci. Eng. Technol.* 6 (1), 116–122
- Marcilla, A; Garci, A; Quesada, JC; Sanchez, S; Ruiz, R (2005). *JAAP*. 74: 387-392
- Miskolczi, N; Bartha, L; Deak, G; Jover, B; and Kallo, B (2004). Thermal and thermo-catalytic degradation of high-density polyethylene waste. *JAAP*.. 72 235–242
- Mudgal, S; Lyons, L; Bain, J (2011). Plastic Waste in the Environment – Revised Final Report for European Commission DG Environment. Bio Intelligence Service, Downloadable from <u>http://www.ec.europa.eu/environment/waste/studi</u> es/pdf/plastics. pdf 10-09-17

- Muhammad, A. B., Obianke, M., Hassan, L. G. and Aliero, A. A. (2016). Optimization of Process Variables in Acid Catalysed in-situ Transesterification of Hevea brasiliensis (rubber tree) Seed Oil into Biodiesel. *Biofuels*. 00; 1-10.
- Nachenius, RW; Ronsse, F; Venderbosch, RH; & Prins (2013). Advances in Chemical Engineering, 42, Burlington: Academic Press, pp. 75-139.
- Park, DW; Hwang, EY; Kim, JR; Choi, JK, Kim, YA; Woo, HC (1999). Catalytic degradation of polyethylene over solid acid catalysts; *Polym. Degrad. Stab.* 65. 193–198.
- Saha, B; Chowdhury, AK; Ghoshal, AK (2008). "Catalyzed Decomposition of Propylene and Hybrid Generic Algorithm for Kinetics Analysis". *Appl. Catal. B: Environ.* 83:265-276.
- Sannita, B. Aliakbarian, A.A. Casazza, P. Perego, Busca G (2012), Mediumtemperature conversion of biomass and wastes into liquid products. A Review of Renewable and Sustainable Energy. 16:6455–6475.
- Seung, KR; Woon KL; Jin, P (2004). Thermal Decomposition of Hydrated Copper Nitrate [Cu(NO3)2·3H2O] on Activated Carbon Fibers. *Carbon.* 5 (4) 180-185
- Shah, J; Jan, MR; Mabood, F; Jabeen, F (2010). Catalytic pyrolysis of LDPE leads to valuable resource recovery and reduction of waste problems. *Energy Conversion and Manage*. 51:2791-2801.
- Stefanis, AD; Patrizia, C; Fortunata, G; Elisabetta, B; Agostina, N and Giorgio, P (2013). Catalytic pyrolysis of polyethylene: A comparison between pillared and restructured clays; JAAP. 104:2013
- William, AR and David, JW (2016). Disinfection and Sterilization in Health Care Facilities: An Overview and Current Issues. *Infect. Dis. Clin. North Am.* 30(3):609-37