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Characterization of Liquid Produced from Catalytic Pyrolysis of Mixed Polystyrene and Polyethylene Terephthalate Plastic

Abstract- *Plastic wastes accumulation increased each year in the environment. Plastics types are different such as polystyrene (PS), polyethylene terephthalate (PET), polypropylene (PP), low-density polyethylene (LDPE), high-density polyethylene (HDPE) and polyvinyl chloride (PVC). In this paper, catalytic pyrolysis of Polystyrene and Polyethy terephthalate were studied to find the effect of PET on the pyrolysis of PS. The reaction took place in stainless batch tubular reactor to determine the effect of temperature and residence time. The maximum liquid products yield at optimum temperature and heating time(60 min) was 77% , 67.56%, 54% and 37.48% for PS, 10%PET + PS, 20%PET + PS and 30%PET + PS respectively. The liquid produced were characterized by GC-MS at optimum condition. The component of the liquid are styrene monemer, toluene, alpha-methylstyrene, 1,3 Diphenylpropane, 1-Phenylnaphthalene, 4-phenyl-1 butene. Styrene monomer was found to be the main product in the pyrolysis of PS, 10%PET+PS, 20%PET+PS and 30%PET+PS.The physical properties such as density, viscosity, and caloric value of the produced liquid was investigated ,the results was 0.9 g/cm*^{3} *,2-3 Cp, and 40-45 MJ/kg respectively.*

Keywords- *Catalytic, Pyrolysis, polystyrene,*

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1. Introduction

According to the new living standards and drastic increase in use of plastics, it's products had strong effect on the environment. Plastics have now become necessary materials for modern life style and the demand is continually increasing, as there are many types with a lot of advantages and attractive applications in household and industries. Plastics after use led to high proportion of waste and this amount is increasing around the environment. Hence accumulated waste plastics pose a very serious environmental challenge because of increasing quantity of waste plastics, they do not biodegrade for very long time [1,2]. Plastic wastes can be classified as municipal plastic wastes (MWP) and industrial depending on their origins; these groups have different qualities and properties and are subjected to different management strategies [3, 4]. The most promising technique of reusing is pyrolysis.

The pyrolysis process can be defined as thermal cracking of the wastes without oxygen. In pyrolysis process, the waste plastics are heated to high temperatures, so their long chain monomers structures are broken into smaller molecules and produce a wide range of light hydrocarbons. These pyrolytic products are: a gas fraction, liquid fraction, solid residues [5]. Thermal pyrolysis may occur between 350ºC to 900ºC. The plastics with lower activation energy will decomposed easily, [6].

Advantages of pyrolysis process [7] are:

(a) Significantly reduce the waste (<50–90%).

(b) The products out of pyrolysis are solid, liquid, and gaseous fuel.

(c) The obtained fuel can be easy storage/transport.

(d) Reduce the environment problems.

(e) From economy view the capital cost is low.

There are two types of pyrolysis – thermal cracking and catalytic cracking.

Pyrolysis is a process in which hydrocarbons such as crude oil are subjected to high heat and temperature to break the bond and molecular weight of the substance being cracked, the process carried out at inert gas such as Nitrogen or Helium.

In waste plastic pyrolysis, catalyst is used in the reaction, in order to reduce the temperature and time of the reaction or increasing the liquid yield. The catalytic process results much narrower product distribution of carbon atoms and increase lighter hydrocarbons at lower temperatures. The cost of catalytic pyrolysis are lower than thermal pyrolysis that make the catalytic process more attractive from an economic perspective. Poisonous catalyst can be reused, and catalysts

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ratio to waste plastic must be optimized. The suggested process can be developed into commercial recycling process for solving the acute environmental problem of disposal of plastic waste. It also offers the higher cracking ability of plastics, and the lower concentration of solid residue in the product [8].

Catalytic pyrolysis of original and waste plastics has been extensively studied and a number of studies have been reported in the literature on thermal degradation, Saker et al studied mixed plastic of PS and PVC using ZnO catalyst the fuel yield was 50.08% (C3_C32) [9], Rashid et al studied 50% mixed plastic (LDPE, PP and PS) with 50% tire using $Fe_2(CO_3)$ as catalyst the fuel yield was 47.4% (C_3-C_{20}) [10], Saker et al studied mixed plastic of PS, LDPE, HDPE and PP using ZnO as catalyst, the fuel yield 87.19% (C_3-C_{36}) [11], Almutapha et al studied catalytic pyrolysis of HDPE in fixed bed reactor, the fuel yield was 34.31% [12], Mabood et al studied catalytic pyrolysis of LDPE in batch reactor, the fuel yield was 69.73% [13]. Panda et al studied catalytic pyrolysis of PP; the fuel yield was 87.5% [4].

This paper will study the influence of adding polyethylene terephthalate (PET) to polystyrene (PS) pyrolysis.

2. Experimental Work

I. Catalyst and materials

The polymers used in this research were waste PS with particle size of (0.2-0.3) cm and waste PET (soft drink bottle) with particle size (0.4-0.5) cm. They washed with water before filled to the reactor. The proportion of polyethylene terephthalate and polystyrene in the mixture were denoted as xPET+ PS were x represents the wt% of PET of PET with respect to PS. Three different mixtures were prepared: 10% PET + PS, 20% PET + PS, 30% PET + PS, moreover catalytic pyrolysis reaction was performed for each of PS and PET alone.

The catalyst used for the pyrolysis experiments was Al_2O_3 (alumina) with a percentage 7% of the feed representing mass ratio. The alumina used in the present work is from Riedel-dehaën Company with PH 4.5, bulk density 0.9 g/ml, grain size 50-200 µm and specific surface 200 m²/g.

II. Pyrolysis procedure

Cylindrical stainless steel reactor (Figure 1), was horizontally placed, the main cylinder has an inner diameter of 40 mm, a thickness of 5 mm and a lenght of 340 mm. The control thermocouple (type K) was inserted in the middle of tubular reactor. Heating was provided by 3500-watt external electrical heaters, which is rolled on cylinder reactor to get the required reaction temperature. At one end of the reactor, a tubing system was connected with copper tubes of 6 mm diameter, nitrogen enters the reactor was measured through one end, at the other end the reactor was connected to condenser. Liquid produced was collected at the collector.

For the catalytic pyrolysis and degradation reaction, 50 gm of polymers (PS & PET) and 7% Al_2O_3 mixed with plastic feed as a catalyst were put inside the reactor. To carry out the pyrolysis reaction under no-oxygen environment, nitrogen gas was supplied to the reactor with sufficient quantity so that the reaction was performed under nitrogen environment

The nitrogen gas was fed to the reactor at rate of 30 ml/min and pressure of 1 bars. After controlling the possible gas leakage, the reactor temperature was adjusted to the desired reaction temperature. The settled heating rate of the electrical heater was 16°C/min. Cooling water supplied by chiller was set at temperature 3°C to ensure the sufficient cooling for the condensation of products. The product separated at the condenser to non-condensable gases leaving from the top of the condenser out of laboratory and liquid (contains sediment) collected from the bottom of condenser in flask. The liquid collected was cooled down to room temperature and separated by using filter paper then weighted and kept into container for the tests.

III. Thermogravimetric analysis (TGA)

Thermo-gravimetric analysis (TGA) is defined as thermal analysis technique that measures the weight loss of material as function of temperature in controlled nitrogen environmental. TGA can show in the range of degradation temperature of the material (the start and the end temperature). Thermo-gravimetric analysis (TGA) was carried out using STA PT-1000 Linseis Company.

IV. Liquid and wax product analysis

The fraction of liquid products was analyzed using a gas chromatography-mass spectrometry GC-MS, Shimadzu model AOC - 20i / AOC - 20s auto injection. The GC-MS operating conditions were the column oven temperature and injection temperature were 100℃, 260 ^{0} C respectively and split injection mode. Helium was used as the inert gas.

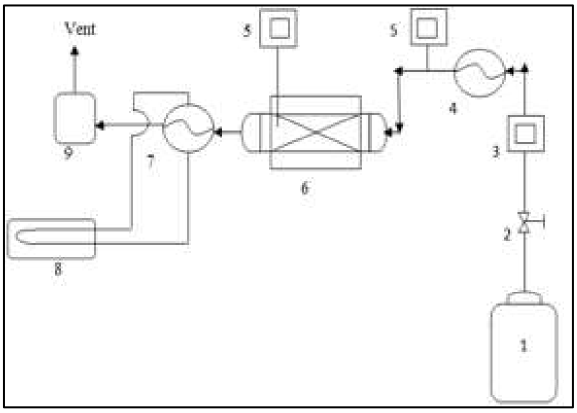

Figure 1: Schematic diagram of the experimental apparatus 1) Nitrogen cylinder, 2) Gate valve,3) Gas flow meter,4) Preheater, 5)Temperature reader, 6) Reactor, 7)Condenser, 8)Cooling system, 9) Liquid collector

3. Results and Discussion

I. Thermogravimetric Analysis (TGA)

Figure 2 and 3 shows TGA analysis for PS and PET respectively. From Figure 2 the PS one-step degradation started at 300 °C and completed at 463 °C the heating rate was 10°C /min. For the degradation of PET shown in Figure 3 one-step weight-loss was observed.

II. Effect of Temperature on products distribution in catalytic pyrolysis

All experiments were conducted in absence of air with heating rate 16 °C/min, 7% $Al_2 O_3$ (catalyst) and residence time 90 min.

Figures 4 and 5 shows the effect of pyrolysis temperatures (350°C, 400°C and 450°C) on the liquid and wax yields for PET, PS and XPET + PS. Catalytic degradation of PET produces wax as product (no liquid). PET plastic composition contain about 33% oxygen , oxygen may react with hydrocarbon and produce carbon monoxide and carbon dioxide ,thus PET cracking produced mainly benzoic acid and non-condensable gases, that referred by GC-MS of the wax out of experiments. The Fig.4 show that the amount of wax significantly increased from 6.6% at 350°C to 20.25°C at 450°C.

The liquid yield at 350°C was lower than that obtained at other temperature. As seen from Figure 4 the liquid yield properly decreased with increase the PET%. The yield of liquid increased with the increase in temperature run to its maximum of 98.4% 82.6 % and 72.5% at 450°C in the case of Polystyrene, 10% PET + PS and 20% PET + PS, respectively.

When the percentage is 30% PET + PS the liquid at first increased up to a maximum of 45.4% and 55.8% at 400°C, respectively but increased in the pyrolysis temperature decrease the liquid product. The total yields in the cases of PS, 10PET + PS, 20PET + PS and 30PET + PS at optimum temperature were 98.4% at 450 °C, 82.6 % at 450 °C, 72.5 % at 450 °C and 55.8 % at 400 °C, respectively.

Polystyrene pyrolysis gives higher amount of liquid than 10% PET + PS, 20% PET + PS and 30% + PS. Polystyrene is mainly converted into stable aromatic components as liquid phase and this is clear in the mixture state (polystyrene addition increases the oil yield).

For wax, the yields increased when the temperature increase in the pyrolysis of PET and XPET + PS. The maximum wax yields in the cases of PET, 10% PET + PS, 20% PET + PS and 30% PET + PS was 15.56wt.% at 450 °C, 1.58 % at 450 °C, 1.64% at 450 °C and 3.24 % at 450 °C, respectively.

Generally adding PET to PS reduce liquid yields because of that PET Pyrolysis normally produce non condensable gases and waxes, and carbon residue, when polymer cracked to short hydrocarbon chain some of these chains are recombination's together forming carbonaceous deposits rather than liquids.

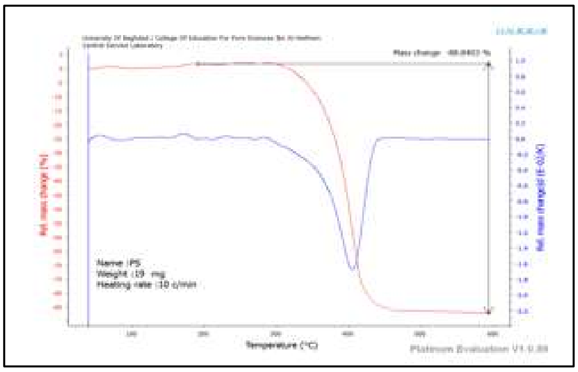

Figure 2: TGA for PS

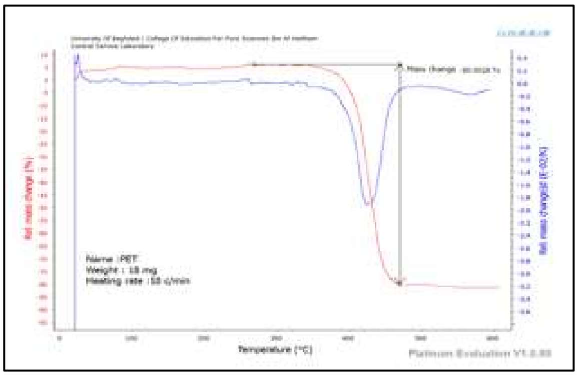

Figure 3: TGA for PET

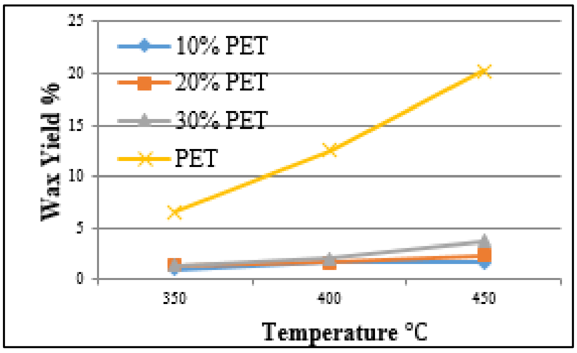

Figure 4: Effect of temperature on the liquid produced from catalytic pyrolysis of PS and XPET + PS

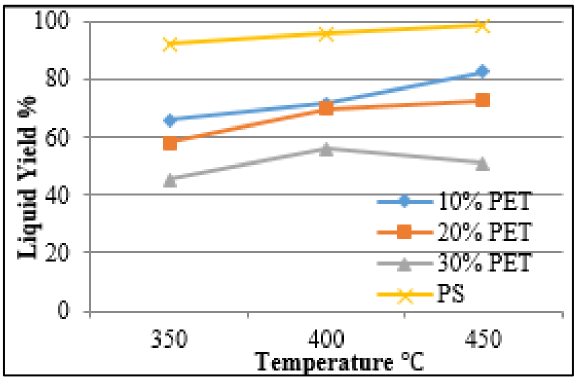

Figure 5: Effect of temperature on the wax produced from catalytic pyrolysis of PET and XPET + PS

III. Liquid analysis

The produced liquid at the experiments was tested to investigate its properties; results of test are given in Table 1. The density for the liquid in all cases was approximately about 0.9 g/cm^3. The values for API gravity were found to be in the range of 16–17. Viscosity and kinematic viscosity values both for PS and PS+ XPET were measured it was in the range 2 centipoises and 2–3 c.st respectively.

Table 2-show Comparative study of physical properties between the liquid produced from catalytic pyrolysis and standard physical properties the conventional oil fractions (gasoline, gasoil and kerosene), the obtained liquid physical properties close to gas oil other than other fractions.

The liquid product obtained from the catalytic pyrolysis of polystyrene (PS), and polyethylene terephthalate (XPET), optimized conditions were specified by GC_MS. The liquid and wax products out from the pyrolysis of waste PS, PET and XPET+PS gave mainly aromatic hydrocarbons. The analysis aimed to study the effect of temperature on the main components distribution.

The GC-MS of wax obtained from the catalytic pyrolysis of PET gave mainly terephthalic acid, benzoic acid, Dibenzoyl-L tartaric acid anhydride ($C_{18}H_{12}O_4$) and Ethylene glygol dibenzoate ($C_{16}H_{14}O_4$). Benzoic acid was the dominated product in wax obtained from PET pyrolysis. It seem terephthalic acid is produced from the cracking of polyethylene terephthalate plastic on the ester bond, which on decarboxylation produces benzoic acid. PET polymer monomer is contains 33% oxygen for that alcoholic compounds appeared in pyrolysis products.

The GC-MS analysis for liquid produced from PS and 10%PET + PS shows that the main products were styrene (C_8H_8), toluene(C_7H_8), and ethylbenzene (C_8H_{10}), 1,3 Diphenylpropane ($C_{15}H_{16}$), α- methylstyrene (C_9H_{10}) and 4-phenyl-1 butene ($C_{10}H_{12}$). The monomer styrene is the dominate product.

The results of liquid produced form 10%PET + PS approximately as the same as been found with 100% PS because the PET percentage is low therefore the effect of PET on PS degradation is low.

From GC-MS analysis (Figure 6), new chemical compounds appeared in liquid produced from catalytic pyrolysis of 20% PET + PS and 30%PET + PS such as Benzaldehyde (C_7H_6O), 1-Phenylnaphthalene ($C_{16}H_{12}$), 1,3-Diphenyl-1-butene ($C_{16}H_{16}$), 1,4-Diphenylbenzene ($C_{18}H_{14}$) as a results of PET percentage increase.

4. Conclusions

The maximum liquid yields from catalytic pyrolysis of polystyrene, 10%PET +PS, 20%PET +PS and 30%PET +PS was 98.4% at 450 °C, 82.6 % at 450 °C, 72.5 % at 450 °C and 55.8 % at 400 °C, respectively.

The pyrolysis of PET led to acid compounds like benzoic acid, terephthalic acid, ethylene glygol dibenzoate and Dibenzoyl-L tartaric acid anhydride as the main components.

Mostly, the liquids yield products decreased with the increase for terephthalate. GC–MS analysis of liquid produced from polystyrene and XPET + PS showed the formation of single ring aromatic hydrocarbons (C6–C9) fraction. Styrene monomer was the major product. The increasing concentration of aromatics (C_{12}_C_{24}) and due to increasing of polyethylene terephthalate percentage many new oxygenated hydrocarbons are formed. The physical properties of the produced liquid was closely to gas oil specifications.

Table 1: Derived liquid properties out of catalytic pyrolysis of PET and PS samples

Temp.℃	Type of plastic	Density (g/cm³)	API	Dynamic Viscosity	Kinematic Viscosity at 40℃, c.st	Color
450	PS	0.9469	17.79	2.575	2.7194	Brown yellow
450	10% PET + PS	0.9496	17.37	2.78	2.9358	Yellow
450	20% PET + PS	0.9550	16.52	2.721	2.8492	Yellow
400	30% PET + PS	0.9493	17.41	2.72	2.8652	Yellow

Table 2: Standards parameter of gasoline, gasoil and kerosene oil

Parameters	Gasoline	Gasoil	Kerosene	Obtained Liquid
Density (g/ml)	0.736/0.725	0.834	0.78_0.82	~0.9
Viscosity (C.P)	0.775_0.8394	2_4.5	0.9_1.5	2_3
Calorific value (MJ/kg)	42.8	41.1_42.9	43.5	40_45
Pour point	-	6	-47	-16_>-28

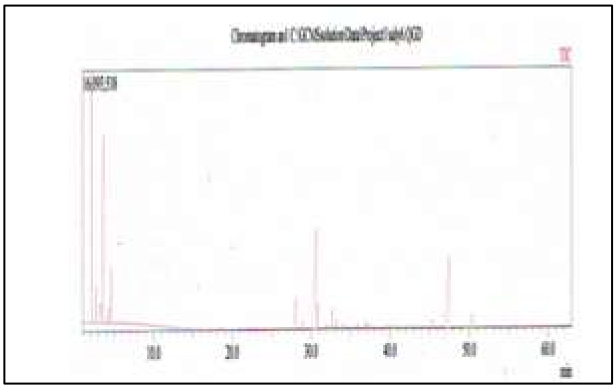

Figure 6: GC-MS of liquid produced from catalytic pyrolysis of PS at 450℃

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