



## Low temperature conversion of plastic waste into light hydrocarbons

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### ABSTRACT

Advance recycling through pyrolytic technology has the potential of being applied to the management of plastic waste (PW). For this purpose 1 l volume, energy efficient batch reactor was manufactured locally and tested for pyrolysis of waste plastic. The feedstock for reactor was 50 g waste polyethylene. The average yield of the pyrolytic oil, wax, pyrogas and char from pyrolysis of PW were 48.6, 40.7, 10.1 and 0.6%, respectively, at 275 °C with non-catalytic process. Using catalyst the average yields of pyrolytic oil, pyrogas, wax and residue (char) of 50 g of PW was 47.98, 35.43, 16.09 and 0.50%, respectively, at operating temperature of 250 °C. The designed reactor could work at low temperature in the absence of a catalyst to obtain similar products as for a catalytic process.

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### 1. Introduction

Consumption of plastic products has increased many folds over the past few decades [1–3]. Current statistics for Western Europe estimate the annual total consumption of plastic products at 48.8 million tonnes for 2003 corresponding to 98 kg per capita. The same quantity a decade before, i.e. in 1993 was approximately 64 kg/capita [4,5].

This trend has resulted in the generation of large quantities of plastic waste (PW) particularly polyethylene bags (poly-bags) that needs to be properly managed to avoid environmental damage and utilize the potential energy and chemical value of the waste plastic [6,7]. PW component of the Municipal solid waste is quite problematic because this is non-biodegradable and therefore can stay in the environment for a considerable length of time proving hazardous in nature [8]. Increasingly stringent international legislation may require new standards for the solid waste disposal that may encourage a novel recycling technologies for absorbing large amount of such wastes.

Chemically polyethylene plastic is mainly composed of carbon and hydrogen. Some plastics may contain other elements, for example, polyethylene tetra-phthalate (PET) contains oxygen, polyvinyl plastic (PVC) contains chlorine and nylon contains oxygen as well as nitrogen. The higher is the relative carbon content, the higher is the calorific value of the plastic [9]. The calorific value of common fuel

oils is approximately 20,900 Btu/lb. While the polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene tetra-phthalate (PE) and polyvinyl plastic (PVC) contain 2000, 19,300, 17,900, 9290 and 8170 Btu/lb, respectively. Coal, news paper, wood, yard waste, food waste and typical MSW may contain 11,500, 7200, 6700, 4650, 3000 and 2600 Btu/lb, respectively [9]. Therefore, the PE, PP, PS and PET have high calorific values that are very close to that of the fuel oils. Consequently, the conversion of these waste plastics into other products valuable for energy recovery and feed stock chemicals should be desirable to offset the disposal costs of these wastes substantially.

The management of PW through controlled combustion (incineration) is not environmentally friendly and sustainable since this may release carbon dioxide, a major contributor to global warming. Landfilling with PW is also not desirable since plastic is non-degradable and no economic value would have been derived from the waste in that case [8]. The best option for sustainable plastic waste management is through recycling [10,11]. This is because the recycling of PW is environmentally friendly compared to the other methods of waste disposal. Through recycling of PW, we can have material and energy recovery. There are three recycling processes namely mechanical recycling, feedstock/chemical recycling and incineration/energy recovery. Over the years different plastic waste management methods have been adopted apart from traditional option of landfills and incineration [10,11].

Catalytic pyrolytic technology is one of such technologies that can also be referred to as advanced recycling. The pyrolytic technology (thermo chemical conversion) seems preferable over other methods of the waste plastic disposal, through which energy and

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feed stock chemicals may be harnessed from these wastes without affecting our environment negatively [12].

Most of the waste plastic conversion research has not been applied commercially as some operating problems have been reported [13,14]. For example, high melting point, green wax formation instead of low melting point brown wax, plugging of product lines as well as condenser tubes etc were encountered in the process. Such problems can be resolved if the reactor is designed to produce relatively low melting point wax and that can operate at lower temperatures to conserve energy. Through innovation the process may be simplified as well as optimized to solve those problems.

Literature review suggested that most of the pyrolytic reactions were conducted at relatively high temperature ( $>500^{\circ}\text{C}$ ). The objectives of this work were to convert waste poly-bags into light hydrocarbons at relatively low temperature in a specially designed pyrolytic reactor that was more suited for operation at lower temperatures to conserve energy.

## 2. Materials and methods

This experiment was conducted at COMSAT Institute (CIIT), Abbottabad, Pakistan. Analytical grade solvents (toluene, xylene and n-hexane) supplied by Merck, Germany and model low-density polyethylene (LDPE) bags polyethylene (PP) obtained from Aldrich were used in this study. The melting points were measured on a Reichert thermometer of F.G. Bode Co., Austria. The oil fraction was analyzed by gas chromatograph (GC) PerkinElmer with FID detector with column (cross band carbowax-PEG—polyethylene glycol as packing material for qualitative characterizations.

### 2.1. Pyrolytic reactor

The pyrolytic reactor and its accessories used in the present study were shown in Fig. 1. This pyrolytic batch reactor had volume of 1 l and was manufactured locally. Retort of the reactor was made by cutting an oxygen cylinder. The retort was connected to the condensation unit with metal pipes for easy handling. The retort (flask) was constructed from mild steel. It had an airtight cover to prevent emission of gases to the atmosphere. A suitable capacity gas burner was placed at the bottom of the retort. A thermostat was used to control temperature. Pressure gauge was also used to observe the internal pressure. The connecting copper pipes were used for the flow of liquid oil and pyrogas. It was totally metallic so it could be applied for commercial purposes and the whole system was totally automatic.

### 2.2. Experimental procedure

The model low-density polyethylene (LDPE) bags polyethylene (PP) feedstock was shredded to volume of  $3\text{ mm} \times 4\text{ mm}$  size to increase the surface area of feedstock. The reactor was loaded each time with 50 g of plastics waste and allowed to operate for 30, 60 and 90 min at a temperature range of 200, 220, 225, 250, 265 and  $275^{\circ}\text{C}$ , respectively, with or without catalyst (zeolite). It was identified that 80 min was optimum operating time. The pressure gauges were used to note the pressure of the vapors of the crack sample. The reactor loading was started at room temperature. At the beginning, time was noted after  $25^{\circ}\text{C}$  rise of temperature. Retention time, temperature and pressure of the vapors were monitored regularly.

#### 2.2.1. Temperature control

Heating jacket was part of reactor system, composed of mild steel (perforated cylinder) that helped to adjust temperature. Thermostat was an important accessory of heating jacket. It was Italian made and had capability to control temperature from  $50$  to  $500^{\circ}\text{C}$ .

Autoignation valve was another accessory of the heating jacket that ensured uniformity of the temperature of the reactants in the reactor. Burner in heating jacket was an injector type with 90 mm diameter.

#### 2.2.2. Catalyst

In case of catalytic PW pyrolysis, zeolite catalyst was used with an area of  $58.5\text{ m}^2/\text{g}$ . The reactor was filled with 1.0 g of the zeolite catalyst while PW (50 g) was placed on the top. Glasswool was placed in the bottom of the reactor, the top of the piston and inside the bed in order to separate the catalyst and the PW.

Condenser composed of copper pipe was used to collect the oil products. Pyrolytic oil in form of vapors collected in copper pipe and condensed in a container embedded in an ice container. The gas produced during the experiment was collected by water displacement and was tested for combustibility by connecting the gas storage unit to Bunsen burner. The wax produced at the bottom of the reactor was separated from solid residues (mainly char) by vacuum filtration. The mass of oil, wax, pyrogas, and char was measured in grams and then converted into mass in percentage. The mass balance of each component, i.e., pyrolytic oil, wax, pyrogas and residue (char) was presented in Table 1. The relation between product yield of pyrolytic oil, wax, pyrogas and char with different temperatures was also studied. Melting point of wax produced was also determined.

## 3. Results and discussions

### 3.1. Reactor performance

Pyrolytic technology (tertiary recycling) is a way of harnessing the energy from PW. Moreover, it is very suitable technology to clean PW from the environment. For this purpose a batch reactor with volume of 1 l was manufactured locally and its performance was tested. The amount of cracking of waste poly-bags increased with the increasing temperatures; moreover, condensable vapors and fuel gases also increased inside the reactor. These vapors and gases exerted pressure on the auto open/close valve that pushed the valve open causing the movement of vapors and gases into the copper pipe (condenser). The vapors condensed into light oil (mixture of hydrocarbons) and collected into a vessel while non-condensable gases passed through another tube which were also tested for combustibility and analyzed through conventional chemical techniques. Gases analyzed were found light hydrocarbon gases with small volume of  $\text{CO}_2$  and hydrogen gas. Greater hydrogen gas produced when catalyst was used. The products of the pyrolysis were identified as condensed oil (pyrolytic oil), wax, char (residue), and pyrogas in varying proportions as shown in Tables 1 and 2. The production of gases and light oil started at  $170^{\circ}\text{C}$  in the presence of zeolite as catalyst while non-catalytic thermal cracking occurred at  $200^{\circ}\text{C}$ .

### 3.2. Product yields of non-catalytic process

The effects of temperature were studied without catalyst addition. The reaction was carried out at 200, 220, 225, 250, 265, 270, and  $275^{\circ}\text{C}$ . The mass balance of the pyrolytic experiment is presented in Table 1. The results show that the products of pyrolysis were condensed oil, pyrogas, wax and char (residue). At  $200^{\circ}\text{C}$  there was no production of gas and pyrolytic oil. At  $220^{\circ}\text{C}$  the average yield of condensed oil was 18.3%, the average yield of char was 3.9% and the average yield of pyrogas was 24.7%. When temperature was increased to  $250^{\circ}\text{C}$ , the average yields of oil, char, and pyrogas were 35.3, 1.2 and 30.7%, respectively. When temperature was increased to  $275^{\circ}\text{C}$ , the average yield of oil, char and pyrogas was 48.6, 0.6 and 40.7%, respectively.



(A) Assembled Reactor



(B) Cylinder cover with seal.



(C) Main auto open / close valve



(D) Ball Valve



(E) Copper pipe condenser

**Fig. 1.** Reactor and its accessories. (A) Assembled reactor. (B) Cylinder cover with seal. (C) Main auto open/close valve. (D) Ball valve. (E) Copper pipe condenser.

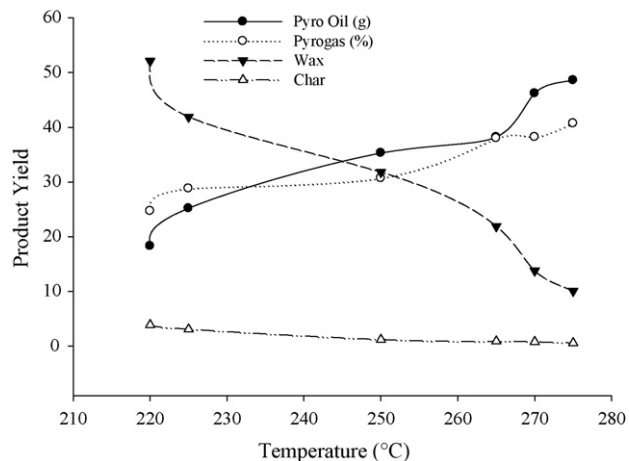
**Table 1**  
Quantities of waste plastic pyrolysis products and the effect of temperature on oil yields with the addition of zeolite as catalyst.

Exp. no.	Duration	Operating temperature (°C)	Waste plastic	Pyrolytic oil (%)	Pyrogas (%)	Wax (%)	Char (%)	Total
1	80	250	50 g	47.98	35.43	16.09	0.50	100
2	80	255	50 g	51.19	35.88	12.50	0.43	100

**Table 2**  
Quantities of waste plastic pyrolysis products and effect of temperature on oil yields without catalyst.

Exp. no.	Duration (min)	Operating temperature (°C)	Waste plastic (g)	Pyro-oil (%)	Pyrogas (%)	Wax (%)	Char (%)	Total
1	80	200	50	Nil	Nil	Nil	Nil	100
2	80	220	50	18.3	24.7	52.1	3.9	100
3	80	225	50	25.2	28.8	41.9	3.1	100
4	80	250	50	35.3	30.7	31.8	1.2	100
5	80	265	50	38.2	38.0	21.9	0.9	100
6	80	270	50	46.2	38.2	13.8	0.8	100
7	80	275	50	48.6	40.7	10.1	0.6	100

The product yield during the thermo chemical conversion of MSW depends on temperature pressure reaction time and added catalysts [15,13]. The products obtained from pyrolysis of PW depend on the type of plastics, feeding arrangement, residence time, temperatures employed, reactor type and condensation arrangement [14,15]. The best results were obtained at 450 °C where the conversion of LDPE into hydrocarbon products was above 90% for a 2 h reaction period [14]. Thermal decomposition rate was very fast at reaction temperature (480 °C), but the oil production was low (40%). Degradation finished between 440 and 475 °C for both plastics [13]. The presence of contaminants, which have some catalytic activity, will no doubt have an effect on the product distribution [16]. Catalyst (zeolites) was used to enhance the quality of desired products as well as to get product at lower temperature to save energy in a minimum time period. Operating temperature was the most critical parameter in the thermochemical conversion of the waste polyethylene–poly-bags. As the temperature was increased, percent yield of both oil and pyrogas increased but the percentage yield of char decreased. The differences in thermal behavior could obviously be attributed to the molecular structure and degradation mechanism. PE thermal degradation consists of free radical formation and hydrogen abstraction steps. Comparison of product yields of non-catalytic process at different temperature identified different amounts of products. At 220 °C the yield of oil (Fig. 2) and gas was too low and wax was too high. At 275 °C the yield of oil and gas tremendously increased with decrease of wax and char.



**Fig. 2.** Quantities of waste plastic pyrolysis products and effect of temperature on product yields without catalyst.

### 3.3. Product yields of catalytic process

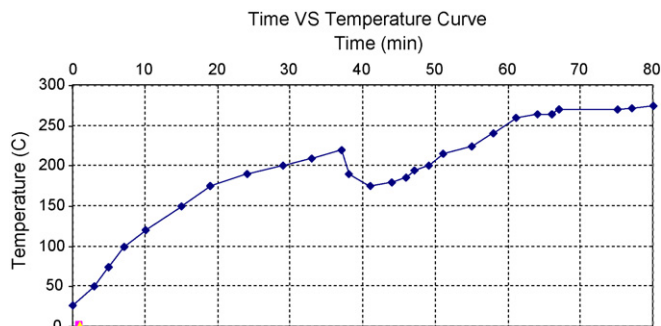
As can be inferred from (Table 1), the average yield of oil, pyrogas, wax and residue (char) of 50 g of PW was 46.9, 35.4, 16.0 and 0.5, respectively, at operating temperature of 250 °C. A slight increase in temperature to 255 °C resulted in the oil yield further of 50.19%. It was observed that as the temperature increased, the amount of pyrolytic oil and pyrogas also increased while the amount of wax and residue (char) decreased.

### 3.4. Changes in temperature with time during non-catalytic process

Operating temperature is the most important parameter in any thermochemical conversion. The temperature was increased from 25 to 275 °C during 80 min. Temperature increased to 220 °C after 37 min and then decreased to 175 °C after 40 min and then again increased to 274 °C (Fig. 3). The maximum pressure observed was 18 psi. Decrease of temperature at 220 °C after 37 min may be due to release of pyrogas and condensable pyrolytic oil from reactor because gases and pyrolytic oil contain heat energy.

### 3.5. Temperature changes through the time during catalytic process

As the time increased, temperature also increased till certain time (Fig. 4). There was increase of temperature from 250 to 255 °C and initial time was 0 min and maximum was 80 min. Temperature increased to 225 °C after 61 min and then decreased to 175 °C after 66 min and then again increased to 255 °C. The maximum pressure observed was 8 psi. In this case gas and oil formation started at 175 °C as compared to non-catalytic process.



**Fig. 3.** Temperature changes with the passage of time without catalyst addition.

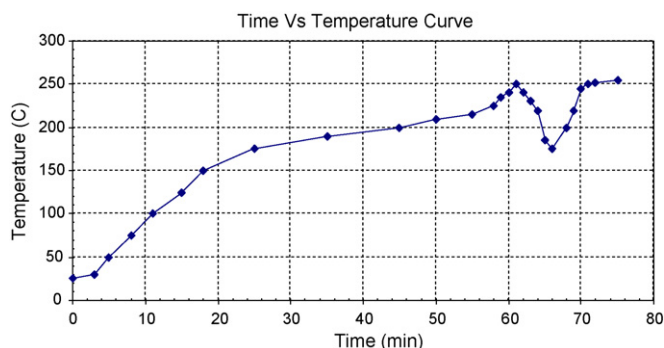


Fig. 4. Temperature changes through the time after the addition of catalyst.

Considerable differences were observed between yields, and composition of products. Both the increase of air flow rate and temperature increased the yield of products. At increasing temperature these differences decreased. Thermal and catalytic oxidative decomposition is a promising technique to degrade low-density polyethylene waste and provide chemical feed stocks for lubricants, surfactants, and other valuable commodities.

The quantitative comparison between catalytic and non-catalytic pyrolysis revealed that catalytic pyrolysis was better option. Comparison of product yields of catalytic pyrolysis at different temperature identified different amounts of products. Same catalyst produced different amounts of products at different temperatures. It was also identified that production of oil and gas was higher during catalytic process.

### 3.6. Effect of reaction time

The reaction time was varied as 30, 60 and 90 min with variable reaction temperatures from 220 to 275 °C of 50 g of loading sample with and without catalyst. It was observed that 30 and 60 min were not sufficient reaction time for completion of reaction. Gas formation started after 30 min of loading reactor at pressure of 8 psi at 220 °C and oil formation started after 50 min at pressure of 18 psi in non-catalytic process. Gas formation ceased after 60 min and oil formation ceased after 80 min. In catalytic pyrolysis the gas and oil formation started after 40 min at the reaction temperature of 175 °C. Gas formation ceased after 65 min and oil formation ceased after 75 min at pressure of 8 psi.

### 3.7. Characterization of pyrolysis products

Functional group chemical analysis of the derived oils and gases and waxes was carried out using conventional elementary analysis. The main hydrocarbon gases were the alkenes consisting of (ethene, propene and butane) and alkanes (methane, ethane, propane and butane). Hydrogen was also formed in significant concentrations.

Tests of hydrogen and carbon dioxide were done. H<sub>2</sub> gas in non-catalytic process was insignificant but in case of catalytic process was significant. In catalytic process H<sub>2</sub> produced exploded with air when flame was applied. Chemical analysis was done for saturated and unsaturated hydrocarbons. Test for alkanols (e.g. ethanol) and carboxylic acids were also done.

More hydrogen gas was observed during catalytic process as compared to non-catalytic pyrolysis. Small amount of carbon dioxide gas was also observed during analysis. Over all more pyrolytic gases and pyrolytic oil produced during catalytic activity. Analysis of pyrolytic oil observed both saturated and unsaturated hydrocarbons but quantity of unsaturated hydrocarbons was meager. Compounds with hydroxyl, acid groups were not observed during analysis.

Pyrolysis of various kinds of plastics at relatively higher temperature (500–700 °C) produced a product containing wax, oil and gas which may be separated by the condensation system. Each fraction is, however, a consequence of the condensation temperature. As the temperature of pyrolysis was increased from 500 to 700 °C there was a marked decrease in the oil and wax fraction and increase in the gas fraction [17]. Catalytic and non-catalytic degradation of low-density polyethylene (LDPE) waste was investigated by Adil et al. [18] in a temperature range of 400–500 °C in pyrex continuous reactor.

Functional group analysis of the derived waxes was also carried out. The wax produced from the pyrolysis of LDPE was very pure aliphatic material, with no aromatic species present and had the potential to be used in catalytic cracker in the petrochemicals industry as substitutes for petroleum derived feedstocks. The color of the wax was blackish brown with low viscosity. The melting point observed was 37 °C. For the pyrolysis run of PE, two main products, namely a green wax with a melting point of about 80 °C and gas were obtained [13]. During its pyrolysis, the most serious operating problem was the plugging of the product lines and condenser tubes by the waxes formed [13]. It was soluble and miscible in n-hexane, ether, acetone and benzene.

For preliminary analysis petrol and kerosene oil were used as standards. Comparing the GC chromatogram of pyrolytic oil with kerosene and petrol, the most of the compounds were in the range of petrol and few were in the range of kerosene oil. Aromatic compounds like benzene and toluene were also observed through gas chromatography. Up to retention time of 2 min on GC chromatogram no peak was seen and there might be low boiling hydrocarbon gases. The composition of this oil fraction is comparable to commercial gasoline fuel. A review on the current trends in chemical recycling of LDPE, HDPE and PP can be found elsewhere [8]. Thus, the present work showed that newly constructed pyrolytic reactor was very useful to recycle PW for energy generation at relatively lower temperatures. This not only saves operational costs but also helps to regenerate useful hydrocarbons to be used as energy source. The present study showed that our designed reactor was efficient to obtain similar results at low temperature and without catalyst requirements as obtained by a reactor working at higher temperature with a catalyst.

## 4. Conclusions

Newly constructed pyrolytic reactor was very useful to recycle PW for energy generation at relatively lower temperatures. Low molecular weight hydrocarbons or fuel oils within the petrol and kerosene oil range were successfully obtained through catalytic and non-catalytic pyrolysis using pure and waste plastics. Additionally wax, pyrogas and char were also obtained. The average yield of the pyrolytic oil, wax, pyrogas and char from pyrolysis of PW were 48.6, 40.7, 10.1 and 0.6%, respectively, at 275 °C with non-catalytic process.

Using catalyst the average yields of pyrolytic oil, pyrogas, wax and residue (char) of 50 g of PW was 47.98, 35.43, 16.09 and 0.50%, respectively, at operating temperature of 250 °C. The oil was the mixture of hydrocarbon in the range of petrol and kerosene oil and could be used as fuel as well as feed stock for industrial chemicals. The char produced could be used as RDF, which can be used for reduction process and as an additive to road building materials.

Pyrogas produced during the process can be used as fuel for the pyrolytic process itself and domestic purposes. Advance recycling through pyrolytic technology has the potential of being applied to the management of PW in MSW which is cost effective supply of feed stock for alternate energy generation. The designed reactor could work at low temperature in the absence of a catalyst to obtain similar products as for a catalytic process.

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