

COMPARISON OF FUEL OIL FROM THERMAL AND CATALYTIC CRACKING OF HIGH DENSITY POLYETHYLENE [HDPE]

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Abstract

Thermal and catalytic cracking of waste high density polyethylene, HDPE (Discarded yoghurt bottles), using CuO/Al₂O₃ catalyst at 430-520°C into fuel oils were carried out using a self-designed stainless steel laboratory reactor. Waste HDPE was cracked into liquid fuel oil, solid residue and gaseous hydrocarbon products. It was observed that catalytic cracking, using CuO/Al₂O₃ catalyst, had lower degradation temperature, faster gaseous and liquid product generation rate and higher yield of paraffinic hydrocarbons than thermal cracking. In contrast, thermal cracking had higher yield of liquid product and more olefinic hydrocarbons than catalytic cracking. GC-MS analysis results gave the compositions of the liquid products of thermal and catalytic cracking to be in the range of C₈-C₂₄, and distributed between paraffinic and olefinic hydrocarbons.

Key words: Comparison, Thermal Cracking, Catalytic Cracking, High Density Polyethylene

Introduction

Plastic wastes are significant environmental pollutants owing to their extremely slow landfill degradability, light weight and combustible nature. Their effects on the environment range from: obstruction of natural and man-made drainage systems – creating floods mainly in urban areas; pollution of water bodies, causing death of aquatic life through suffocation; emission of greenhouse gases such as methane and carbon dioxide during combustion or degradation in an uncontrolled manner; etc. There is therefore a need to effectively manage plastic wastes in order to reduce the burden on the environment and to conserve the finite natural resources from which they were made [1,2]. This can be done through efficient plastic recycling processes which include mechanical recycling and a variety of treatments including chemical depolymerisation, gasification, thermal cracking and catalytic conversion [3-5].

Thermal cracking, or pyrolysis, involves the degradation of polymeric materials by heating in the absence of oxygen to produce lighter hydrocarbons. The process is usually conducted at temperatures between 500-800°C and results in the formation of a carbonised char and a volatile fraction that may be separated into condensable

hydrocarbon oil and a non-condensable high calorific value gas [4].

Catalytic cracking of plastic wastes takes place at much lower degradation temperature and results in lower energy consumptions and higher conversion rates. In addition, the shape selectivity exhibited by some microporous catalysts, allows the process to be directed towards a narrow distribution of hydrocarbon products with a higher market value [6-7].

This study was designed to investigate the thermal and catalytic cracking of waste high density polyethylene product (discarded yoghurt bottles), with a view to providing useful, added value, fuel oil products which can be added to the existing fuels or used as intermediate feedstock in oil refineries.

Materials and Methods

Sample Collection and Preparation

The polyalkene, HDPE, particularly, the discarded yoghurt bottles, were obtained from household and municipal wastes. They were washed, dried and shredded into small sizes for easy handling and faster reaction.

Catalyst

The CuO/Al₂O₃ catalyst used in this work was self-synthesized using copper (II) nitrate trihydrate, Cu(NO₃)₂·3H₂O as the metallic precursor and prepared according to a procedure described in the literature [8]. The catalyst was characterized by Atomic Absorption Spectrophotometric (AAS) analysis.

Thermal Cracking of HDPE

The thermal cracking reactions were carried out in an inert atmosphere of Nitrogen. 100g of shredded HDPE was placed in a cylindrical stainless steel reactor which has a length of 220mm and i.d. 122mm. The reactor was rendered air tight, purged with Nitrogen gas for 20 minutes and then heating commenced. The reaction temperature was measured and controlled by means of a thermocouple. After 50 minutes and at about 424°C, evolution of gas started slightly. After 60 minutes, the temperature increased to 434°C, evolution of gas increased and it was accompanied with drops of condensed phase. Liquid and gaseous products leaving the reactor were separated using an ice trap maintained at 4°C. The condensed product that was retained in the ice trap was collected and weighed as the liquid product after the reaction. Heating and product collection continued for 2hr 30min at 520°C, after which evolution of vapour effectively ceased. The residue solidified to dark soft solid mass and its weight was obtained. The gaseous product that was non-condensing at 4°C was eluted without collection and its weight was found from the difference between the liquid and solid products and the weight of HDPE feed [9].

Catalytic Cracking of HDPE

The catalytic cracking reactions were also carried out in an inert atmosphere of Nitrogen. 100g of shredded HDPE was placed in the cylindrical stainless steel reactor and 10g of CuO/Al₂O₃ catalyst was arranged in sandwich layers within the HDPE in the reactor. 200ml of toluene was added. The reactor was covered air tight, purged with Nitrogen gas for 20 minutes and then heating commenced. Also, a stream of hydrogen gas was passed into the reactor throughout the cracking process. After 40min of reaction and at about 300°C, evolution of gas started slightly. As the temperature rised to 380°C, liquid product started forming and evolution of vapour increased vigorously. Both liquid and condensable gaseous products were collected using an ice trap. The non-condensing gases at 4°C escaped un-trapped. Heating and product

collection continued until after 2hr 15min and at 450°C, when evolution of vapour effectively ceased. The weights of the products were obtained as described above [9].

GC-MS Analysis of Liquid Products

The liquid products of the thermal and catalytic cracking reactions were characterized using Gas chromatographic – Mass spectrometric (GC-MS) analysis which produced chromatograms containing peaks which were identified as olefinic and paraffinic hydrocarbons in the Carbon number range of C₈ – C₂₄.

Results and Discussion

Products of Thermal and Catalytic Cracking of HDPE

The percentage yield of liquid, gaseous and solid products obtained from the thermal and catalytic cracking of HDPE are given in Table 1.

Table 1: Yield of Products, Wt(%)

Products	Thermal Cracking	Catalytic Cracking
Liquid	50.64±0.35	44.89±0.38
Gas	15.74±0.40	24.54±0.22
Solid	33.62±0.31	30.57±0.25

The cracking reactions produced three distinct products which include: condensed phase (liquid), non-condensing phase (gas) and the residue (solid) as shown in Table 1.

The liquid products obtained from both thermal and catalytic cracking reactions were very light and oily. They both have golden brown colour, but, the liquid product of thermal cracking was darker than that of catalytic cracking. Their appearance can be likened to those of common fuels such as kerosene and gasoline, but they have a characteristic smell that is different from either gasoline or kerosene. Also, the solid residue product of thermal cracking was very soft and grease-like while that of catalytic cracking was both greasy and waxy in nature. The gaseous products obtained from these reactions consisted of light hydrocarbons that were non-condensing at 4°C and were combustible when contacted with flame.

Also, it was observed that the conversion rate for catalytic cracking was higher than that of thermal cracking as most of the HDPE feed was converted to liquid and gaseous products at a shorter time and at a lower temperature.

Result of GC-MS Analysis of Liquid Products

The GC-MS analysis results characterized the liquid products of thermal and catalytic cracking to paraffinic and olefinic hydrocarbons only and they are in the carbon number range of C₈-C₂₄. Table 2 below indicates the percentage yield of the hydrocarbon compounds present in the liquid products of thermal and catalytic cracking while Table 3 below gives the relative abundance of alkanes and alkenes in the liquid products.

Table 2: Yield (%) of Hydrocarbons in the Liquid Products of Thermal and Catalytic Cracking

Hydrocarbons	Yield (%)	
	Thermal Cracking	Catalytic Cracking
C ₈ -C ₁₂	17.38	30.42
C ₁₃ -C ₁₈	49.66	46.74
C ₁₉ -C ₂₄	32.96	22.84

Table 3: Relative Abundance (%) of Alkanes and Alkenes in the Liquid Products of Thermal and Catalytic Cracking

Reaction		Alkane	Alkene
Thermal	Cracking	54.81	45.19
Catalytic	Cracking	61.70	38.30

From Table 2, it was observed that the liquid product of catalytic cracking consists of more of lighter hydrocarbon compounds in the C₈ – C₁₂ than liquid product of thermal cracking. This is in accordance with the expectation that the catalyst should enable breaking down of the HDPE feed to lighter fractions than if the catalyst was not present at all. Also, both thermal and catalytic cracking reactions produced higher yield of paraffins than olefins as shown in Table 3, but, the yield of paraffins was more in catalytic cracking. This was in line with our expectation as the catalyst will promote the hydrogenation of alkenes to produce saturated hydrocarbons.

This result was compared with that earlier reported in the literature in which products in the C₄-C₅₀ range obtained was analyzed into fractions which include: petrol, C₄ to C₁₂;

kerosene, C₁₀ to C₁₈; diesel, C₁₅ to C₂₅; fuel oils, C₂₀ to C₅₀ and shown to conform to the hydrocarbon products from refineries[10]. Therefore, from the GC-MS results, we can infer that the liquid products obtained in this work would also conform to those in the main hydrocarbon products from refineries and may be a blend of petrol (gasoline), C₄ to C₁₂; kerosene, C₁₀ to C₁₈; and diesel (gas oil), C₁₅ to C₂₅. This suggests that the products produced could be suitable either for adding to the existing fuels or used as intermediate feedstock in a refinery.

Conclusion

Liquid fuel oils were produced from thermal and catalytic cracking. The catalytic cracking, using CuO/Al₂O₃ catalyst, had lower degradation temperature and faster gaseous and liquid product generation rate than thermal cracking. In contrast, thermal cracking had higher yield of liquid product than catalytic cracking. The GC-MS analysis result showed the compositions of the liquid products of thermal and catalytic cracking to contain only alkanes and alkenes in the range of C₈-C₂₄. Catalytic cracking had higher yield of alkanes than alkenes and more of lower molecular weight hydrocarbons than thermal cracking. The solid residue of catalytic cracking was also harder and more homogenous than that of thermal cracking and therefore, it could be of a better quality.

This study has demonstrated that thermal and catalytic cracking are effective methods that could be used to achieve 100% conversion of waste plastics into useful fuel products. If well developed it will help in controlling environmental and resource problems posed by plastic wastes disposal and therefore, resources will be conserved and the burden on the environment will be reduced.

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