

# CATALYTIC DEGRADATION OF WATER SACHET WASTE (LPDE) USING MESOPOROUS SILICA KIT-6 MODIFIED WITH 12-TUNGSTOPHOSPHORIC ACID

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## Abstract

The work investigated the feasibility of the catalytic degradation of water sachet waste (which is a low density polyethylene) to produce valuable chemicals using 12-tungstophosphoric acid (HPA) and 12-tungstophosphoric acid supported on KIT-6 as catalysts. The reaction was carried out at 400°C for 30 minutes at atmospheric pressure. The gas and liquid products obtained were analyzed using a gas chromatograph. For the liquid product using HPA-KIT-6, about 69 mol% of fractions between C<sub>10</sub>-C<sub>17</sub> (kerosene fraction) was obtained; 32 mol% of which was C<sub>16</sub> fraction while for the gas product 93 mol% propane fraction was obtained. A low amount of gas (mainly C<sub>3</sub> fraction) resulted from the reaction using HPA-KIT-6 while cracking over HPA gave high yield of gas product (C<sub>2</sub> and C<sub>3</sub> fractions). Catalytic degradation using HPA/KIT-6 is therefore a promising route for obtaining valuable fuels and petrochemicals while at the same time reducing the environmental problems arising from water sachet waste.

**Keywords:** Water sachet waste (LPDE); KIT-6; catalytic degradation; HPA; kerosene; propane.

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## 1. Introduction

Water sachet is a low density polyethylene (LPDE) use to package purified potable water in Nigeria. It is very cheap and hardy, thus attracting patronage from the low to middle strata of the populace. Water sachet wastes are dumped indiscriminately and therefore constitute huge environmental menace. The recent unprecedented flood witnessed in some cities of Nigeria was largely attributed to the clogging of drainages by water sachet waste. The challenge posed by water sachet waste and other polymer or plastic waste is particularly daunting due to their non-biodegradable nature. This is further compounded by their large volume per unit mass and short life span. Panda et al., [1] reported that plastics in municipal waste streams make up only 7-9% of the weight of the total waste stream; by volume they may represent 20-30%.

There are several methods for disposal of LPDE waste namely landfill, incineration, true material recycling and chemical recovery. Land filling is increasingly becoming unacceptable because of a decrease in landfill availability and cost increase. Incineration of waste polymers results in environmental danger of emissions of various combustion products. True material recycling which entail converting the waste into products that can be reused, though can reduce cost of disposal, is generally agreed not to be a long term solution to treat waste LPDE.

Thermal degradation or pyrolysis usually leads to wide product distribution and requires high temperatures, usually 500 – 900°C [2-10]. Catalytic degradation using suitable catalysts has the ability to control both the product yield and product distribution in addition to reduced reaction temperature [11-22]. Acidic catalyst favors products of shorter hydrocarbons. Silica, alumina, calcium carbide, etc, have been investigated [23]. Mesoporous materials due to their large pore diameter seem to be especially suitable as catalyst support for waste polymer degradation. Examples of mesoporous materials that have been investigated include MCM-41, KFS-16 and SAPO-37 [24-31]. Silica mesoporous molecular sieves show very low acidity and are usually modified with suitable acidic materials to facilitate the cracking process.

In this paper, we present an investigation on the degradation of water sachet waste (LPDE) performed over mesoporous silica KIT-6 modified with 12-tungstophosphoric acid ( $H_3PW_{12}O_{40}$ ) HPA. For comparison, the acid was also applied alone as catalyst for the degradation.

## 2. Experimental

### 2.1 Preparation of the support

The mesoporous silica was synthesized as follows [32]; typically, 6g P123 was dissolved in 217g of deionised water and 11.628g of 37 wt% conc. HCl solution with stirring at 35°C. After complete dissolution, 6g of butanol was added at once with vigorous stirring. After 1h of stirring, 12.9 g of TEOS was added at once to the homogenous clear solution while still stirring. The mixture was left under vigorous and constant stirring for 24h at 35°C. Afterwards, the mixture was placed in an oven at 100°C and left for 24h under static conditions (in a closed polypropylene bottle). The solid product obtained after hydrothermal treatment was filtered while hot and dried at 100°C without washing. To complete the synthesis, the template was removed by extraction in an ethanol-HCl mixture; this was done by stirring the filtrate for 1- 2h in a mixture of 300 – 400ml ethanol with 20 – 30ml 37% conc. HCl followed by calcination in air at 550°C for 6h.

### 2.2 Grafting of the 12-tungstophosphoric acid on KIT-6 catalyst support

3g of 12-tungstophosphoric heteropolyacid (HPA) was supported on 0.5g of KIT-6 from methanol solution by means of refluxing for 3 hours. The brownish mixture obtained was centrifuged in order to obtain a considerable amount of the solids. This solid was dried in an oven for two hours at 100°C and calcined in a furnace at 450°C for another two hours. A white coloured powder was obtained.

### 2.3 Analysis of the solid acid

Following synthesis, the materials were characterized to determine the particle and pore structure. The characterizing techniques used are the low angle powder X-ray diffraction (XRD) and the Energy-dispersive X-ray spectroscopy (EDX). Diffraction techniques supplied insight to the degree of structural order while the EDX gave the elemental analysis of the functionalized catalyst. The X-ray diffraction techniques ensure that the original Ia3d structure and pore sizes are not distorted after functionalization.

### 2.4 Catalytic degradation of water sachet waste

A batch reactor is used to investigate the degradation of water sachet waste using heteropoly acid catalyst supported on mesoporous silica (KIT-6). The water sachet waste were cut into small pieces. 2g of the polymer was mixed intimately with 1g of the HPA/KIT-6 in the first run. The reaction temperature was kept at 400°C for 30 minutes. A similar procedure was repeated in the second run using HPA only.

A tube was connected to the flask to transfer the gas to the inverted measuring cylinder as shown in Figure 1. The gas was collected over water. A syringe was connected to the tube to collect the gas along the line. Some gaseous products condensed and collected as liquid sample. The gaseous and liquid samples were extracted using chloroform before analysis using a capillary column Buck Scientific Gas chromatograph (GC) model 910.

The products are usually classified into three groups:

- Liquid products which are condensable at room temperature.
- Gaseous products
- Residues, which include carbonaceous species and waxy compounds.

### 2.5 Analysis of degraded product

The products obtained were cleaned-up using chloroform. This was done to selectively extract the hydrocarbons that are to be analysed using the gas chromatograph. The gaseous products were bubbled into the chloroform while the liquid samples were thoroughly mixed with the chloroform. This mixture was then put in vials (Plastic bottles were not used to prevent reaction that usually occur with components of the plastic). Samples were injected into the GC. The carrier gas used was helium at a pressure of 10 psi.

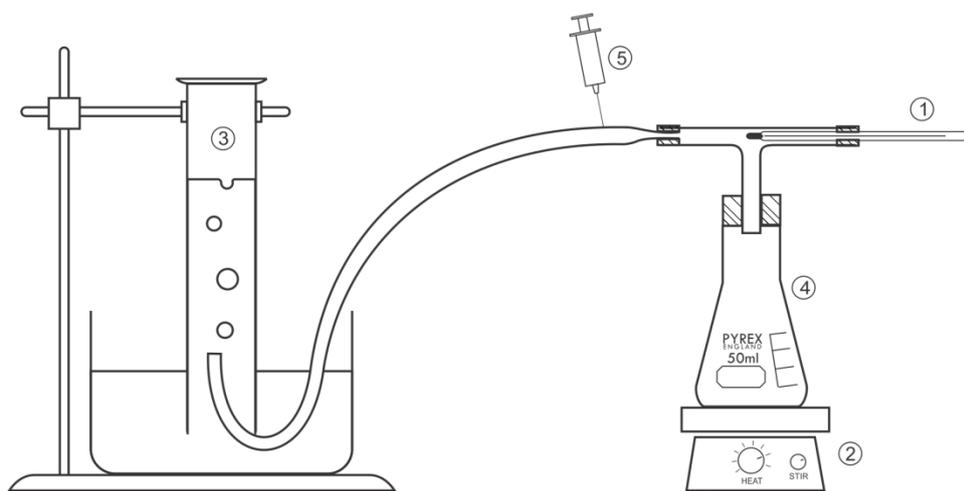


Figure 1 A schematic representation of the experimental set-up

1- Thermometer, 2-Heating mantle,3- Gas product,4-Flask, 5-Injection for gas collection

### 3. Results and discussion

The transmission electron microscopy image of the mesoporous silica KIT-6 prepared and used for this study is shown in Figure 2. This clearly reveals the large domains of ordered pores. Its surface area was determined to be  $694.67 \text{ m}^2/\text{g}$  using the nitrogen adsorption and desorption method. The material therefore provides enormous surface to support cracking reaction. To enhance the availability of active sites (acidic centres) needed for cracking, 12-tungstophosphoric acid (HPA) was grafted on the KIT-6.

Figure 3 shows the volume of gas produced during the two runs, i.e., degradation of water sachet waste (LPDE) over HPA alone and in the presence of HPA/KIT-6. It can be observed that cracking over HPA gives a higher yield of gas product. This indicates that the acid supports cracking of polyethylene more into the shorter chain hydrocarbons. The HPA/KIT-6 produced more of liquid product.

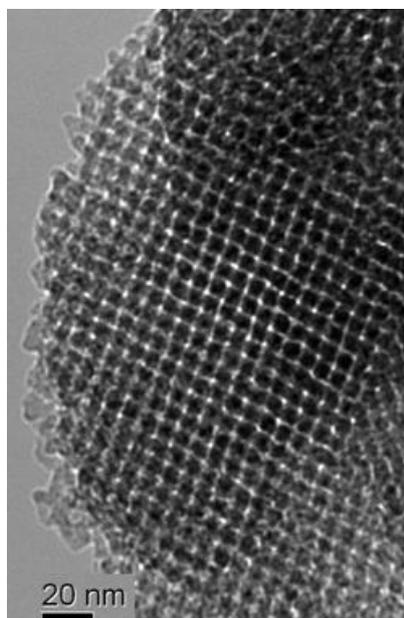


Fig. 2 The transmission electron microscopy image of KIT-6 showing the ordered pores

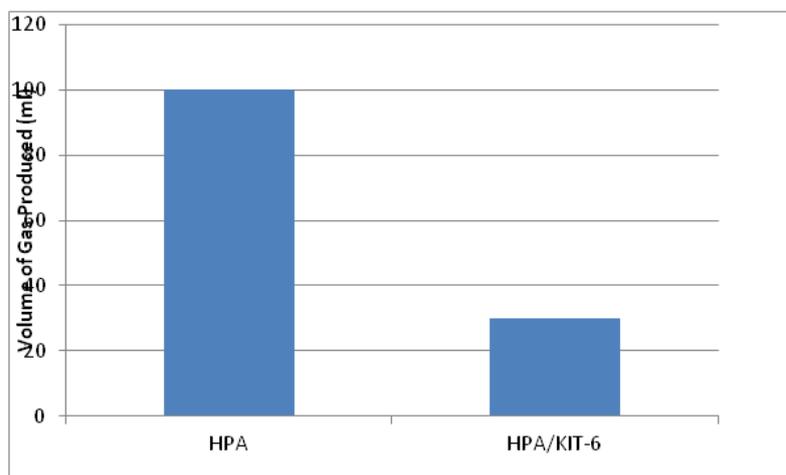


Fig. 3 Gaseous product distribution of water sachet cracking performed in the presence of different catalysts under atmospheric pressure

Figure 4 shows the carbon number distribution of the gas product as analyzed by GC model 910. Degradation with HPA produced mainly  $\text{C}_2$  and  $\text{C}_3$  hydrocarbons while cracking over HPA/KIT-6 produced mainly  $\text{C}_3$  hydrocarbon with trace amount of  $\text{C}_4$  hydrocarbon.

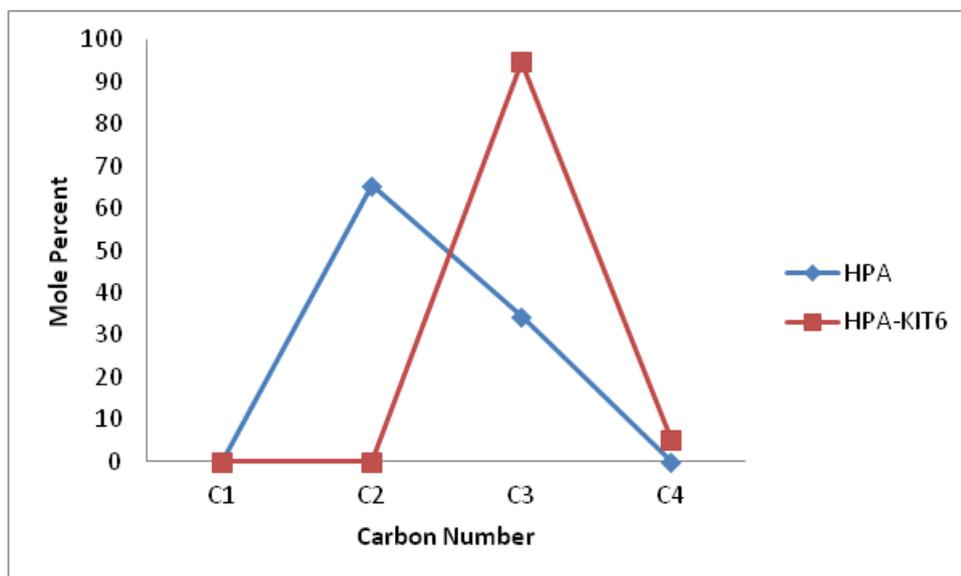


Fig. 4 Carbon number distribution of gaseous product from catalytic degradation of LDPE

The carbon number distribution of the liquid product obtained from the two runs is shown in Figure 5. Cracking over HPA show wide product distribution ranging from C<sub>5</sub> to C<sub>20</sub> hydrocarbons with significant amount of petrol-like hydrocarbons, C<sub>6</sub> – C<sub>12</sub> fractions. Degradation over HPA/KIT-6 also shows wide product distribution ranging from C<sub>10</sub> to C<sub>20</sub> with a predominant amount of kerosene-like hydrocarbons, C<sub>10</sub> – C<sub>17</sub> fractions. The kerosene accounts for 69 mol% of the liquid product, 32 mol% of which is C<sub>16</sub> hydrocarbons.

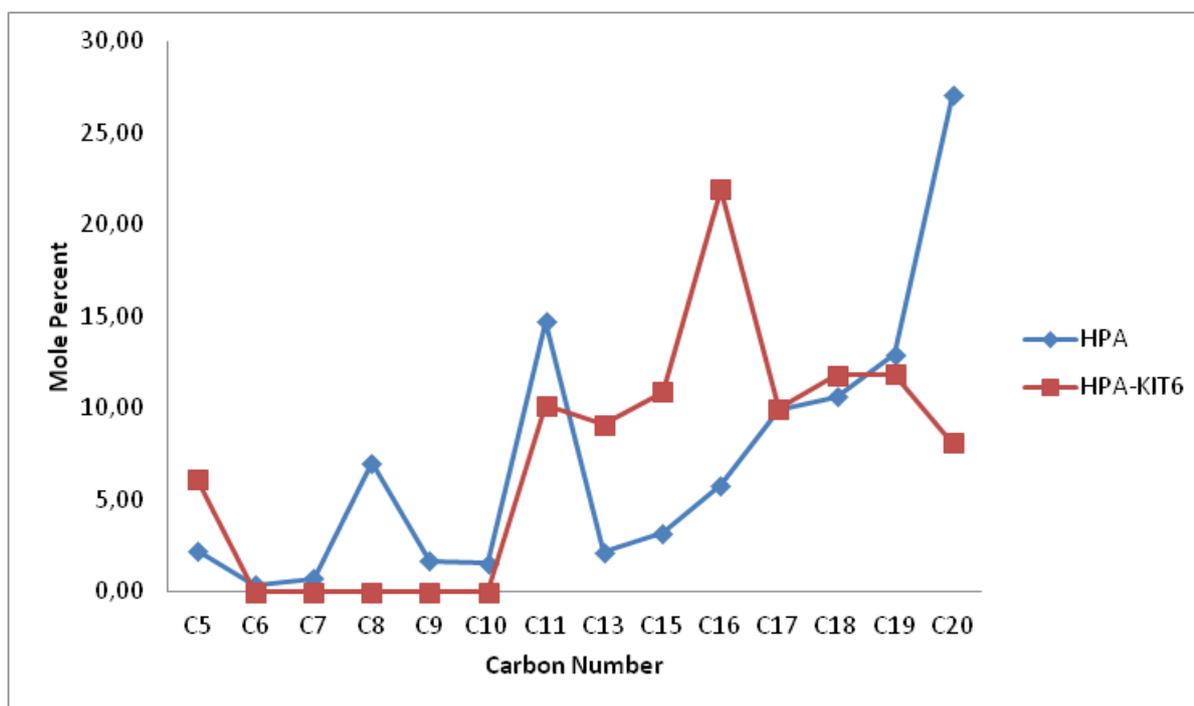


Fig. 5 Carbon number distribution of liquid product from catalytic degradation of LDPE using HPA and HPA-KIT-6.

Gaca et al. [30] reported that catalytic degradation of spent LPDE over HPA/MCM-41 produced gas product containing mainly C<sub>1</sub>, C<sub>2</sub> and C<sub>3</sub> hydrocarbons with only traces of C<sub>4</sub> hydrocarbon. Their liquid product did not show clear maximum; however, the petrol fraction (C<sub>6</sub> – C<sub>12</sub>) made up 62 %. In comparison with this study, cracking over HPA/KIT-6 rather produced liquid product containing 69% kerosene fraction and gas product containing mainly C<sub>3</sub> hydrocarbon. There is agreement in both studies in terms of the selective higher yield of liquid product relative to the gas product. Also the liquid products from both HPA/MCM-41 and HPA/KIT-6 contain only aliphatic hydrocarbons (paraffins and olefins).

Gaca et al. [30] also reported that polyethylene degradation over ZSM-5 zeolites produced liquid containing mainly aromatic hydrocarbons, while gas product formed in high yield was predominantly composed of C<sub>3</sub> and C<sub>4</sub> hydrocarbons. In comparison with this study, cracking over HPA catalyst produced liquid containing only aliphatic hydrocarbons and gas product composed of C<sub>2</sub> and C<sub>3</sub> hydrocarbons. There is agreement in both cases for selectively producing predominantly high yield of gas relative to the liquid product. This affirms the highly acidic nature of zeolite catalyst.

#### 4. Conclusion

Catalytic degradation of water sachet waste over HPA/KIT-6 is a promising route for obtaining clean fuel and intermediates for the chemical and petrochemical industries. It is evident that this technique can be harnessed to re-use water sachet waste which have been causing blockage of drains and resultant flooding. This way, environmental problems arising from water sachet waste can be reduced drastically while yielding useful products in the fuel oil range. HPA-KIT-6 showed a high selectivity toward the production of propane which can be used in the production of cooking gas while the liquid product is mainly kerosene fraction. The product yield (gas/liquid product) and composition is dependent on the catalyst employed.

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