Thermal and Catalytic Pyrolysis of Low-Density Polyethylene (LDPE) Wastes into Useful Fuel Oils: Comparative Studies

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Abstract: *Catalytic and non-catalytic (thermal) conversion of polyolefinic wastes into useful liquid fuel oils rich in paraffinic and olefinic hydrocarbons were attempted using a self-designed stainless-steel laboratory reactor. For the catalytic process, the waste polymer was degraded in an organic solvent (Toluene) by a bi-metallic catalyst (CoMo/Al$_2$O$_3$) into solid residue, liquid fuel oil and flammable gaseous hydrocarbon products after 1¼ hr of the catalytic reaction at temperature range of 260 – 325°C. The thermal process yielded identical products but at a longer reaction time (2hrs) and higher temperature range of 474-520°C. The smell, characteristics and the hydrocarbon distribution of the liquid fuels of both processes overlap with the existing hydrocarbon fuels obtainable in the refineries in that they contain C$_8$-C$_{24}$ hydrocarbons. The solid residue exhibits the characteristics of grease while the highly volatile gaseous product was eluted without collection due to technical difficulties. Closed-system reaction operations of this nature can be utilized to achieve 100% conversion of polyolefinic wastes to desirable hydrocarbon products that can serve as alternatives to existing fuels thereby reducing the burden of plastic wastes on the environment.*

Keywords: *Polyolefinic waste, Low Density Polyethylene, Thermal cracking, Catalytic cracking, Bi-metallic catalyst*

1. INTRODUCTION

There has been remarkable progress in polymer cracking in the last decade and research is still ongoing to be able to get the most utilization of plastic wastes. Polyethylene, particularly Low-density polyethylene (LDPE) has been principally targeted because of its numerous applications especially in packaging as well as insulation [1] and its excellent source of hydrocarbon products but it is highly resistant to thermal degradation; requiring a temperature of above 400°C in order to exhibit sufficiently high degradation rates. Most of the previous studies were carried out on thermal pyrolysis but these processes require very high temperatures, are less sensitive than catalytic processes to dirt as well as critical impurities (such as Chlorine, Sulphur, Nitrogen and heavy metals), and the end products are mostly of lower quality thus lesser value [2,3]

Thermal pyrolysis also consumes large amounts of energy due to the low thermal conductivity of polymers coupled with the endotherm of cracking [4]. Thus, catalytic technologies have been proposed to promote cracking at lower temperatures, reduced energy consumption and higher conversion rates [5,6]. Furthermore, use of specific catalysts allows the process to be directed towards the formation of a narrower distribution of hydrocarbon products with a higher market value [5,7]. The advantages of catalytic pyrolysis over thermal degradation include lower degradation temperature and a narrower hydrocarbon product distribution [8].

Hydrocracking of plastics is a potential alternative for breaking down the polymer chain in that it can considerably lower the energy requirement of pyrolysis reaction. It can equally promote a more selective as well as a narrower hydrocarbon product distribution leading to the formation of highly saturated products and avoiding the presence of olefins in the liquid fractions which favours their use as fuels without further treatments. Moreover, hydrogenation promotes the removal of hetero atoms, such as chlorine (Cl), nitrogen (N) and sulphur (S), in the form of volatile compounds. A typical hydrogenation catalyst is bi-metallic in nature and often includes transition metals, such as nickel (Ni), molybdenum (Mo) and iron (Fe), supported on acidic solids such as alumina, zeolites or amorphous silica-alumina [7]

The present study was conducted to investigate the efficiency of a hydrocracking catalyst under hydrogenation conditions to degrade low density polyethylene in a self-designed laboratory reactor to achieve maximum optimization of the catalytic pyrolysis process and this could only be estimated appropriately by making comparisons with a non-catalytic process (thermal pyrolysis)

2.   MATERIALS AND METHODS

2.1 Sample Collection and Preparation

The waste polyolefin film (discarded table water sachets) collected from household and municipal wastes were washed, dried and shredded into smaller pieces to aid the degradation.

2.2 Catalyst preparation

The catalyst used, CoMo/Al_2O_3 was prepared by stepwise impregnation of molybdenum and cobalt salts on alumina support in a procedure similar to that described in literature [9]. Ammonium heptamolybdate ((NH_4)$_6Mo_7O_{24}$) and Cobalt nitrate hexahydrate (Co(NO_3)$_2$· $6H_2O$) salts, both of analytical grade from BDH chemicals were utilized for the two-step process. A 30 g of the alumina (support) was soaked first in an aqueous solution containing 9 g of ammonium heptamolybdate. The resulting impregnated catalyst was then dried in an oven at 120 ^{0}C for 6 hours and then calcined at 500 ^{0}C for 4 hours. After the catalyst was allowed to cool, it was further soaked in an aqueous solution containing 3g of cobalt nitrate and later dried as well as calcined at 120 ^{0}C and 500 ^{0}C for 6 hours each respectively after which it was stored in an airtight bottle.

2.3 Cracking experiments

Thermal cracking

The thermal cracking experiments were carried out in an air tight cylindrical stainless-steel reactor of length 210 mm and 22 mm inner diameter fitted with connecting pipes to transfer necessary gases as well as products into and out of the reactor respectively. A condensing flask maintained at 4°C was attached to the outgoing pipe to separate non-condensing and condensing gaseous products. 100 g of waste low density polyethylene film (shredded table water sachets) was arranged in the reactor and heated after an initial purging with nitrogen for 30 minutes. Adequate precautions were made to prevent leakages and the temperature was allowed to rise gradually until evolution of gases was observed at 474°C. This occurred at 45 minutes into the reaction and after this, oil droplets started collecting in the condensing flask. The collection proceeded for another 1 hr 15 minutes after which the reaction was discontinued when evolution of gases effectively ceased. The overall temperature range for the experiment was between 474-520°C which were the temperatures at the first visual sign of evolution of gases and at the end of the experiment respectively. The heat was removed and the reactor residual content was overturned into a metal plate where it rapidly cooled into a grease-like substance that was weighed. The weight of the oil was also determined and the weight of the gaseous product was estimated by material balance [9,10]. The grease remained soft and stains the finger when touched even after several weeks. The composition of the oil was determined by Gas Chromatography/Mass Spectromerty (GC-MS).

Catalytic cracking

The experimental set-up was similar to the one described above only that 10 g of the prepared catalyst was put between successive layers of the waste polymer film and 200 mls of the solvent (toluene) was added before the experiment commenced. In this case also, adequate precautions were made to prevent leakages and all the steps required for purging were duplicated. After the purging, a steady flow of hydrogen gas was introduced into the reactor and this was maintained for the duration of the experiment which lasted for 75 minutes. The overall temperature range for the reaction was 260°C – 325°C which as mentioned above were the temperatures at the first visual sign of evolution of gases and at the end of the experiment respectively. The weights of the products were determined as above and the oil products from all the experiments were analyzed by Gas chromatography/Mass spectrometry technique specifically GCMS-QP2010 PLUS. The compositions of the oils were determined from the results obtained from the analysis.

N₂ gas for purging and thermal cracking experiment
H₂ gas for catalytic hydrocracking experiment

Stainless-steel reactor

Condenser maintained at 4°C
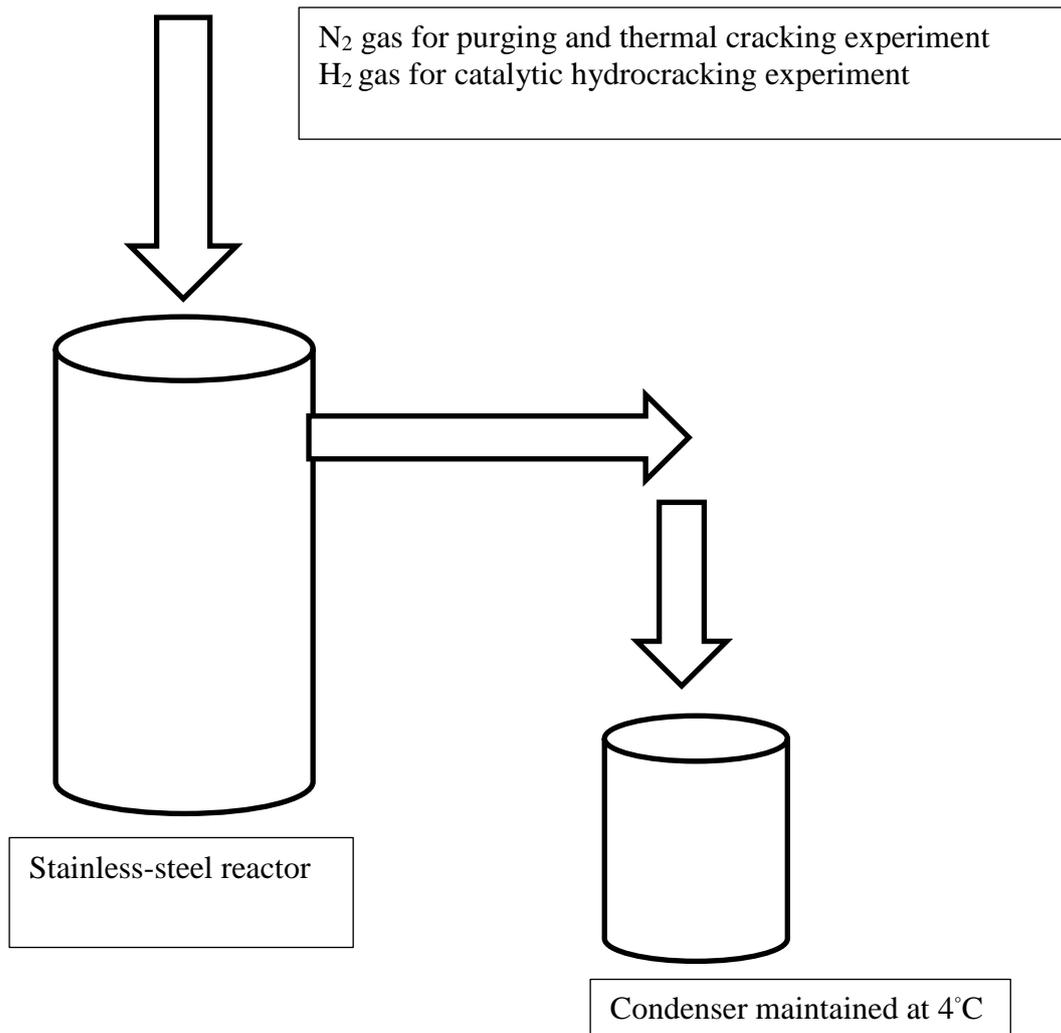
Figure 1: Simple schematic representation of the experimental set-up

3.   RESULTS AND DISCUSSION

The percentage products as well as the hydrocarbon distributions of the oils from the two experiments were obtained through the following calculations [11] and summarized in Table 1 as well as Figures 2&4;

$$\% \ mass \ of \ solid \ product \ = \ \frac{total \ solid \ produced (Kg)}{total \ plastic \ fed \ (Kg)} \times 100$$

$$\% \ mass \ of \ liquid \ product \ = \ \frac{total \ solid \ produced (Kg)}{total \ plastic \ fed \ (Kg)} \times 100$$

$$\% \ mass \ of \ gaseous \ product \ = \ \frac{100 - (solid + liquid) \ produced (Kg)}{total \ plastic \ fed \ (Kg)} \times 100$$

$$\% \ overall \ conversion \ = \ \frac{total \ solid + liquid \ produced (Kg)}{total \ plastic \ fed \ (Kg)} \times 100$$

$$\% \ selectivity * = \ \frac{mass \ of \ specific \ hydrocarbon \ compound}{total \ mass \ of \ all \ hydrocarbons \ produced} \times 100$$

$$\% \ saturation \ or \ un-saturation * = \frac{mass \ of \ specific \ olefinic \ or \ paraffinic \ compound}{total \ \ mass \ of \ all \ paraffins \ and \ olefins} \times 100$$

*The relative concentration as determined by GCMS

Table 1: Yield of products, Wt (%)

Products	Thermal Cracking	Catalytic Cracking
Solid	34.89 ± 0.29	37.03 ± 0.25
Liquid oil	22.03 ± 0.33	35.23 ± 0.38
Gas	43.08 ± 0.42	27.74 ± 0.24
% overall conversion	56.92	72.26

The gaseous products of all the experiments were all non-condensing at 4°C and this indicates the presence of lower hydrocarbons that was confirmed by flame tests [12]. The solid products obtained from the thermal cracking experiments were grease-like and softer than those of the catalytic cracking processes which bore close resemblance to a wax but the reverse was expected. The liquid products of all the experiments were oily and light with golden brown colour but those of the catalytic processes were paler. The GC/MS analysis results of the oils suggest wide product distributions ranging from $C_8 – C_{24}$ and $C_7 – C_{20}$ hydrocarbons for the thermal and catalytic processes respectively. The compounds identified which were mainly aliphatic hydrocarbons (normal alkanes, iso alkanes, normal and iso alkenes) are illustrated by the following figures;
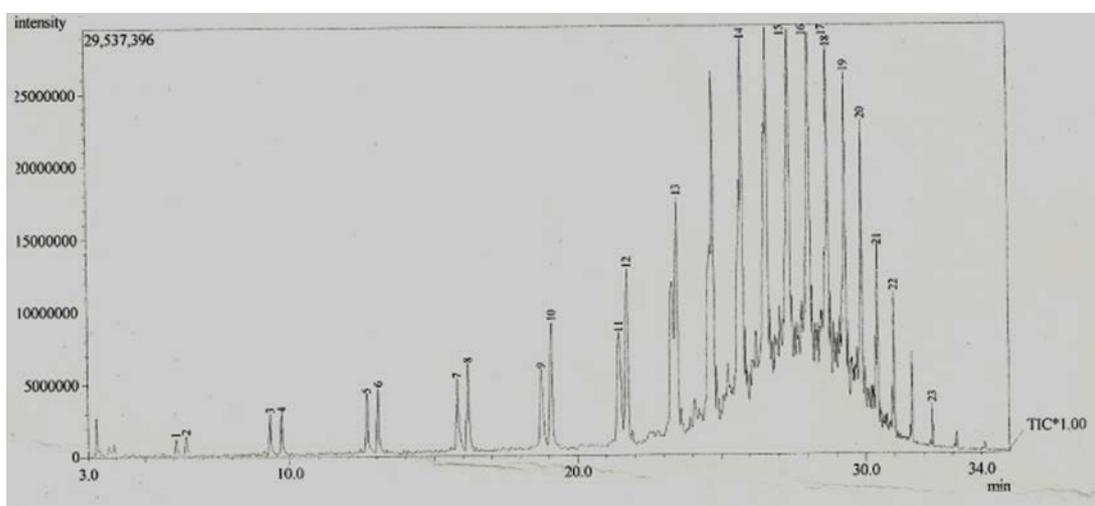
Figure 2: GC-MS Chromatogram of the Liquid Product of Thermal Cracking of LDPE
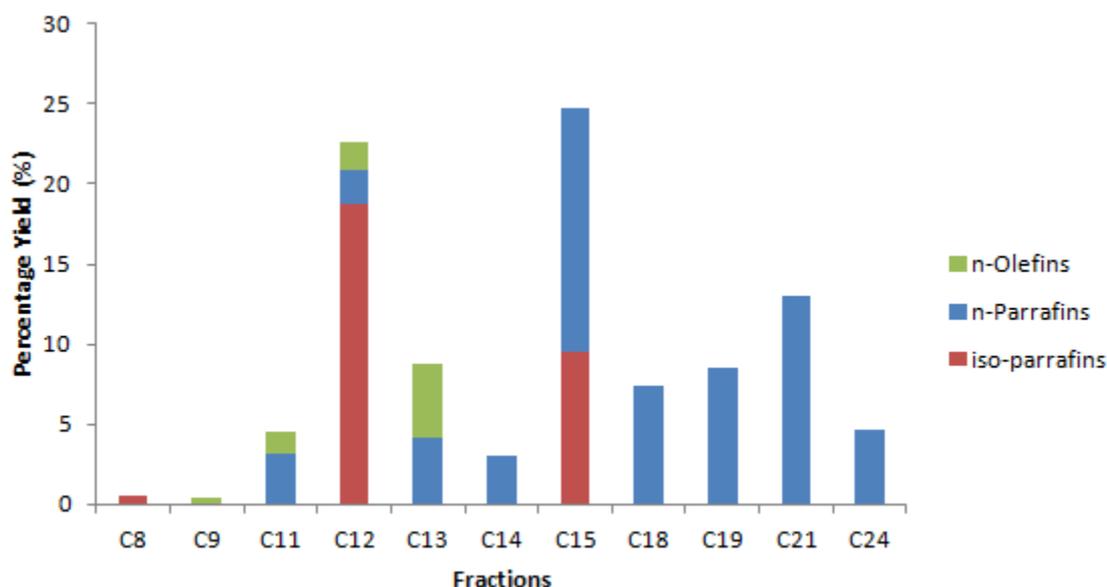
Figure 3: Hydrocarbon distribution of the liquid product of thermal cracking of LDPE
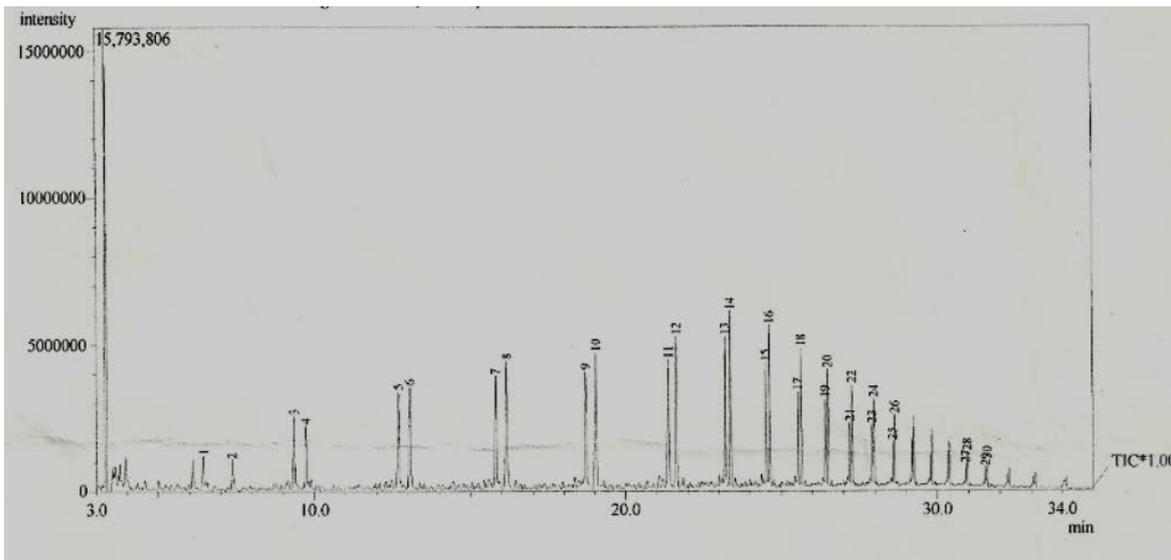
Figure 4: GC-MS Chromatogram of the Liquid Product of Catalytic Cracking of LDPE
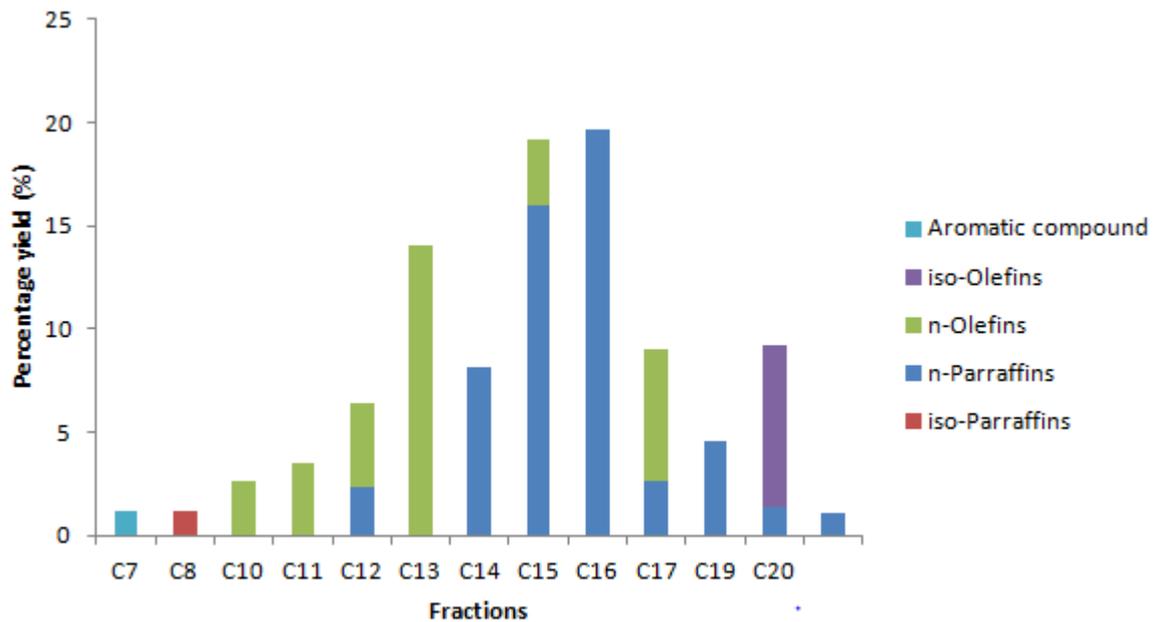
Figure 5: Hydrocarbon Distribution of the Liquid Product of Catalytic Cracking of LDPE

The oil yield of the catalytic process was higher than that of the other process while the reverse is the case for the gaseous product and this agrees with what was obtained in a similar experiment where $NiMo/Al_2O_3$ was used [13]. The compositions of the oils were similar in the sense that higher percentages were observed in the $C_{10} - C_{15}$ regions for both cases. The catalytic process produced more olefins than the thermal process most of which were alpha olefins with some amounts of iso-olefins. The yield of paraffins from the non-catalytic process was however higher than that of the catalytic and the reverse was also expected in this case because of the expected hydrogenating ability of the catalyst. According to literature [11], likely hydrogenation reactions between unsaturated compounds and H_2 molecules produced from the cracking process itself can enhance the generation of paraffins which seems to occur more in the thermal process thereby giving the indication of low activity of the catalyst probably due to poor activation [8].

The cracking of some plastics or mixtures of them have been reported to be possible or enhanced by the use of a suitable hydrogenation catalyst as well as solvent [14]. It has also been discovered that improved solvent blending of polymer and catalyst using a solution slurry method in toluene promotes the degradation of polyethylene with claims that the first weight loss was observed just above 200°C [15]. This is in agreement with what was obtainable in the catalytic cracking experiment of the present study as the conversion started at a lower temperature (260°C) than observed for the thermal cracking

experiments. The solvent probably promoted interactions between the catalyst and the waste polymer. An aromatic compound was produced from the catalytic process which could be due to interference of the solvent since aromatic fractions are supposed to be obtained at high temperatures [7]

The oils products of this study were found to be similar to those obtained in previous studies where iso and straight chain hydrocarbon fractions [16] are reported to be identical in composition to the petroleum fractions obtainable in the refineries: $C_4 - C_{12}$ (petrol), $C_{10} - C_{18}$(kerosene) and $C_{15} - C_{25}$ (diesel) [9]; $C_5 - C_{10}$ (gasoline), $C_{10} - C_{16}$ (kerosene) and $C_{14} - C_{20}$ (diesel oil) [12] and ($C_6 - C_{12}$) (petroleum fraction) and $C_{10} - C_{17}$ (kerosene fraction) [17] hence the oils from the present study are comparable to existing fuels in the refineries.

4. CONCLUSIONS

Through this investigation, waste low density polyethylene film was successfully converted by thermal and catalytic processes into solid, oil and gaseous products using a self- designed stainless-steel laboratory reactor. The catalyst increased the oil yield but without much selectivity as expected. In terms of the compositions of the oils produced, the thermal process gave a better result than the catalytic process whereas the contrast was expected, and this is an area that could be further researched.

REFERENCES

[1] Socci, J., Osatiashtiani, A., Kyriakou, G & Bridgwater, T. (2019). The Catalytic Cracking of Sterically Challenging Plastic Feedstocks over High Acid Density Al-SBA-15 Catalysts, *Applied Catalysis A, General,* 570, 218–227
[2] Ylä-Mella, (2005). Recycling of Polymers; Environmental Catalysis. [Online]. Available: www.oulu.fi/resopt/PlastRec.pdf
[3] Gandidi, I. M., Susila, M. D., Mustofa, A. & Pambudi, N. A. (2018) Thermal and Catalytic Cracking of Real MSW into Bio-Crude Oil, *Journal of the Energy Institute*, 91, 304-310
[4] Achilias, D. S., Antonakou, E., Roupakias, C. Megalokonomos, P. & Lappas A. (2008). "Recycling Techniques of Polyolefins From Plastic Wastes" *Global NEST Journal*, 10, (1),114-122
[5] Al-Salem, S. M., Antelava, A., Constantinou, A., Manos, G. & Dutta, A. (2017). A Review on Thermal and Catalytic Pyrolysis of Plastic Solid Waste (PSW), *Journal of Environmental Management*, 197, 177-198
[6] Miandad, R., Barakat, M. A., Rehan, M., Aburiazaiza, A.S., Ismail, I.M.I. & Nizami, A.S. (2017) Plastic Waste to Liquid Oil through Catalytic Pyrolysis Using Natural and Synthetic Zeolite Catalysts, *Waste Management* 69, 66–78
[7] Aguado, J. & Serrano, D., (1999), *Feedstock Recycling of Plastic Wastes*. Royal Society of Chemistry, (Series Editor J.H. Clark), Cambridge, United Kingdom
[8] Rodd L., (2000), Catalytic Cracking of Polyethylene over Mesoporous Materials, Individual Inquiry, Department of Chemical Engineering, University of Queensland, Brisbane. [Online] Available: http://www.cheque.uq.edu.au/ugrad/theses/2000/iitheses/L_Rodd.pdf,
[9] Kareem, S.A & Kadiri, A.O., (1998), Hydrogenation of Thevetia Peruviana Seed Oil using Cobalt Oxide-Molybdenum Oxide Catalyst Supported on Activated Carbon, *Nig. J. Pure & Applied Sciences*, 13, 629-635.
[10] Low, S. L., Connor, M. A. & Covey, G. H. (2001). "Turning Mixed Plastic Wastes into Useable Liquid Fuel". Paper Presented at the 6th World Congress of Chemical Engineering, Melbourne, Australia, 23-27 September, 2001.
[11] Auxilio, A. R., Choo, W., Kohli, I., Srivatsa, S. C. & Bhattacharya, S. (2017) An experimental study on thermo-catalytic pyrolysis of plastic waste using a continuous pyrolyser, *Waste Management* 67, 143–154
[12] Osueke, C. O. & Ofondu, I. O. (2011). "Conversion of Waste Plastics (Polyethylene) To Fuel by Means Of Pyrolysis" *International Journal of Advanced Engineering Sciences and Technologies*,4(1), 21 - 24
[13] Ademiluyi, T. & Akpan, C. (2007). "Fuel gases from pyrolysis of waste Polyethylene sachets" *J. Appl. Sci. Environ. Manage.*,11 (2), 21 – 26
[14] Deng, G.S., McClennen, W.H. & Meuzelaar, H.L.C., (1997), Catalytic Degradation of High-Density Polyethylene and Waste Plastics Below 200^{0}C, Symp. Feedstock Recycling of Waste Polymers, Las Vegas. 42, (4), 972-977
[15] Wann, J.-P. A., Kamo, Y., Yamaguchi, H., & Sato, Y., (1997). Effect of Ferric Oxide Catalyst on the Cracking of Polystyrene and Polyethylene, Symp. Feedstock Recycling of Waste Polymers, Las Vegas. 42, (4) ,972-977
[16] Sivakumar, P. & Anbarasu, K. (2012). "Catalytic Pyrolysis of Dairy Industrial Waste LDPE Film into Fuel" *Int J Chem Res,*3, (1), 2012, 52-55
[17] Usman, M. A., Alaje, T. O., Ekwueme, V. I. and Adekoya, T. E. (2012). "Catalytic Degradation of Water Sachet Waste (LDPE) Using Mesoporous Silica Kit-6 Modified With 12-Tungstophosphoric Acid" *Petroleum & Coal*, 54, (2) 85-90.