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Original Article

Production of Hydrocarbon Fuels from Polyethylene Plastic Wastes Using Thermal and Catalytic Pyrolysis

Dan Kica Omol [1*], Ongwech Acaye [1], Fred David Okot [1], Ocident Bongomin [2]

[1] Department of Chemistry, Faculty of Science, Gulu University, Gulu, Uganda.
[2] Department of Manufacturing, Industrial and Textile Engineering, School of Engineering, Moi University, Eldoret, Kenya.
* Correspondence: omolokica2017@gmail.com; Tel.: +256782550568

Abstract: Plastics have become an indispensable part of modern life today. The global production of plastics has gone up to 299million tones in 2013, which is believed to be increasing in the near future. The utilization of plastics and its final disposal pose a tremendous negative significance impacts on the environment. The aim of this study was to investigate the thermal and catalytic pyrolysis for production of hydrocarbon fuel from the polyethene plastic wastes. Catalysts used in the experiment were acid activated clay mineral and aluminum chlorides on activated carbon. The clay mineral was activated by refluxing it with 6M Sulphuric acid for 3hours. The experiment was conducted in three different phases: the first phase of the experiment was done without a catalyst where 88mL oil was obtained at a maximum temperature of 39 ℃ and heating rates of 12.5℃/minutes, reaction time of 4hours. The second phase involves the use of acid activated clay mineral where 100mL of oil was obtained and heating rates of 12.5℃/minutes and reaction time of 3hours 30minutes. The third phase was done using aluminum chlorides on activated carbon and 105ml oil was obtained at a maximum temperature of 400℃ and heating rates of 15.5℃ reaction time of 3hours 10minutes. From the results, catalytic pyrolysis is more efficient than purely thermal pyrolysis and homogenous catalysis (aluminum chlorides) shows a better result than solid acid catalyst (activated clay minerals) hence saving the energy needed for pyrolysis and making the process more economically feasible.

Keywords: plastics wastes, pyrolysis, catalyst, Activation, hydrocarbon fuel, polyethylene

1. Introduction

Inevitably in the modern world today plastics have interwoven our life and life without plastics is impossible [1]. The global production of plastics increased by over 4% in 2012 and reached about 299 million tons in 2013 [2]. Plastic wastes are the third major component of municipal wastes in East African cities after organic waste and paper wastes. By 2011 plastic waste levels in East Africa was approaching 10% net weight of the total solid waste flows in major urban centres [3, 4]. The most common ways in which plastics have been disposed of within Africa and the western world has been through the Municipal Solid Waste (MSW) stream. This has most commonly entailed landfill or incineration [5]. However, both methods are recognized as posing negative impacts on the environment and are ultimately unsustainable [6]. Until now landfill has been the predominant method of disposing of plastic solid wastes (PSW) [7]. Understanding this problem led to development of several methods including chemical depolymerization, gasification, pyrolysis and catalytic degradation [8–11]. The products from tertiary recycling are often hugely varied depending on the process parameters utilized in the plastic production [12–14]. As such, much research has been performed to ascertain the conditions which produce the highest value product yields.

This process can be further manipulated through the adjustment of process parameters or the addition of catalyst so that the production of specific molecular weight compounds can be achieved making the process more economically viable and sustainable [12–14]. In this study the potentiality of activated montmorillonite clay in catalyzing the pyrolysis reaction is investigated and compared with conventional catalyst.

2. Literature Review

In order to understand the available technology on plastics wastes pyrolysis, literature review was conducted. Many studies have been conducted on High Density Polyethylene (HDPE) Pyrolysis at different operating parameters to investigate the product yield obtained. Ahmad et al [15] explored the pyrolysis study of HDPE using micro steel reactor. The pyrolysis temperatures were within 300–400 ^{0}C at heating rate of 5–10 ^{0}C/min. Nitrogen gas was used as the fluidizing medium. From the experiment, they found that the highest total conversion happened to be at 350 ^{0}C with liquid was the dominant product yield (80.88 wt. %). The solid residue was very high at 300 ^{0}C (33.05 wt. %) but the amount was reducing to0.54 wt. % at the highest temperature of 400 ^{0}C. On the other hand, Kumar & Singh [16] have done the thermal pyrolysis study of HDPE using semi-batch reactor at higher temperature range of 400–550 ^{0}C. It was observed that the highest liquid yield (79.08 wt. %) and gaseous product (24.75 wt %) obtained at temperature of 55^{0}C while wax started to dominate in product reaction at higher temperature of 500–550 ^{0}C. The dark brownish oil obtained from the pyrolysis had no visible residue and the boiling point was from 82 to 352 ^{0}C. This suggested the mixture of different oil component such as gasoline, kerosene and diesel in the oil that matched the properties of conventional fuel. Besides, the sulfur content in the HDPE pyrolytic oil was very low (0.019%) that made it cleaner to the environment.

As one way to recover energy and reduce waste, pyrolysis of Low Density Polyethylene (LDPE) to oil product has received much attention by vast researchers in the recent years [17–22]. Bagri & Williams [23] have investigated the LDPE pyrolysis in fixed-bed reactor at 500 ^{0}C with heating rate of 10^{0}C/min. The experiment was done for duration of 20 min and nitrogen was used as fluidizing gas. It was observed that high liquid yield of 95 wt% was obtained with low gas yield and negligible char. In this research, the investigation was carried out on the mixture of LDPE and HDPE and determining the potentiality of chosen catalyst to degrade plastics wastes.

3. Materials and Methods

3.1. *Sample Collection*

The waste plastics used in this experiment consisted of a mixture of 100g HDPE and 100g LDPE resins which were collected from within Laroo division rubbish pit around Gulu University main campus. The samples were manually collected from the designated area, packed in sacks and carried to the chemistry laboratory. From the laboratory, the waste plastics were sorted according to their resin type as indicated by the resin identification codes and placed in different boxes. The dirty plastics wastes were washed with water and detergent solution, dried and then kept for the further processing.

3.2. *Pelletalization Technique*

This is a process of forming plastic pellets from the light to bulky plastic materials. This helps reduced their surface area and makes them easy to be transported and packed inside the reactors. During this process the cleaned plastics were cut in to small pieces and placed on the hot plate heating machine covered by aluminum foil, and heated to a temperature of about 150^{0}C and rolled with a piece of metal into a ball like structure. The pellets were then cooled and stored for the pyrolysis experiment.

3.3. *Catalysts Materials*

Catalyst material used for this experiment was a Lewis acid-based catalyst, Aluminum chlorides supported by activated carbon both obtained from the local market. Natural catalyst in form of gray clay was also used for this experiment. The clay is locally available and was collected from within Gulu municipal swamp valley beds.

3.4. *Preparation of the natural Catalyst*

The clay material was obtained from the local swamp bed in Laroo division massed up using a wooden roller and cut into small cubes (approximately 1cm^3).The cubes were heated in the universal hot air oven at 150^{o}C for six hours, allowed to cool for one day and crushed into fine powder using a mortar and pestle. The mixture was sieved to remove the gravels and small stones and the fine powder mixed with 6M sulfuric acid in a glass beaker, stirred and the mixture refluxed for 3hours and vacuum filtered. The residue in the filter paper were washed thoroughly using distilled water several times, and the clean residue was tested for the presence of sulfates using acidified barium nitrates to ensure that no sulfate ion is present in the activated clay sample. It was placed inside the universal hot air oven for another one day for drying. This activated clay mineral powder was made into a paste with starch powder and some small quantity of distilled water sand rolled into small cubes, dried and kept for the experiment. The advantage of pelletizing the catalyst powder are to put easily in the catalytic bed and reduce the pressure drop, by blending the activated clay with a starch powder, the void fraction between the inter-particles of the catalyst pellets were increased.

3.5. *Laboratory Preparation of Inert Gas*

Since the pyrolysis experiment is carried out under an inert atmosphere, unfortunately the only limitation for this experiment that there is no nitrogen source, this limitation will be overcome by preparing the inert gas in the laboratory by removing all the reactive gases like oxygen, carbon dioxides, water vapor from the atmospheric air using simple laboratory technique.

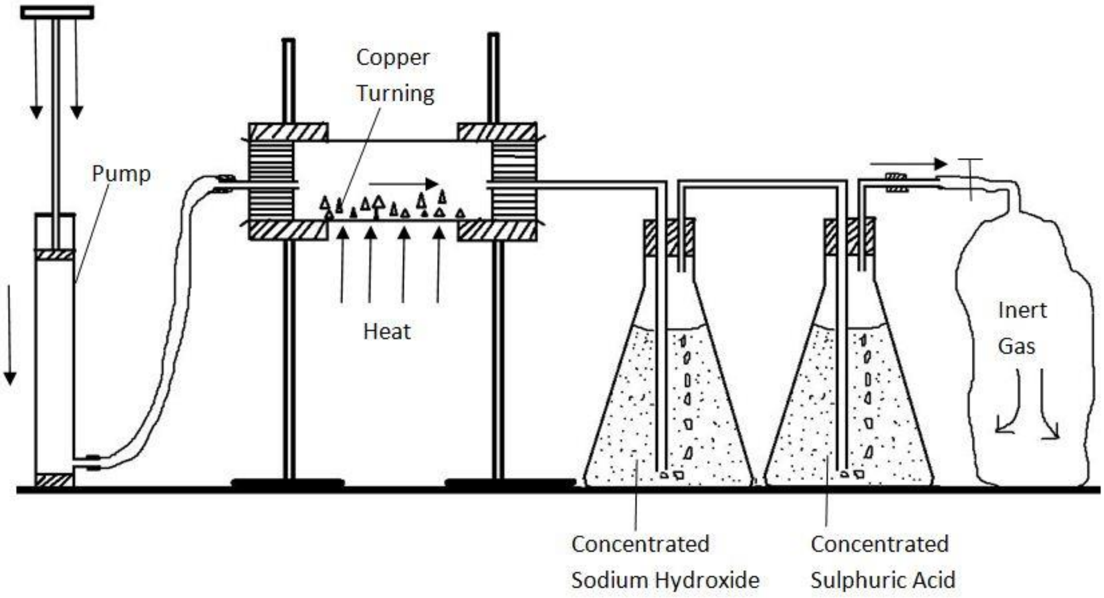

Figure 1: Set up for laboratory preparation of inert gas.

3.6. Experiment setup layout for hydrocarbon fuel production

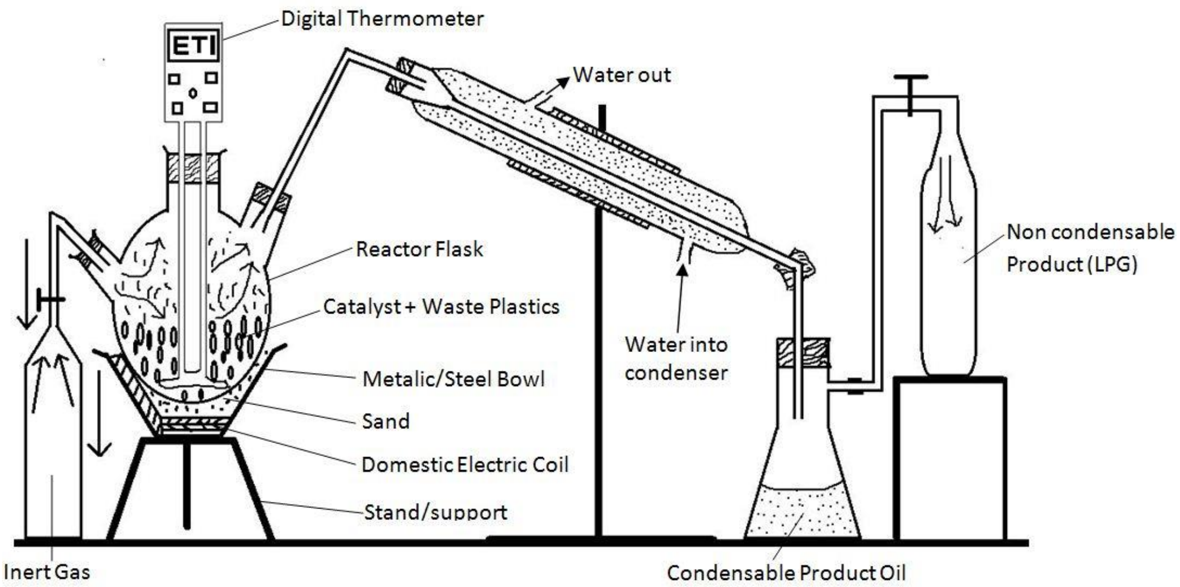

Figure 2: Experimental setup for hydrocarbon fuel production from plastic wastes

3.6.1. Using acid activated clay catalyst.

A mixture of HDPE and LDPE plastic resins (1:1 w/w, 200g) were fed into the reactor flask and 20g of catalyst (10:1 w/w) was added. The electrode of the thermocouple thermometer is inserted in the reactor flask and the tip was immersed in the fed stoke catalyst mixture from the vertical opening and sealed completely as shown in **Figure 2**. The inert gas generated as shown in **Figure 1** was directly fed into set up **(Figure 2**). The reactor flask, placed on sand in a steel basin was heated electrically. The inert gas was allowed to pass through the set up for some time to drive out air and replacing it with the inert nitrogen. After flashing the system, an empty balloon or Teflon bag is connected to the side arm of the conical flask. When all the connection is made the system becomes isolated from the surrounding in terms of air movement. The power was switched on, and the time and temperature taken for the fed stoke to melt were recorded.

3.6.2. Using aluminum chloride on activated carbon

In the second session of the experiment, the procedures in subsection 3.6.1. were repeated but with aluminum chloride on activated carbon as catalyst.

3.6.3. Thermal pyrolysis of plastic wastes

In the third part of the experiment, the procedures of 3.5.1. were repeated but with no material catalyst in place.

3.7. Data analysis method

The data collected were fed on excel and statistically analyzed to determine the correlation between temperature and the amount of oil collected.

4. Results

The results obtained for the pyrolysis experiments are shown in tables 1-3

Table 1: Catalytic pyrolysis using acid activated clay catalyst (heterogeneous catalysis).

Temperature (℃)	**Amount of oils** (mL)
27.0	0
127	0
150	0
200	10
250	25
300	90
350	100
390	100

Reaction heating rates = 10.5℃/min

Table 2: Catalytic pyrolysis using aluminum chloride catalyst (homogeneous catalysis)

Temperature (℃)	**Amount of oil (mL)**
27	0
75	0
110	0
150	0
200	15
250	65
300	88
350	105
400	105

Reaction heating rates = 15.5℃/min

Table 3: Thermal pyrolysis of plastic wastes

Temperature (℃)	**Amount of Oil (mL)**
27	0
127	0
172	0
222	5
272	7.4
322	30
372	76
384	80
386	88

Reaction heating rates = 12.5℃/ minute

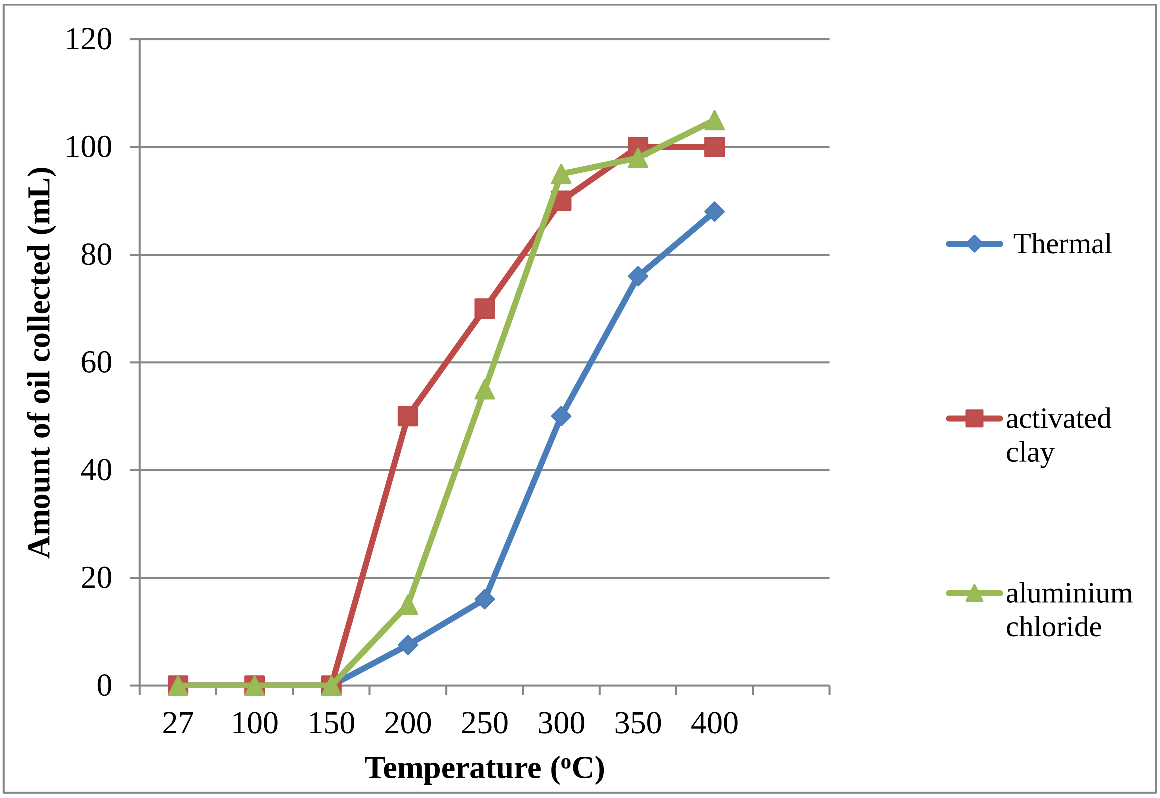

Figure 3: Line graph showing variation of amount of oil collected with pyrolysis temperature

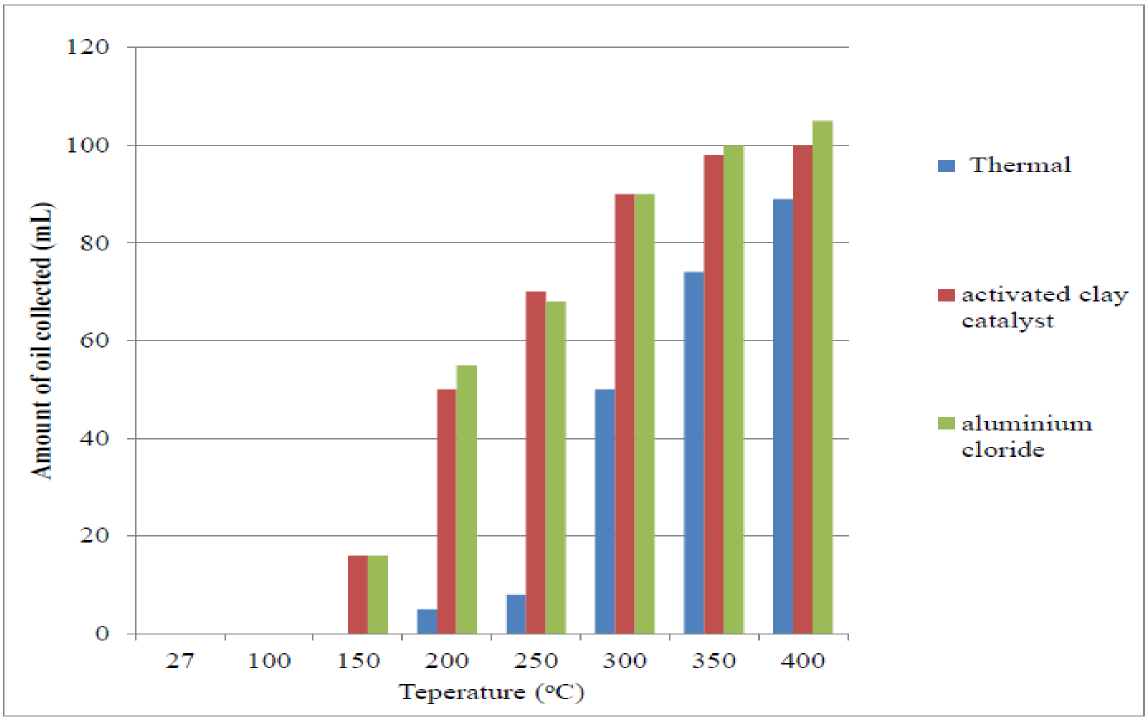

Figure 4. Bar graph showing amount of oil collected at varying temperatures

5. Discussion

Tables **1-3** indicate that the yields attained after cracking a mixture of HDPE and LDPE at varying temperatures. The degradation of plastic wastes started at temperatures above 150℃ for all the three conditions investigated. For the purely thermal pyrolysis the degradation started at the temperature of 205℃ and a slight increase in temperature from 205-222℃ at an average heating rate of 12.5°C increased the volume of oil collected by 5mL. The reaction took about 5 hours to go to completion. Generally, for catalytic pyrolysis the drop of oil started at much lower temperatures (170°C) and (185°C) using aluminium chlorides catalyst and acid activated clay minerals respectively. But an increase in temperature from 170℃ to 200℃ produced 15 mL of oil which is 7.5% conversion with aluminium chloride catalyst. When using acid activated clay, 10mL of oil was collected which is 5% conversion for the temperature increase from 185℃ to 200℃. These figures were however much lower than those obtained by Motevasel et al [12] who found out that thermal degradation of a mixture of plastic wastes start at 370℃ with less that 10% conversion but with up to 40% conversion when using a catalyst. The big difference is due to variation in temperature distribution in the reactor hence the plastics in contact with the reactor absorbs heat faster and start degrading. At some points, even when melting and volatilization had already started, the thermo-couple would still be indicating quite law temperatures. Nevertheless, it was possible to determine that for thermal pyrolysis, the degradation temperature is higher compared to those of catalytic degradations. This is basically because the catalysts offer alternative pathways of lower activation energies (**Figure 3**). The same figure also indicates that catalytic degradations registered higher amount increase in volume of oil collected for corresponding increase in temperature.

From **Figure 4**, it can be seen that for every temperature increase attained, the quantity of liquid product is grater for the catalytic conversion compared to thermal conversion process. This is in line with the results obtained by Motevasel et al [12] who found increase in the product yield with increase in temperature using catalyst. However, at very higher temperatures (350 – 400°C), even thermal degradation becomes almost as efficient as catalytic degradation Therefore it can be concluded that catalytic degradation is a more efficient method of the pyrolytic conversion of plastic wastes in to fuel. Moreover, **Figure 4** also indicates that catalytic conversion using aluminum chloride (homogenous catalyst) yielded slightly higher amounts of oil compared to using activated catalyst (heterogeneous catalysis). This is because the heterogeneous catalyst having a solid particulate matter interferes with the heat conductivity in the reactor which affects the overall distribution of heat in the reactor and cause low degradation at a particular temperature.

The aluminum chlorides used as catalyst works in the homogenous state. On adding the catalyst in the reacting vessel it gets dissolved in the molten plastics and becomes in a uniform phase as the reacting mixture hence the process of heat conductivity is not interfered with therefore heat conductivity and distribution will be faster compared to when using a solid acid (heterogeneous catalyst), so the product formed at a specific temperature will be higher compared to when using a solid acid catalyst in heterogeneous phase.

The only problem with using homogenous catalyst in the pyrolysis reaction is that it is unrecoverable after the reaction therefore its disposal is unsafe to the environment. Solid acid such as activated clay catalyst is recoverable after the reaction and can be used again and its disposal does not cause any damage to the environment. It is green chemical transformation.

5. Conclusions

The pyrolysis of plastic wastes was investigated as an effective approach to recycle plastics in the municipal plastic wastes. Plastic wastes can easily be converted into hydrocarbon fuels using locally available materials. In the experiments conducted it was found that more oil product was obtained using catalytic pyrolysis at the specific temperature and the degradation of the plastics started at lower temperature compare with purely thermal pyrolysis. Therefore, catalytic pyrolysis is a better method of conversion of plastic wastes to fuel.

Acid activated clay mineral is a good heterogeneous cracking catalyst since it is recoverable after use and its final disposal poses no threats to the environment. Moreover, it has good catalytic activity compared to a homogenous catalyst which is unrecoverable after use and the disposal of the residue poses a significant negative impact on the environment. The degradation of plastics is favored at a higher temperature of 340-400°C, this is the temperature ranges where more liquid oil products is form.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

A B

A: Pellets of a mixture of HDPE and LDPE plastic wastes
B: Waste plastics pyrolysis oil sample (WPPO)

C D

C: Raw montmorillonite clay minerals
D: Acid activated montmorillonite clay mineral.

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