

Research Article

An Experimental Study on Catalytic Cracking of Polyethylene and Engine Oils

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Abstract: The utility of plastics and engine oils is very important due to their wide application in the packaging and automotive industries respectively and as such their continued use has led to an increase in plastics and oil waste. However, the huge amount of plastic and engine oil waste produced may be treated with thermal catalytic methods to produce fossil fuel substitutes. In this research, the co-processing of polyethylene resin with petrol engine oil into high value hydrocarbons using thermal catalytic cracking (consisting of initial pyrolytic stage followed by a catalytic reforming stage) was investigated. Plastic resins and petrol engine oil were loaded in the thermal reactor and HZSM-5 zeolite catalyst placed in the catalytic chamber. The system was purged with nitrogen at temperatures between 400 and 520°C. The resulting products were compared with those obtained in the absence of a catalyst. At temperatures greater than 460°C the conversion into liquid and gas fuels is above 70% wt. At similar temperatures and in the absence of catalyst, thermal cracking of low density polyethylene generated majorly liquid products with a low calorific value. The use of HZSM-5 as a catalyst caused a significant increase in the proportion of gaseous hydrocarbons that consisted mainly of light fraction olefins and liquid oil with calorific value of 43.9 MJ/kg and also comparable to regular petrol fuel. This study focuses on developing a method of conversion that can be adopted by industries as a means of converting waste plastics and waste oils into resources rather than waste.

Keywords: HZSM-5, oils, plastics, thermal catalytic

INTRODUCTION

In modern world, the extensive use of plastics and oils, treatment of polymer and oil wastes has become an important issue from environmental and energy point of view (Williams and Williams, 1999). Europe generates 15 million tonnes of post consumer plastic wastes (Williams and Williams, 1999) while USA generates about 20 million tonnes of plastic waste material (Yanik *et al.*, 2001). The amount of plastic waste in Japan is about 15 million tonnes (Saito and Narita, 1999). Saudi Arabia produces plastic waste approximately 6 million metric tonnes per annum (Siddiqui and Redwins, 2009).

Kenya produces about 4000 tonnes of thin flexible bags per annum. They are produced, mainly as products for shopping purposes of which less than 10% is recycled for the material recovery (Oyugi, 2007). Nairobi alone with a population of 3 million people generates 2,400 tonnes of garbage daily (an average household generate 253 kg/year). The garbage is composed of 20.6% plastics and 79.4% organic and food waste respectively. Waste generation projection in Nairobi will be 1.4 million tonnes of solid waste per year in 2015 (Ministry of Environment, 2009).

In addition to the plastic waste, almost 13,000 tonnes of oil waste is generated each year in Kenya

posing several environmental problems as a result of its metal compounds and high sulfur content due to additives, dispersants and oxidation inhibitors and from sulfur existing naturally. Repair and maintenance services: garages, petrol stations and repair shops are sources of waste oil and oil-contaminated solid wastes that are often disposed of in dumpsites. Less than 10% (1,300 tonnes/year) of waste oil generated is actually collected and recycled (Ministry of Environment, 2009).

The number of landfill sites is decreasing as a result of waste plastics and oils, thus it becomes more expensive and desirable for many localities to curb the problem (Oyugi, 2007). Another profound problem of all is what scientists have warned for decades: that destroying the world's petroleum supplies, in the form of burning gasoline, making the oil unavailable for future production of plastic, rubber, oils and transport fuels. It has been predicted that, at some point, mankind will deeply regret this irreversible loss of such a valuable commodity (Ross, 2007; Panda *et al.*, 2010).

The world's proven reserves of oil amounts to 1,349,417,153,000 barrels (215 trillion litres), distributed among 97 countries against a consumption of 30,036,303,800 barrels (4.78 trillion litres) per annum (Global Resource Corporation, 2007). At that

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burning rate all the oil will have been depleted in less than 45 years! Kenya consumes 1.6 million tonnes of crude oil per year.

Plastics waste recycling can be categorized into four modes namely: primary, secondary, tertiary and quaternary recycling. Primary recycling is the reprocessing of scrap plastic. Secondary recycling or mechanical recycling is the remolding of plastic waste into new plastic products with a lower quality level. Tertiary recycling is the conversion of plastic waste to petrochemical feedstock or fuel oil. Quaternary recycling retrieves energy from wastes through combustion. An example of the fourth type is incineration of waste for power generation (Williams and Williams, 1999).

Primary recycling involves repair and mending, resulting in products of poor quality.

Secondary recycling, which involves grinding, remelting and reforming of the waste materials into low-value products such as fillers and fibres, has been a more common practice for recycling. Combustion (Quaternary recycling) is an alternative to landfill disposal of plastic wastes but this practice is expensive and often generates problems with unacceptable emissions of gases such as nitrous and sulphur oxides, dust, dioxin and other toxins. However, the products from these processes are of limited use and of low value (Ramdoss and Tarrer, 1998).

Waste oil is primarily paraffinic (C_{2n+2}) and can provide good solvency for the straight chain common thermoplastics (Leidner, 1981; Anderson and Berger, 1993). Average Hydrogen to Carbon ratio (H/C) of these materials is greater than 1.8 suggesting that the effective breakdown of polymeric structure and stabilization of the fragments can result in high quality fuel oil without external addition of molecular hydrogen requiring high reaction pressure. Thus simultaneously processing of mixed waste plastics with waste oil has synergistic effects which can increase the production (yields) of fuel oils or chemical feedstock of environmentally acceptable grade (Taguchi, 1995; Aguado *et al.*, 2000).

The efficient use of catalyst over cracking processes such as pyrolysis, hydro cracking and gasification improves the quality of fuel oils. Zeolite HZSM-5, which exhibit strong catalytic activity and therefore reducing the degradation temperature was used (Aguado *et al.*, 2007).

Tertiary recycling is gaining momentum as an alternative method which produces higher value hydrocarbon products (basic chemical or feed stocks and fuel oils) from plastic wastes (Ali and Siddiqui, 2005; Aguado *et al.*, 1999). Especially, co-processing of co-mingled waste plastics with waste oil through a tertiary recycling technique (thermal catalytic process) can achieve the purpose of waste recycling into commercial viable chemicals or fuel oils and hence the

basis for this research. The thermal-catalytic degradations of plastics/waste oil into fuel oil is one of the possible routes among the various utilization of plastic and oil wastes available for Kenya and the world.

MATERIALS AND METHODS

Materials: Polyethylene LDPE granules were sampled from Laminated Tube Industries (LTI), Eldoret, Kenya. HZSM-5 Zeolite catalysts. The acid catalyst was employed and was purchased from Kobian Kenya Limited, Nairobi Petrol engine oil. Unused petrol engine oil was purchased for the experiment to represent the waste oil. Nitrogen gas, which is an inert gas, was purchased from British Oxygen Company (BOC), Eldoret, Kenya. This prevents oxidation in the cracking of plastics.

Cold water was used for cooling of the vapour generated after heating the plastic and oil. The water was kept in a refrigerator to a temperature of less than 5°C before being used to provide effective cooling. The furnace in automotive laboratory, School of Engineering, Moi University was used to heat the plastics and oils to the required temperature. The furnace has Temperature control devices.

Methods: The thermal-catalytic experiment, consisted of a cylindrical reactor was continuously purged with nitrogen, contained the plastic and petrol engine oil for its thermal cracking. The vapours so generated were passed over HZSM-5 catalyst in the catalytic reactor where reforming takes place (Fig. 1).

The thermal reactor unit for loading LDPE plastic and oil mixture were weighed before the runs to determine the mass. (50.0 g) of plastic resins and 50.0 g of unused oil were loaded in the thermal reactor and 20.0 g of HZSM-5 zeolite catalyst were placed in the catalytic chamber. The system was purged with nitrogen at controlled rate (150 mL/min) to prevent oxidation of the burning mixture. The reactor was heated from room temperature up to a final temperature of 400°C or above that was kept constant for one hour. The hydrocarbon products leaving the catalytic reactor were passed through a water condenser cooled by cold water/cooling water to separate the liquid products from the gas fraction. The thermal reactor unit for loading LDPE plastic and oil mixture were weight after the runs to determine the mass balance. Liquid yields were determined by weight from the amount of hydrocarbons collected in the condenser. Experiments using similar conditions but in the absence of catalyst were also conducted for comparative purposes.

RESULTS

Conversion and product yield: When the reaction was conducted at 430°C, only 43.8% wt of the original

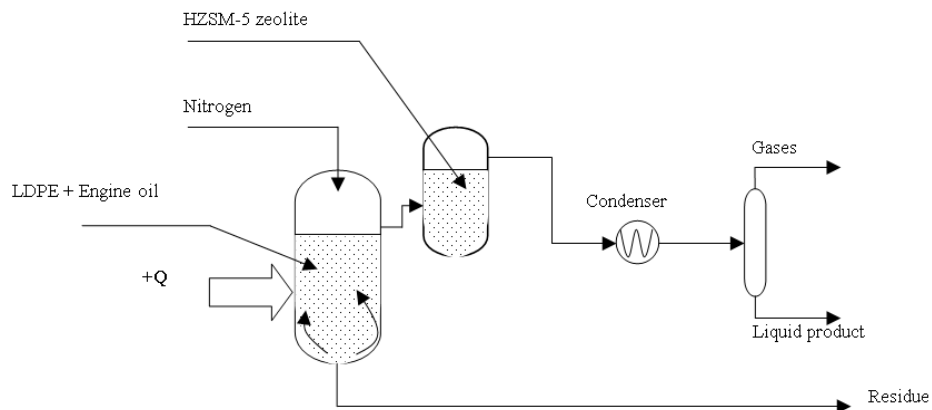


Fig. 1: Experimental procedure

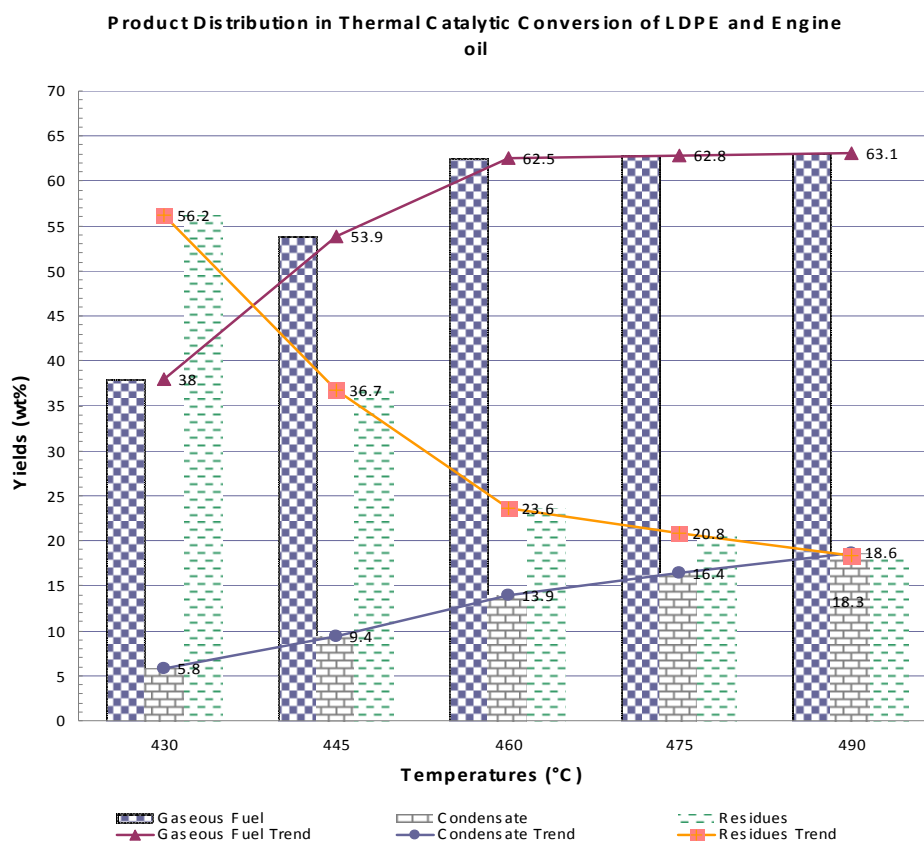


Fig. 2: The conversions and product yields resulting from thermal-catalytic reforming of LDPE and engine oil

plastic was collected as hydrocarbon products in the condenser or as a gas. The remaining 56.2% wt was unable to pass through the reaction system and stayed in the thermal reactor as liquid oil. A marked increase in the conversion values (between 75 and 80% wt) was observed at 460°C and the reaction was 82.6% wt complete at 490°C to liquid and gas fuels as shown in Fig. 2.

With respect to product yields, it was observed that the amount of residue products was limited at temperatures of above 460°C. This has been attributed

to the characteristics of the reaction system, which does not allow large molecular weight species to proceed through the system and remain in the pyrolytic reactor until they have been sufficiently cracked.

In the absence of HZSM-5 catalyst (Fig. 3) conversion of LDPE and engine oil at temperature of 460°C resulted in the formation of a high proportion of liquid hydrocarbons (63% wt of the original plastic mass), while the gas fraction represented only 13.8% wt of the total. The use of higher temperature of 490°C favored the formation of gases (23.6% wt) and

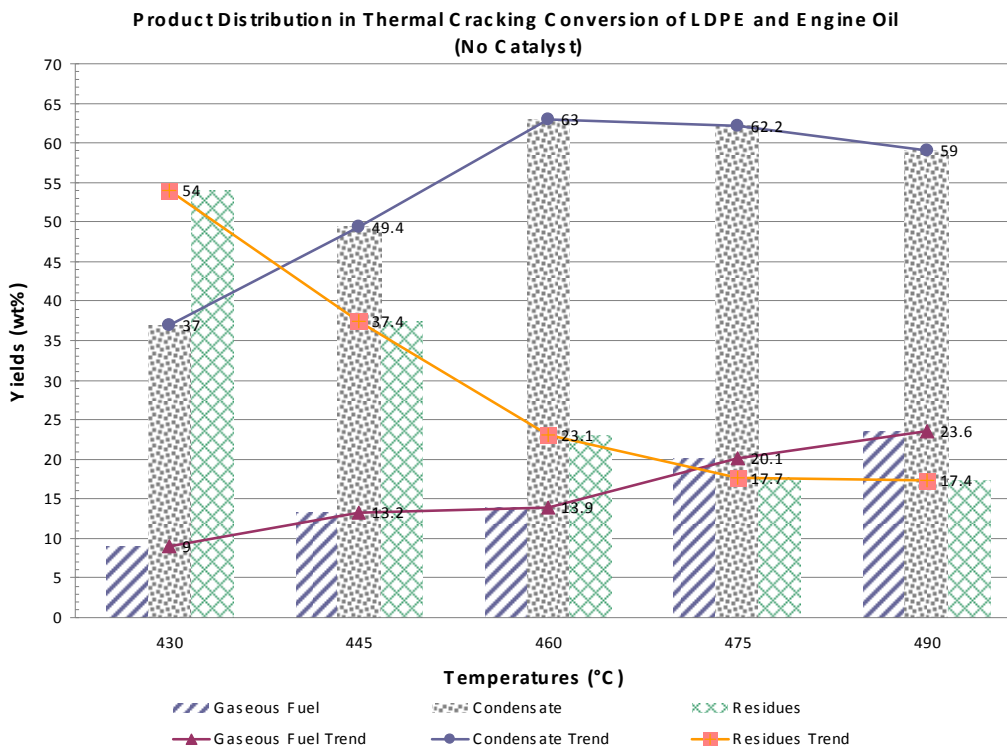


Fig. 3: The conversions and product yields resulting from the thermal cracking

reduced the proportion of liquid products which was associated with a more intense cracking effect on the plastic and engine oil products.

The use of HZSM-5 as catalyst led to a significant increase of the gas fraction as seen at five temperature points. At the optimum reaction temperature of 460°C, the gas yield amounted to 62.5% wt of the original plastic mass and almost a similar proportion was generated at 490°C, although the proportion of liquid hydrocarbons was slightly higher (18.6% wt) at 490°C as compared to 13.9% wt at 460°C.

Effects of temperature and HZSM-5 catalyst:

Generally, it was noted that at 430°C large amount of the waxy compound was obtained instead of gas or liquid because of insufficient temperatures. In the presence of a catalyst, there is catalytic after thermal cracking of long chained polymers/hydrocarbons which results in more gaseous (less complex components) being produced and hence less liquid oils.

Conversion of plastics and oils increases with increase of temperature resulting in decrease of unconverted plastics and engine oils in the reactor. Also, higher operating temperature and high heating rates both enhance bond breaking and favor the production of small molecules. It was observed that gaseous products increases and liquid products decrease with increase in temperatures.

Effect of residence time on product yield is more pronounced at lower than higher temperatures. The

Table 1: Comparison of waste plastic/oil fuel from thermal catalytic cracking to regular petrol

Properties	Regular gasoline	Plastics and oil fuels
Color	Orange	Pale yellow
Specific gravity	0.75	0.73
Calorific value (MJ/kg)	43.70	43.90
Sulphur content (by mass)	≈ 0.10	<0.01

catalytic degradation was practically complete within one hour at 460°C with a yield of 14% wt, it took another 1 h to reach a liquid yield of 18.6% wt at 460°C (an increment of 4.6% wt).

Characterization by hydrocarbon properties:

Analysis of products by hydrocarbon properties is essential to ascertain their potential value as fuels or refinery feedstock. Property characterization analysis was used to determine the type of hydrocarbon products generated from the thermal-catalytic conversion of LDPE and engine oil at a temperature of 460°C.

Properties of liquid from thermal-catalytic cracking were: Viscosities of 0.70 centipoise, Specific gravity of 0.73, Residue in the flask was waxy and Pale yellow in color.

The hydrocarbons generated from the thermal cracking of LDPE have broad product distribution range (C₅-C₂₅) and correspond almost exclusively, to parafins (C₂H_{2n+2}) and polyethylene olefins (C₂H_{2n}) over a wide range of molecular weights. The formation of these products has been associated with the random

scission mechanisms involved in the thermal cracking of this polymer.

Results of thermal and catalytic reforming over HZSM-5 catalyst generated a similar range of products regardless of the reaction temperature employed. This effect has been related to the strong acid character of the catalyst that provided a catalytic activity sufficiently high to ensure a complete reforming of the hydrocarbon products even at low (430°C) temperatures.

The liquid products conform to those in the main hydrocarb on products from refineries as shown in Table 1. For example; typical carbon numbers of some products include cooking gas, C₁ to C₄ and Petrol, C₅ to C₁₂.

CONCLUSION

The process resulted in elimination of heavy petroleum types (C₁₃-C₂₂) and the formation of a high proportion of gasoline (C₅-C₁₂) fraction of approximately 20% wt feed products. The composition of oil fraction is comparable to regular petrol fuel, making this oil (condensate) suitable for blending with conventional transportation fuels and therefore use of these products directly as a fuel or for reprocessing in a refinery therefore appears possible.

Kenya which produces over 4000 tonnes of waste plastics and 13,000 tonnes of used engine oils, can save approximately 1520 tonnes of petrol fuel through the thermal-catalytic cracking (0.095% wt of total crude oil imported annually). The research study performed provided important information showing the prospects of thermal catalytic cracking to deal with waste plastics and waste engine oils.

Depletion of non-renewable source of energy such as fossil fuel demands the improvement of this technique. This sets the future trends in plastics and oil waste thermal-catalytic recycling as an Industry.

RECOMMENDATIONS

- Thermal-catalytic offers a technology that is environmentally friendly and Process of preparing a catalytic catalyst for conversion of waste plastic and waste oil to higher olefins cheaply and locally need be researched on
- Investigations on the following are required:
 - Ways to remove PET and PVC from mixed plastics wastes because of their dangerous emissions such as chlorine, PCDD, PCDF and PCB along with highly corrosive hydrochloric acid
 - Cost analysis of one litre of new fuel
 - Establishing the extent to which patterns of thermal decomposition of plastic/oil mixtures conform to those of the individual polymers present

- The impacts of additives and/or contaminants on the ways in which plastics/oil mixtures decompose. Plastic additives include: fillers, plasticizers, lubricants, flame retardants, colourants and carbon black

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