

Research Article

## Catalytic Conversion of Hospital Plastic Waste in to Liquid Fuel Using Kaolin Base-Supported Catalysts

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### ARTICLE INFO:

#### Keyword:

Conversion,  
Hospital,  
Plastic Waste,  
Liquid fuel,  
Kaolin

### ABSTRACT

Thermal and Catalytic conversion of hospital plastic waste into liquid fuel using kaolin base supported catalysts was conducted, the plastic waste samples were collected from Usmanu Danfodiyo University teaching Hospital Sokoto, which encompassed Drip bags (Linear low-density polyethylene LLDPE), Hand gloves (Polyethylene terephthalate PET) and Urine bags (Polyurethane PU). Uncatalyzed pyrolysis was first carried out using thermal cracking only at 300, 350, and 400°C. Catalyzed pyrolysis was also conducted using three different active catalyst mounted on same support and equal catalytic ratio of active catalyst to support. CuO/Kaolin (CAT.A), Fe<sub>2</sub>O<sub>3</sub>/Kaolin (CAT.B) and CaO/Kaolin (CAT.C). The catalytic activities of all the three synthesized catalysts were successfully tested in the conversion of hospital plastic waste into liquid fuel. However, the pyrolysis using (CAT.B) was found to be more promising than the others in terms of the liquid selectivity (yield) and the nature of hydrocarbon related compound in the liquid fraction. The results indicated that CAT.B has lower coking tendency than the others. The FTIR and GC/MS analysis revealed the chemical composition and carbon number distribution of the liquid fraction which indicate the presence of paraffinic, naphthenic and olefins hydrocarbon compounds as the dominant component in the liquid fraction obtained. Thus, the liquid fraction obtained has potential to be used in various energy and transportation applications after further refining process.

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## INTRODUCTION

The drastic increase in the production and everyday use of plastics over the past decades has made plastic waste disposal a serious environmental challenge. (Ioannis *et al.*, 2017). Since its first synthesis in early 1900s, plastics have substituted many types of materials such as metals, 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.*, 2004; Dilih *et al.*, 2011). Other than the mentioned advantages of plastics, studies have shown that plastic-based products are responsible for reduction in cost of production in different fields of human endeavor (Luitel and Khanal, 2010). 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). Despite the 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.*, 2004, Angayal *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 in 2025 will increase to 13 % of total municipal waste, which again varies according to country (Sannita *et al.*, 2012). Generally, wastes are categorized into Hospital, industrial, municipal, and agricultural waste. Hospital plastic wastes were chosen in this research because they 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 the 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). Polyvinyl chloride (PVC) which is use in the production of blood bag. The development of different viable recycling technologies for plastic waste materials is becoming increasingly important due to the growing interest in thermolysis and catalytic polymer degradation as methods of producing various fuel fractions from polymer wastes. Pyrolysis is one of the best methods for preserving valuable petroleum resources in addition to protecting the environment by limiting the volume of nondegradable waste (Stefan & Richard 2006). Pyrolysis of waste plastics is favored because of the high rates of conversion into oil, which can be obtained. The gaseous products coming from the pyrolysis process with high caloric value may be used as fuel in the process (William & paul 2006). PE is the most abundant waste plastic (50-60 wt %), followed by PS (16-20 wt %). Polypropylene (PP) is the third-most-abundant waste plastic (10-16 wt %). There has been considerable work conducted on pyrolysis of polymers, some of which aimed at pyrolytic recycling of plastics to monomers and fuels. The chemistry of plastic pyrolysis was reviewed by Wall *et al.*, 2005 and Mercilla *et al.*, 2005, who concluded that thermal treatment at sufficiently high temperature results in breaking polymer

chains and subsequent formation of smaller molecules. Some polymers, e.g., acrylics, decompose thermally and generate high yields of monomers. However, the most common plastics such as polyethylene and polypropylene do not appear to give high yields of monomers but rather a mixture of many different hydrocarbons with proportions depending on the process conditions mostly temperature and catalyst, (Ali *et al.*, 2002, Stefan & Richard 2006, Serrano *et al.*, 2005). Therefore research on plastics to different products, including chemicals and fuels using different type of catalysts have been published (Lin *et al.*, 2010; Lin 2009), cited in Al-mustapha and Andresen (2012). Different catalysts were reported for catalytic conversion of plastic wastes. These include ZSM-5 (Park *et al.*, 1999; Miskolczi *et al.*, 2009), silica alumina (Shah *et al.*, 2010), basic catalysts, such as  $\text{BaCO}_3$  (Jan *et al.*, 2010), Bimetallic catalyst, Al-Zn composite (Tang *et al.*, 2003), Fluid catalytic cracking catalyst (Miskolczi *et al.*, 2006; Huang *et al.*, 2010), and mesoporous catalysts, such as Al-MCM-41 (Saha *et al.*, 2008). So, all these reported catalysts 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 A-lmustapha and Andresen (2012). Therefore, this work was aimed to develop an indigenous capacity to synthesize a very simple Kaolin-base supported catalyst with low gaseous product in the material balance, low aromatic content in the liquid fraction, and less expensive with short resident time. Consideration will be given to higher selectivity to liquid product and its quality.

## 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. Then, the sample mixture was 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 (60 g) of kaolin powder was weighed and soaked into of distilled water ( $500 \text{ cm}^3$ ) contained in a beaker ( $1000 \text{ cm}^3$ ) 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  $105 \text{ }^\circ\text{C}$  in an oven for eight hours (Edomwonyi, *et al.*, 2013; Seung *et al.*, 2004). The entire process was repeated to obtain 120 g of clean kaolin.

### Preparation of Reagents

#### 50wt % of $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$

A catalyst precursor ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) of (20.25 g) was accurately weighed and dissolved into a glass beaker ( $250 \text{ cm}^3$ ) containing distilled water ( $50 \text{ cm}^3$ ). This is equivalent to (10 g of  $\text{Fe}_2\text{O}_3$ ), the mixture was stirred until the salt was completely dissolved. The salt solution was

transferred into a volumetric flask (250 cm<sup>3</sup>) 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 cm<sup>3</sup>) using distilled water (Edomwonyi, *et. al.*, 2013; Huang, 2001).

#### **50wt % of [Cu(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O]**

To obtained ten gram (10 g) of CuO of the catalyst material, (37 g) of the catalyst precursor (Cu(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O) was dissolved into a glass beaker (250 cm<sup>3</sup>) containing distilled water (50 cm<sup>3</sup>). The mixture was stirred until the salt was completely dissolved. The salt solution was transferred into a volumetric flask (250 cm<sup>3</sup>) the beaker was washed three times with distilled water and the washings was transferred into the volumetric flask containing the salt solution and

#### **Catalysts Synthesis Processes**

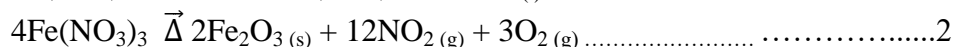
The catalyst combination consists of active catalysts material such as calcium oxide, copper oxide and iron oxide each one mounted on net kaolin as supportive catalyst. That's the kaolin-base supported catalyst, may include Fe<sub>2</sub>O<sub>3</sub>/Kaolin, CuO/Kaolin and CaO/Kaolin.

#### **Preparation of Kaolin-base supported Catalyst**

An accurately measured washed kaolin powder (50 g) was soaked into ethanol solution (1wt %) contain into a glass beaker (500 cm<sup>3</sup>). The content was allowed to soak for 2 hours with constant stirring of 200 rpm. Then the mixture was suction to dry (Haung 2001). The process was repeated to a constant weight (100 g) of net kaolin.

#### **Impregnation of the Catalysts**

The impregnation method was used in preparing the heterogeneous catalyst as reported by Cecilia *et.al.*, (2019), Hadi *et., al* (2017) and Schuth and Unger (1997) with little modification.



the volume of the salt solution was adjusted to the mark (250 cm<sup>3</sup>) using distilled water (Edomwonyi *et. al.*, 2013).

#### **50wt % of [Ca(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O]**

A catalyst precursor [Ca(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O] of (42.14 g) was accurately weighed and dissolved into a glass beaker (250 cm<sup>3</sup>) containing distilled water (50 cm<sup>3</sup>). 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 cm<sup>3</sup>) 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 cm<sup>3</sup>) using distilled water (Edomwonyi *et. al.*, 2013; Huang, 2001).

Impregnation method is a method commonly used for the synthesis of heterogeneous catalyst in which the volume of the solution is either equal or less than the pore volume of the support (Schuth and Unger 1997, Bhaskar *et al.*, 2003).

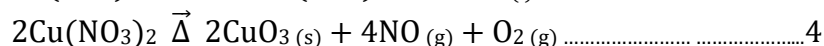
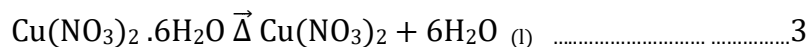
#### **Impregnation of 50 wt % Fe<sub>2</sub>O<sub>3</sub>/Kaolin**

Prepared kaolin, Ten gram (10 g) was transferred into a glass beaker (500 cm<sup>3</sup>). And already prepared solution (250 cm<sup>3</sup>) containing (25.25 g) of Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O was added to it gently to form homogeneous mixture. The mixture was ultra-sonicated 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 was obtained. The decomposition of Fe(NO<sub>3</sub>)<sub>3</sub>. During calcination was given by Eq. 1 and 2

**Impregnation of 50wt % CuO/Kaolin**

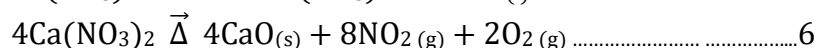
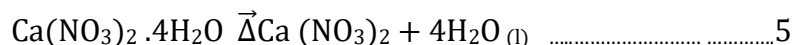
Ten gram (10 g) of kaolin was transferred into a glass beaker (500 cm<sup>3</sup>). And already prepared solution (250 cm<sup>3</sup>) containing (37 g) of Cu(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O was added to it gently to form homogeneous mixture. The mixture was ultrasonicated for 5 minutes at 80 °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 °C for 3 hours and the dried mass then pulverized. The pulverized mass was calcined at 600 °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(NO<sub>3</sub>)<sub>2</sub> during calcination was given by Eq. 3 and 4

**Impregnation of 50 wt % CaO/Kaolin**

Prepared kaolin, Ten gram (10 g) was transferred into a glass beaker (500 cm<sup>3</sup>). And already prepared solution (250 cm<sup>3</sup>) containing (42.14 g) of Ca(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O was added to it gently to form homogeneous mixture. The mixture was then 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. It was then oven dried at 105 °C 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 differences were also obtained. The decomposition of Ca(NO<sub>3</sub>)<sub>2</sub> during calcination was given by Eq. 5 and 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 µm internal diameter and 0.25 µm film thickness. The temperature was held at 50 °C for 5 minutes then increased to 300 °C at the rate of 7 °C/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 °C. 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 database 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<sup>-1</sup> 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  $\alpha=0.05$  at 95% confidence level, (Muhammad *et al.*, 2016).

**Table 1:** The reaction variables investigated and their respective levels

S/No	Variables	Symbols	Lower level	Middle level	Upper level
1.	Temperature (°C)	( $\theta$ )	300	350	400
2.	Catalyst Type	(T)	CuO/Kaolin	Fe <sub>2</sub> O <sub>3</sub> /Kaolin	Ca/Kaolin
3.	Time (mins)	(m)	60	60	60

### 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 into 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. 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 ice-cooled 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 (3.1).

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

## RESULTS AND DISCUSSION

### RESULTS

**Table 2:** Summary of material balance obtained for uncatalyzed Pyrolysis of hospital plastic waste conducted at different temperaturre.

S/No.	TEMPERATURE (°C)	GASEOUS (%)	LIQUID (%)	RESIDURE (%)	CONVERSION (%)
1.	300	08.30±0.126	65.36±0.045	26.34±0.005	73.66
2.	350	10.49±0.098	74.83±0.050	14.74±0.081	85.32
3.	400	11.82±0.052	75.86±0.049	12.18±0.012	87.68

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

## DISCUSSION

### Thermal pyrolysis of hospital plastic waste at varying Temperatures

Table 2: Shows summary of material balance obtained for uncatalyzed Pyrolysis of hospital plastic waste conducted at different temperatures. In the thermal pyrolysis, the influence of temperature 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 influences 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). Because in this research, the first pyrolysis operates at a temperature of 300, 350 and 400 °C, while the other operates at a higher temperature of 703, 727 and 746 °C.

**Table 3:** Summary of material balance obtained for catalyzed pyrolysis of hospital plastic waste at constant catalyst loading (50 wt%)

S/No.	TEMPERATURE (°C)	CATALYST TYPE (%)	GASES (%)	LIQUID (%)	RESIDURE (%)	CONVERSION (%)
1.	300	CuO/Kaolin	08.23 $\pm$ 0.055	63.96 $\pm$ 0.024	21.31 $\pm$ 0.013	78.69
2.	350	CuO/Kaolin	08.62 $\pm$ 0.077	64.80 $\pm$ 0.38	26.58 $\pm$ 0.66	73.52
3.	400	CuO/Kaolin	09.51 $\pm$ 0.022	65.91 $\pm$ 0.051	24.58 $\pm$ 0.066	75.42
4.	300	Fe <sub>2</sub> O <sub>3</sub> /Kaolin	07.57 $\pm$ 0.126	63.54 $\pm$ 0.016	28.84 $\pm$ 0.022	71.11
5.	350	Fe <sub>2</sub> O <sub>3</sub> /Kaolin	07.87 $\pm$ 0.132	65.94 $\pm$ 0.034	26.89 $\pm$ 0.029	73.79
6.	400	Fe <sub>2</sub> O <sub>3</sub> /Kaolin	08.16 $\pm$ 0.042	74.94 $\pm$ 0.022	16.80 $\pm$ 0.018	83.10
7.	300	CaO/Kaolin	07.92 $\pm$ 0.046	64.89 $\pm$ 0.035	27.19 $\pm$ 0.034	72.81
8.	350	CaO/Kaolin	08.01 $\pm$ 0.022	64.87 $\pm$ 0.043	27.12 $\pm$ 0.028	72.88
9.	400	CaO/Kaolin	08.86 $\pm$ 0.042	69.84 $\pm$ 0.022	21.80 $\pm$ 0.018	79.10

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

### 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 net kaolin as supportive catalyst which involve, CuO/Kaolin (CAT.A), Fe<sub>2</sub>O<sub>3</sub>/kaolin (CAT.B) and CaO/Kaolin (CAT.C). 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.A at a temperature of 300, 350 and 400 °C were found to be 63.96, 64.80 and 65.91 % while for CAT.B is 63.54, 65.94, 74.94 % and 64.89, 64.87, 69.84 % for CAT.C respectively. The residue formed using CAT.A at same temperatures were found to be 21.31, 26.58, 24.58, for CAT.B 28.84, 26.89,

16.80 and 27.19, 27.12, 21.80% for CAT.C. 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 and gaseous product obtained from catalyzed pyrolysis using CAT.B found to be higher than that of CAT.A and C catalysts and the residue were found to be much lower than that of CAT.A and C at same temperature. This results clearly indicates that the CAT.B catalyst has slow coking tendency than the other catalysts which is a characteristic of a very good catalyst, because the lower the coking tendency the higher the liquid and gaseous product and vice versa.

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

S/No.	COMPOSITION	CATALYSED PYROLYSIS (%)			
		UCP	CAT. A	CAT. B	CAT. C
1	Naphthenes	44	42	38	40
2	Paraffins	25	28	26	28
3	Olefins	23	20	28	22
4	Others	8	10	8	10

[Key: CAT.A= Catalyst A (CuO/Kaolin ratio 1:1), CAT.B= Catalyst B (Fe<sub>2</sub>O<sub>3</sub>/Kaolin ratio 1:1), CAT .C = Catalyst C (CaO/Kaolin ratio1:1), others =Aromatic and hydrocarbon containing hetro atom].

### GC-MS profile of liquid fraction obtained from hospital plastic waste

From the GCMS compound list, the liquid fraction obtained from catalyzed and uncatalyzed pyrolysis of the sample contained more hydrocarbon related compounds. The main compound obtained include naphthenic, paraffinic and olefins compound such as 1,4

cyclohexadiene, 1,4 heptadiene, Hexadiene heptane, and other heteroatom. Figure 1-4 in appendix compares the chromatograms of the liquid fraction obtained from catalyzed and uncatalyzed degradation of Hospital plastic waste using three different catalysts in which CuO/Kaolin is designated as CAT.A, while Fe<sub>2</sub>O<sub>3</sub>/Kaolin is designated as CAT.B and



CaO/Kaolin is designated as CAT C, that is Catalyst A, B and C. while Figure 4 are chromatograms obtained from uncatalyzed pyrolysis. The peaks were identified by NIST MS library and the data was used to determine the types of hydrocarbon and carbon number distribution obtained from the liquid fraction. The analysis revealed different compositional hydrocarbon of the liquid product obtained from both catalysts. 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, the emphasis is to improve the percentage yield of olefins and paraffins hydrocarbon which are industrially more attractive, while reducing the proportion of naphthenic and hetroatom in the liquid fraction. And the catalyzed pyrolysis were also presented, the amount of the reaction over CAT.A the percentage yield were found to be 42, 28, 20 and 10 %. Over CAT.B are 38, 26, 28 and 8 %, then CAT.C 40, 28, 22 and 10%.The results shows that the reaction using CAT.A the amount of naphthenic hydrocarbons was significantly decreased to about 2 % while increasing the formation of the paraffinic hydrocarbons by 3 % compared to other catalysts and also reduced the

percentage of olefinic hydrocarbon by 3 %, while using CAT.B the amount of naphthenic hydrocarbons was decreased by 6 %, and increases the formation of paraffins by 1 %, another good property of CAT.B when use, the amount of olefins was improved by 5 %.While the reaction over CAT.C the amount of naphthenic and olefins hydrocarbons was also decreased by 4 and 1 % respectively, as well as improving the percentage of paraffinic hydrocarbon by 3 %. Each catalyst has different effect toward the formation of various hydrocarbon group which should be because of different degradation mechanism as reported by Lee and Shin (2007). However, the emphasis is to improve the percentage of paraffinic and olefins hydrocarbon while reducing the percentage of naphthenic and other heteroatoms compound. CAT.B promoted the formation of higher amount of olefins compared to CAT.A and C which can be use as feedstock for petrochemical industries, and olefins compounds are industrially more attractive than even the pure saturated compounds (Almustapha and Andresen 2012; Buekens and Huang 1998), as they are the intermediaries of many valuable and expensive chemicals.

**Table 5:** Carbon number distribution determined from liquid product obtained.

S/No	Carbon Range	Catalysed Pyrolysis (%)			
		UCP	CAT. A	CAT. B	CAT. C
1.	C <sub>5</sub> ----- C <sub>14</sub>	9	9	10	10
2.	C <sub>15</sub> ---- C <sub>20</sub>	20	22	26	23
3.	C <sub>21</sub> -----C <sub>25</sub>	22	25	28	18
4.	C <sub>26</sub> -----C <sub>31</sub>	27	22	15	27
5.	Above C <sub>31</sub>	22	22	21	22

[Key: UCP= Uncatalysed pyrolysis, CAT.A= Catalyst A (CuO/Kaolin ratio 1:1), CAT.B= Catalyst B (Fe<sub>2</sub>O<sub>3</sub>/Kaolin ratio 1:1), CAT .C = Catalyst C (CaO/Kaolin ratio1:1).

Pyrolysis products usually are straight chain hydrocarbons which contain much heavier molecular weight components, so the main

purposes of the catalysts is to shorten the carbon chain length of the pyrolysis products and thus to decrease the boiling point of the products

(Williams and Willianms, 1998). The result of Carbon number distribution determined from liquid fraction are provided in Table 3.6, which also indicate that the catalysts 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 evaluated as follows, C<sub>5</sub>-C<sub>14</sub>, C<sub>15</sub>-C<sub>20</sub>, C<sub>21</sub>-C<sub>25</sub>, C<sub>26</sub>-C<sub>31</sub> and Above C<sub>31</sub>, are 9, 20, 22, 27 and 22. While the reaction over (CAT.A) is 9, 22, 25, 22, and 22%, then the reaction over CAT.B are 10, 26, 28, 15 and 21 %, and that of CAT.C are 10, 23, 18, 27 and 22% respectively. It can be seen that CAT.A has not improve the amount of lower carbon range (C<sub>5</sub>-C<sub>14</sub>), but enhanced the yields of the middle range hydrocarbons i.e. C<sub>15</sub>-C<sub>20</sub> and C<sub>21</sub>-C<sub>25</sub> by 2 and 3%, while decreases formation of high carbon range hydrocarbons i.e. C<sub>26</sub>-C<sub>31</sub> and by 5

% respectively. While CAT.B also enhanced the yields of the lower and middle range hydrocarbons (C<sub>5</sub>-C<sub>14</sub>, C<sub>15</sub>-C<sub>20</sub>, C<sub>21</sub>-C<sub>25</sub>) by 1, 6 and 6 %, whereas as also reduced the yield of high carbon range hydrocarbon (C<sub>26</sub>-C<sub>31</sub> and above C<sub>31</sub>) by 12 and 1 % . And CAT.C also enhanced the yields of the lower range hydrocarbons (C<sub>5</sub>-C<sub>14</sub> and C<sub>15</sub>-C<sub>20</sub>) by 1 and 3 %, while decreasing the amount of middle hydrocarbon by 4 %, and living the higher hydrocarbon at constant position. 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 nature of the catalyst which did not affect the formation of tertiary carbanion ion yielding more straight chain hydrocarbons in the diesel range (Khowatimy *et al.*, 2014).

**Table 6:** FTIR analysis of the liquid fuel obtained from catalyzed and unanalyzed pyrolysis of Hospital plastic waste at different catalyst loading

No. of Peak	Frequencies	Attribution	Functional Group	Peak Intensity			
				UCP	CAT.A	CAT.B	CAT.C
1	697	C-H bend	Aromatic	ND	M	S	S
2	766	C-H bend.	Aromatic	ND	S	W	W
3	906	C-H bend.	Alkenes	W	S	M	S
4	1100	C-O bend.	Alkoxy	W	M	M	W
5	1150	C-O stretching	Alkoxy	W	M	M	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	M	S
10	2923	C≡C stretching	Alkynes	W	S	S	S
11	2957	C≡C stretching	Alkynes	W	S	w	S

The Peak Intensity is reported as follows; S = Strong, M = Medium, W = Weak, ND = Not detected, CAT.A= catalyst A (ratio 1:1), CAT.B = catalyst B (ratio1:1), CAT.C= catalyst C (ratio 1:1)

### FT-IR Analysis of the liquid fraction obtained from the Pyrolysis

FT-IR analysis was used in studying different functional groups and chemical composition, it has also been reported that this technique is extensively used in characterization of pyrolytic oil obtained from waste polymers, in order to investigate the hydrocarbon types and functional groups in a liquid fractions (Arabiourrutia *et al.*, 2012; Islam *et al.*, 2010). Figure 5-8 of in appendix are FTIR chromatograms of the catalyzed and uncatalyzed pyrolysed liquid products. 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 8. Table 4.5 reveal 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.A (Figure 6 of the appendix) features some strong absorption peaks mostly positioned at 210, 2923 and 2957  $\text{cm}^{-1}$  which can be corresponded to asymmetric stretching of  $\text{C}\equiv\text{C}$ , C-H of  $-\text{CH}_3$  and  $=\text{CH}_2$ , respectively. A weak absorption peak at 1525-1596  $\text{cm}^{-1}$  indicates C=C of olefins ( Islam *et al.*, 2010), and a medium peak centered at 1456  $\text{cm}^{-1}$  shows  $\text{CH}_2$  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. B and C (Figure 7 and 8) shows peaks corresponded to methyl and methylene groups. The peak at 697 and 766  $\text{cm}^{-1}$  were observed in most of the liquid oils obtained using both catalysts, which corresponds to the high concentration of aromatic compounds that include monosubstituted and disubstituted aromatic hydrocarbonds. Two more peaks, which were obvious, and visible around 1466 and 1596  $\text{cm}^{-1}$  correspond to C-C single bond of alkane and C=C double bonds, corresponding to aromatic compounds (Khowatimy *et al.*, 2014)

### CONCLUSION

In this study an indigenous capacity was used and synthesized a simple Kaolin-base supported catalyst with low gaseous product in the material balance, low aromatic content in the liquid fraction, and less expensive with short resident time. The FTIR and GC/MS analysis revealed the chemical composition and carbon number distribution of the liquid fraction which indicate the presence of paraffinic, naphthenic and olefins hydrocarbon compounds as the dominant component in the liquid fraction obtained, Thus, the liquid fraction obtained has potential to be used in various energy and transportation applications after further refining process

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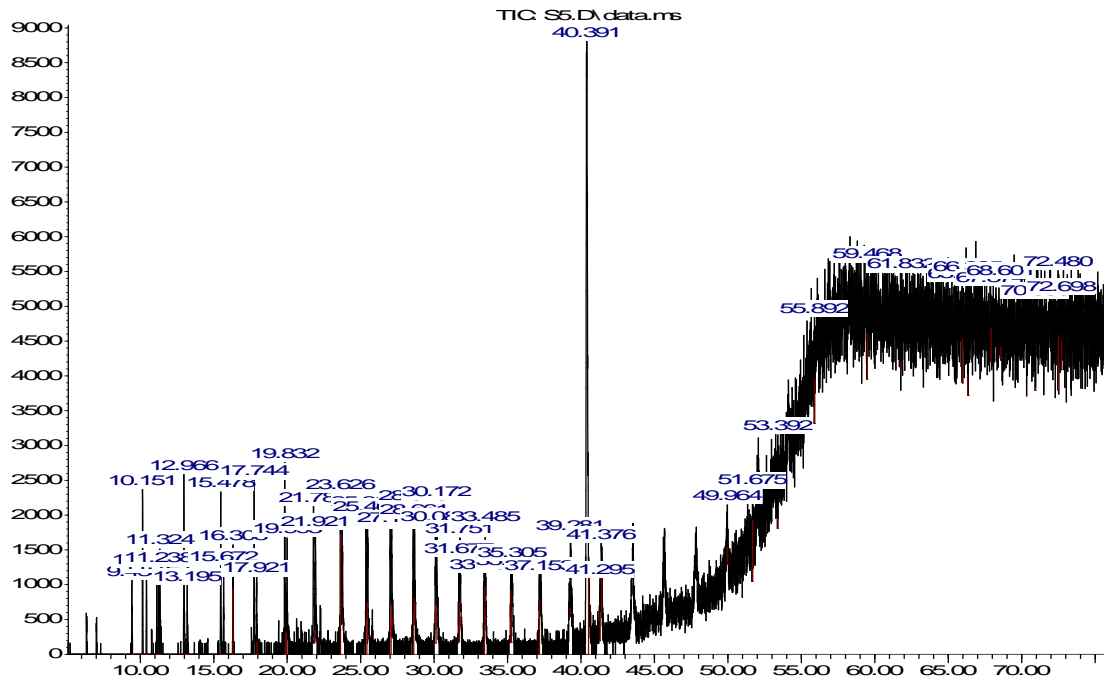
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**APPENDICES**

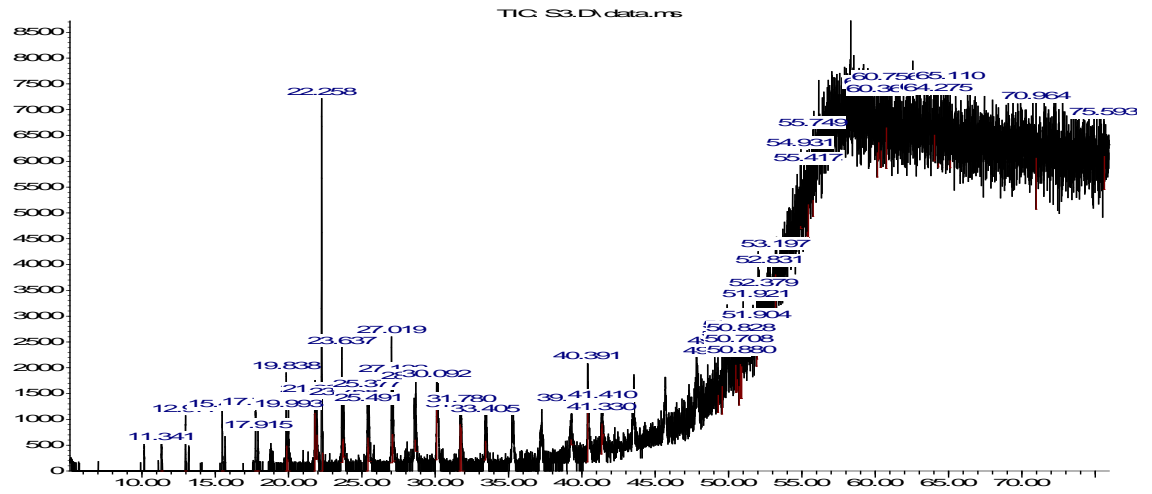
Abundance



Time->

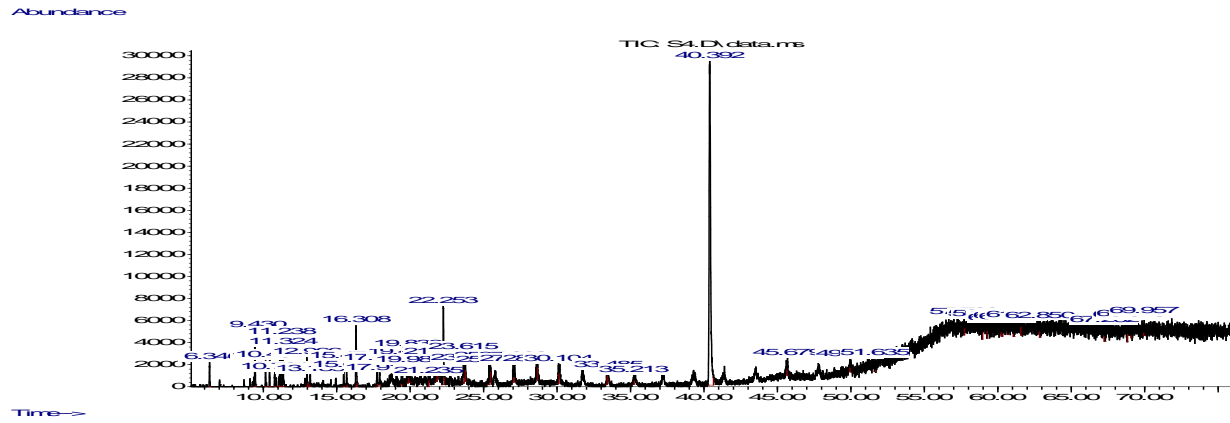
**Appendix 1: GCMS Chromatogram of Uncatalyzed Pyrolysis (UCP)**

Abundance

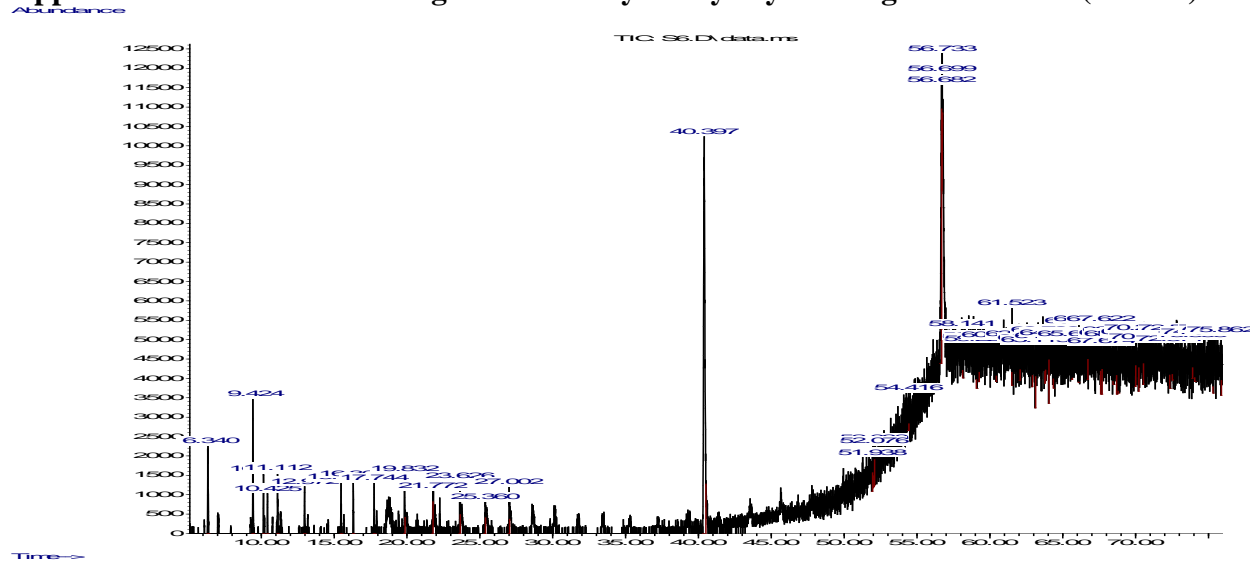


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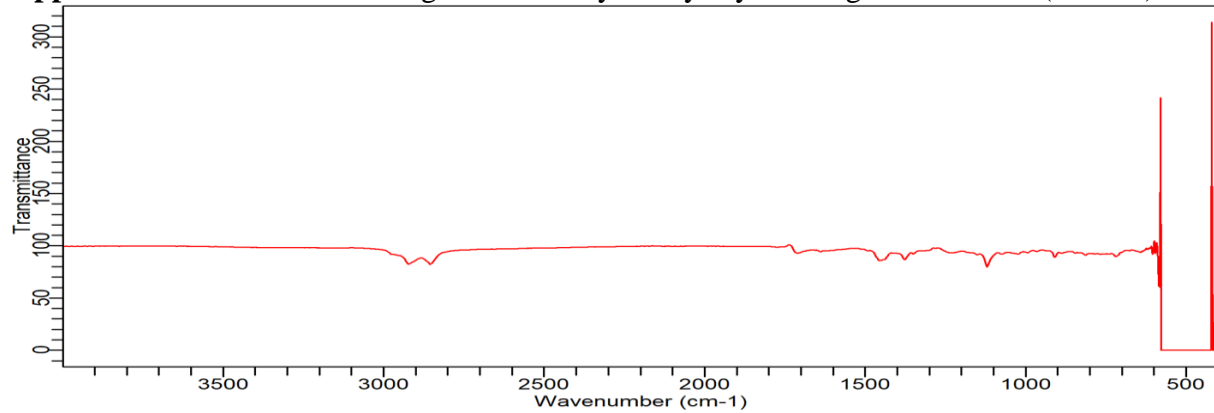
**Appendix 2: GCMS Chromatogram of Catalyzed Pyrolysis using CuO/ Kaolin (CAT.B)**



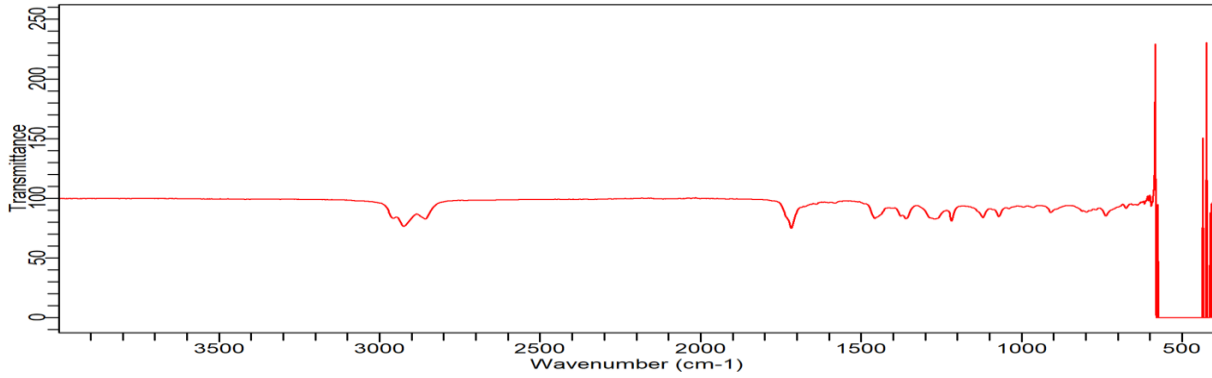
**Appendix 3: GCMS Chromatogram of Catalyzed Pyrolysis using FeO/ Kaolin (CAT.B)**



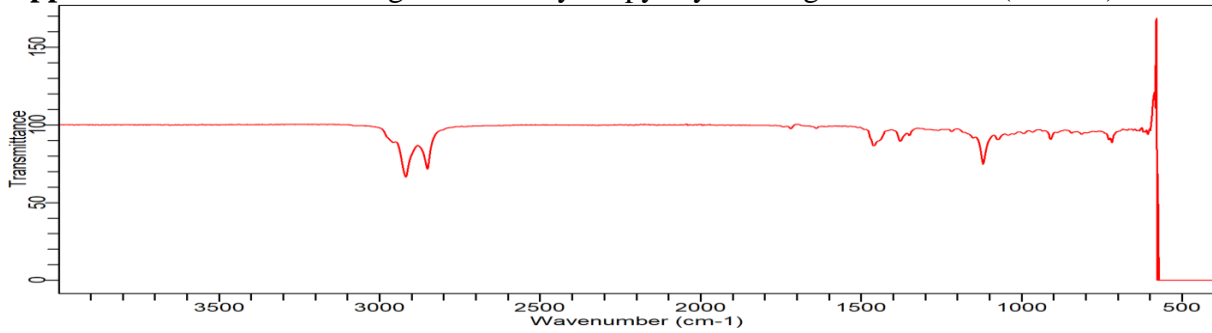
**Appendix 4: GCMS Chromatogram of Catalyzed Pyrolysis using CaO/ Kaolin (CAT.C)**



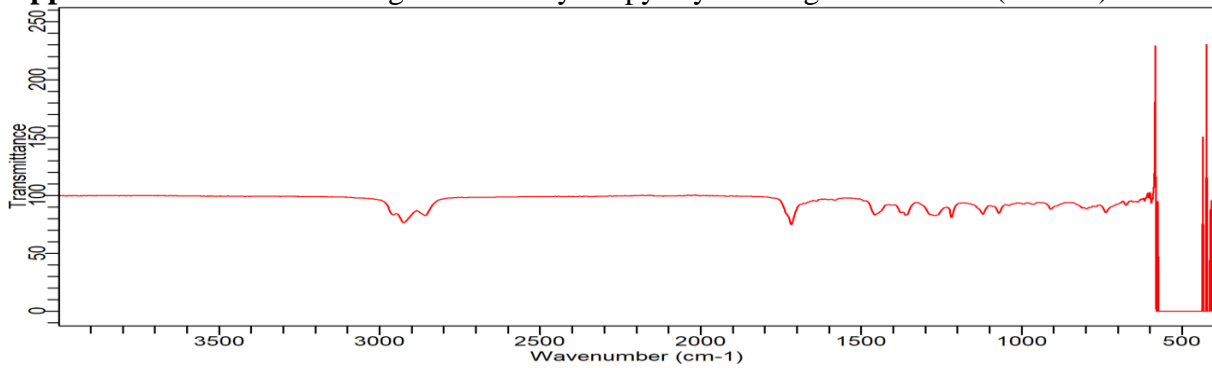
**Appendix 5: FTIR Chromatogram of Uncatalyzed pyrolysis using (UCP)**



**Appendix 6:** FTIR Chromatogram of catalyzed pyrolysis using CuO/ Kaolin (CAT.A)



**Appendix 7:** FTIR Chromatogram of catalyzed pyrolysis using FeO/ Kaolin (CAT.B)



**Appendix 8:** FTIR Chromatogram of catalyzed pyrolysis using CaO/ Kaolin (CAT.C)