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Thermal Pyrolysis of Municipal Solid Waste (MSW)

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Abstract. Plastics are very desired components, used in a lot of fields, from domestic packaging, agrarian, automotive, to building structure. The frequent use of plastic products related to their lightweight, high chemical stability and low cost.

The present work aims to illustrating the thermal pyrolysis of two types of plastic: Polyethylene terephthalate (PET) and polystyrene (PS) in a batch tubular reactor. The reaction indicated that PS and PET were converted more meaningfully into useful liquid products out of thermally route compared to PET pyrolysis. The resulted liquid could be used as fuels or raw materials in chemical industries. Formation of oxygenates and aromatics were noticed. The maximum liquid produced at optimum temperature and optimum heating time (90 min) is 77% , 67.56%, 54% and 37.48% for PS, 10%PET + PS, 20%PET + PS and 30%PET + PS respectively. The liquid product is analysed by GC-MS at optimum condition. The compositions of the liquid produced are styrene monomer, toluene, alpha-methylstyrene, 1,3 Diphenylpropane, 1-Phenylnaphthalene, 4-phenyl-1 butene. The main product in the pyrolysis of PS is styrene monomer, 10%PET+PS, 20%PET+PS and 30%PET+PS.

1. Introduction

Polymers are considered natural or synthetic molecules that consist of a large number of smaller moieties, monomers, which form a long chain by reacting with each other's. Polymers can be classified depending on two main criteria: according to their thermal behavior and polymerization mechanism. The classification of polymer is significant because the most suitable way of degradation for a given polymer is related to the properties of the plastic molecules [1].

In general use, the term 'plastic' is replicated to the term polymer. Nevertheless, all plastics are polymers but not all polymers are plastic. Polymers can be classified to several groups: a) elastomers (rubbers), b) plastics and c) fibers. This categorization is made depend on their physical properties, elastic modulus and degree of elongation [2].

Plastics are inefficient. So they usually do not combine or make bond with other materials. That's mean that plastics do not decompose normally. It requires thousands of years to decompose or to decay in the environment. Some plastics do not decompose at all. They need to throw in the ocean or in the landfill. Therefore, plastics are producing numerous harmful problems for humaneness, for environment, for animal in the mainland of even in the oceans. The increase in plastic manufactures and uses are growing daily. So it became an important matter to dominate this issue [3]

Currently, researchers focus more and more on pyrolysis, which has a great benefit over incineration in producing value-added chemicals, even from mixed feedstock.

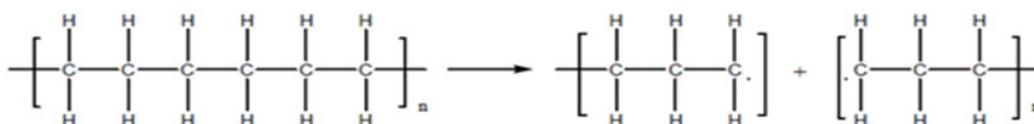


Pyrolysis process has the ability to breakdown polymer chains into low molecular weight compounds. The output of plastic pyrolysis operation could be used as fuels or chemicals. Two kinds of pyrolysis processes (Thermal pyrolysis, Catalytic pyrolysis) are reported correspondingly.

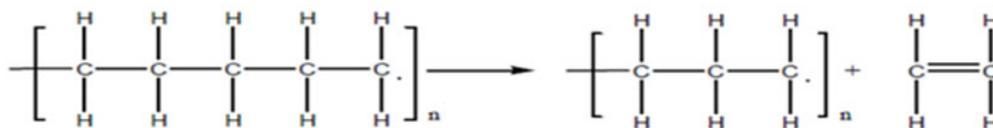
1-1 Thermal Degradation

Basically, thermal degradation normally produces a mixture of low value hydrocarbons having various products, containing hydrogen to coke. Generally, the increase in temperature of pyrolysis cracking led to produce small quantities of liquid fuels and increase the production of Non-condensing gaseous. The yield and composition of the products gained are controlled by the time of the reaction as well as the temperature [4]. General steps of the thermal degradation are described by the following sequence of procedure [5,6]:

1-Initiation step: happens at random scission of the polymer chain and initiating primary radicals Rp (1)

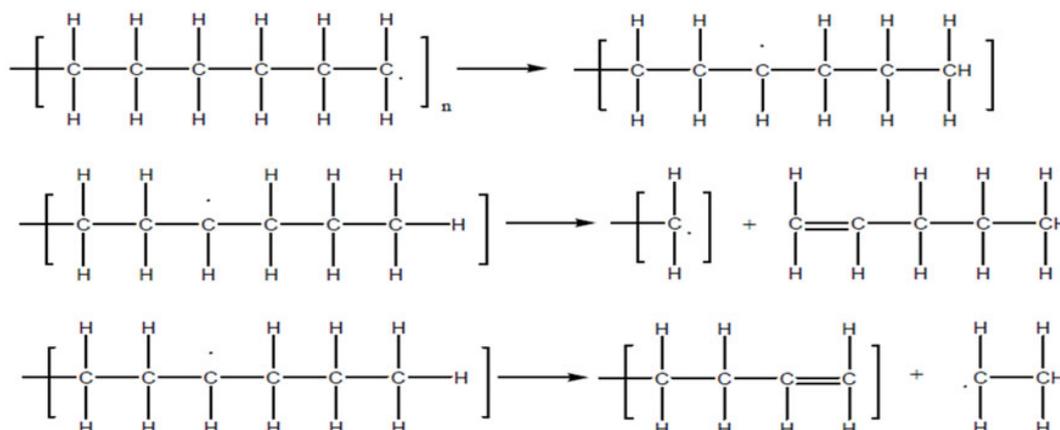


2-Propagation step: olefin monomers are release in this step; it's formed from primary radicals by β -scission which leads to produce predominantly propene (2)

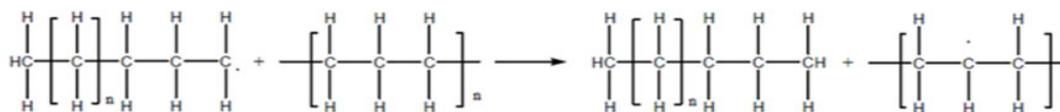


3-Hydrogen chain transfer reaction step: maybe occur as intermolecular or intramolecular (rely upon low or high temperatures) processes.

a. Intramolecular (H) transfers: leads to produce a secondary radical which is more stable. The sequent β -scission of secondary radicals act jointly with the propagation step of the radical chain mechanism since a new primary radical is formed in this process. In addition, the formation of olefins takes place during the process C-C bond hemolysis [1].



b. Intermolecular (H) transfer: secondary radicals maybe formed through H abstraction by an intermolecular transfer reaction



4-Termination step: involves the formation of a neutral molecule by the merging of secondary radicals.



As a result of these reaction steps, the thermal pyrolysis lead to great distribution of hydrocarbon, a C5 C80 range, each fraction being mainly composed of diene, 1-olefin and n-paraffin. Hydrogen formed at high temperature in significant quantity. The products produced from thermal cracking have a finite commercial price, particularly, which is applied as fuel. Where the heavy oils has been proposed, it has been used as a wax [7]. Achieving this great range of products is about one of the main advantages of this technique, which demands temperatures of 500 °C to 900 °C. These factors severely limit its applicability and increase the cost of recycling raw material of plastic waste [8].

The thermal pyrolysis process featured is seem to be a simple process with low costs, but the high energy consumption [9]. A large number of experimental studies have been as listed in Table 1.

Table 1. Recent laboratory experiments on plastics pyrolysis

Author	Experimental steps	Main products and comments
Kiran, Ekinci and Snape (2000) [10]	Thermal pyrolysis of waste and virgin PP plastics & mixtures of waste PP with wastes of polyethylene (PE) and polystyrene (PS)	The liquid yield distribution concerning the aliphatic, mono-aromatic and poly-aromatic compounds varies as the ratio of PP waste increases in the waste plastic mixtures. In addition to this, the alkene/alkane ratio of gas products shows variations depending on the mixing ratio of wastes.
Ballice (2002) [11]	Different LDPE:PP ratios	Maximum product release temperature: 440°C giving straight and branched paraffins and olefins, dienes and aromatics (C1-C27). Increasing ratio of LDPE produced greater amount of C16+ paraffins Produced
Seo & Shin (2002) [12]	Mixed waste plastic pyrolysed at 400-500°C	PE (50-60%), PP (20-30%), PS (10- 20%), PVC (10%) gave pyrolysis oil toluene (49-68%) Aromatics in oil said to be partly due to PS in the feed but likely some other effect in pyrolysis process contributed too.
Faravelli et al. (2003) [13]	PE & PS 370°C and 410°C	HDPE –alkanes, alkenes, dialkenes PS –monomer, dimer and trimer PS degradation independent from presence of PE
Ciliz, Ekinci and Snape (2004) [14]	PE:PP and PS:PP mixes Virgin	polymers gave Ea of 167-181 kJ/mol. PE:PP mix gave high values of gas and residue and low liquid yield. Liquid yield for PE:PP mix reduced with increasing PP, but more C7-C11 aliphatics. Addition of PP increased alkene/alkane ratio for C2 and C3.

1-2. Catalytic Degradation

In this type of pyrolysis a suitable catalyst is used during the pyrolysis to carry out the cracking reaction, the presence of catalyst lead to reduce the temperature of reaction and time. The product distribution of carbon atom number and peak at lighter hydrocarbons in this process is much narrower. To make this

process economically feasible, the cost should be further reduced. The use of effective catalysts in lesser amounts and reuse of catalyst can optimize this option. Catalytic pyrolysis can be improved into a cost-effective commercial polymer recycling process for solving the serious environmental problem of plastic waste. It also offers the higher cracking ability of plastics, and the lower concentration of solid residue in the product [15].

Riyadh et al.[16] studied the catalyst pyrolysis of PS, PET and XPET+PS. 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 catalyst pyrolysis of PET lead to acid compounds like benzoic acid, terephthalic acid, ethylene glycol dibenzoate and Dibenzoyl-L tartaric acid anhydride as the main components.

2- Experimental work

2-1. Materials

The plastics utilized in current paper were waste polyethylene terephthalate (PET) and polystyrene (PS) and their mixture. The PET was actual waste plastic from soft drink, and the waste PS was from disposable foam food containers. Additionally, collected waste PET and PS were washed with soap and water and cut into small pieces. The particle size of PET and PS was (5-6) mm as shown in figures (1) and (2). Soft drink bottle and disposable foam food containers were transparent. Nitrogen gas was supplied from Dijlah Factory, with purity 99%.



Figure 1. waste PS



Figure 2. waste PET

2-2. Thermogravimetric analysis of materials

The weight loss versus temperature curve for thermal decomposition of polyethylene terephthalate and polystyrene under a linear heating rate shows that the decomposition was a single step degradation started at 300°C and completed at 463°C for PS while the degradation of PET started at 350°C to 465°C for PET. The TGA analysis was measured by the laboratories of College of Education for pure Science (Ibn Al-Haitham).

2-3. Liquid Product Analysis

The reaction products (liquid) were analyzed in a GC-MS (shimadzy model AOC-20i / AOC-20s) auto injection that is located in the Ministry of Science and Technology. Temperature 100 °C to 260°C.

2-4. Procedure

The equipment used in the thermal pyrolysis of wastes plastic consists of Batch tubular reactor made of stainless steel of about 340 mm length, 40 mm inside diameter and 45 mm outside diameter. Thermocouple (type K) with digital temperature recorder, connected to the reactor, used to measure the temperature inside the reactor. The heat was supplied to the reactor by 3600 Watt external electrical heaters to get the required reaction temperature. The condensate products are collected from the bottom of the condenser and the gaseous products leave the system at the top of the condenser. The batch reactor was first cleaned with naphtha. 50 g of a certain plastic particles (PS or PET) were weighted by using a four decimal balance, both of weight plastic particles (PS, PET, 10%PET+PS, 20%PET+PS, 30%PET+PS) were fed to the reactor. Nitrogen was supplied several times to purge the air out of the

reactor before the experiment started. The pressure fixed at 1 atmospheric. The electrical heater was turned on to reach the required reaction temperature; the accuracy of temperature readings was about 3°C. zero time was recorded ,when the gases were started to get out of reactor through the condenser. Then, the cooling water was supplied by chiller at temperature 3 to 5°C the condenser was effective enough to drop the temperature of the pyrolysis product to less than 30 °C. The product separated in the condenser to non-condensable gases has left from the top of the condenser to get out of laboratory. Liquid (contains wax) was collected from the bottom of condenser in sealed cylinder. The liquid and the wax weight by four dismal balances. The gas weight was calculated by making difference between initial weight of plastic and summation of products weight (liquid, wax and coke). The time of experiment ends when no further production of liquid and wax (end of plastic inside the reactor). The schematic diagram and photographic of the experimental apparatus are shown in Figures 3 and 4, respectively.

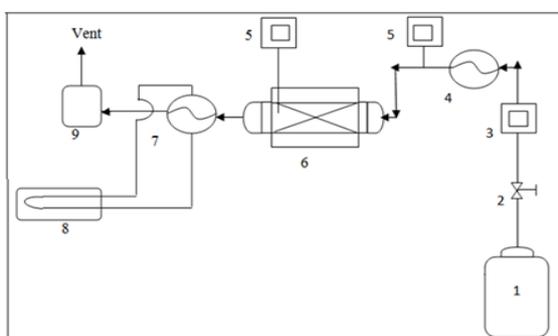


Figure 3. Schematic diagram of the experimental apparatus 1) Nitrogen cylinder, 2) Gate valve, 3) Gas flow meter, 4) Preheater, 5) Temperature reader, 6) Reactor, 7) Condenser, 8) Cooling system, 9) Liquid collector.



Figure 4. Photograph of the experimental

2-5. Experimental Design

The following Table 2 shows the thermal pyrolysis of PS and PS+xPET.

Table 2. Experimental procedure of Thermal pyrolysis

Material	Time (min)	Temperature °C
PS	90	350
		400
		450
PS+ 10%PET	90	350
		400
		450
PS + 20% PET	90	350
		400
		450
PS + 30% PET	90	350
		400
		450

3. Results and discussion

3-1 Effectiveness of reaction Time on Thermal Pyrolysis of PS

The degradation of plastic products has been affected by reaction time. In this study, the test of optimum reaction time was studied between 30 min to 120 min for the pyrolysis of PS by using the maximum decomposition temperature (450°C). The results of the trials are shown in Figure 5. It has been noticed that liquid product increased notably when the reaction time was increased from 30 min to 90 min. The maximum yield was 77% at 90 min. A further increase in reaction time showed no clear change in the yield of liquid products.

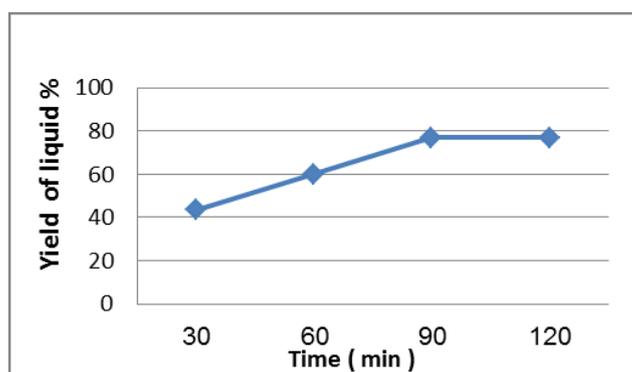


Figure 5. Effect of reaction time on the liquid yield

3-2. Effect of Temperature on Thermal Pyrolysis

Temperature has a strong effect on the characteristics of pyrolysis liquid. The effect of pyrolysis temperature, on the thermal pyrolysis of PS, 10%PET + PS, 20%PET + PS and 30%PET+PS, and PET was studied to know the temperature that gives maximum yield. The liquid produced from waste polystyrene increased from 58.2% to 67.8 %, while the gases and residue decreased from 27.6% to 22 % and 14.2 % to 10.2 %, respectively when the temperature was increased from 350°C to 400°C and the liquid further increased from 67.8% to 77% and further decreased in gases and residue from 22 % to 16 % and 10.2 % to 7% respectively when the temperature was increased from 400°C to 450°C.

For the thermal pyrolysis of 10% PET + PS the yield of the liquid and wax increased from 54% to 58.6 % and from 0.46 % to 0.92 % respectively, while the gases and residue decreased from 22.14 % to 20.5 % and from 23.4 % to 19.98 %, respectively when the temperature was increased from 350 °C to 400 °C. When the temperature increased from 400°C to 450, liquid and wax products further increased from 58.6 % to 67.56 % and from 0.92 % to 1.58 %, respectively and further decreased in gases and residue from 20.05 % to 19.6 % and 19.98% to 11.26%, respectively.

In case of 20% PET + PS, the amount of the liquid and wax increased from 44.6% to 51.4% and from 0.84% to 1.52%, respectively, while the gas and residue decreased from 22.16% to 19% and from 32.4% to 28.08%, respectively when the temperature was increased from 350°C to 400°C, and then the liquid and wax further increased from 51.4% to 54% and from 1.52% to 1.64%, respectively and further decreased in the gases and residue from 19 % to 17% and 28.08% to 27.36% respectively when the temperature increased from 400°C to 450°C. The amount of liquid and wax produced from 30% PET + PS were increased from 27.8% to 37.48% and from 1.96% to 2.02%, respectively, while the gases and residue decreased from 30.04% to 28.9% and from 40.2% to 34% respectively, when the temperature was increased from 350°C to 400°C, but the temperature further increased reduced the yield of the liquid and residue from 37.48% to 30.4% and 34% to 28.9%, respectively and increase of the yield of gases and wax from 26.5 % to 37.46 % and from 2.02 % to 3.24 %, respectively. Fig. 6 show the effect of temperature on the products produced from thermal pyrolysis.

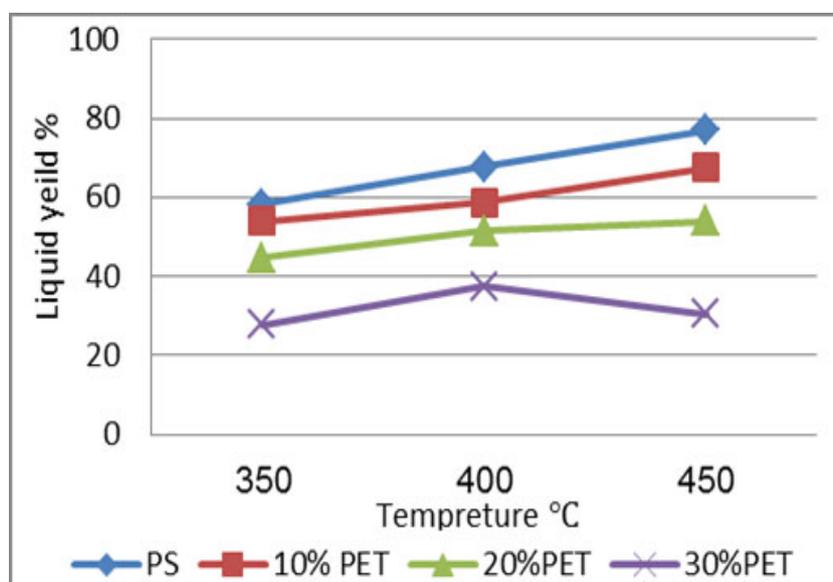
The yield of liquid products reported in the previous study for the catalytic pyrolysis of PS & PS+XPET was calculated in terms of wt.% and the results were compared the thermal pyrolysis, the comparative data are compiled in Table 3.

Table 3. Comparison of liquid yield produced from Plastic conversion in absence and presence catalyst

No.	plastic	Temp., °C	Liquid yield, %	
			Thermal pyrolysis	Catalytic pyrolysis [16]
1	PS	450	77	98.4
2	10 % PET + PS	450	67.56	82.6
3	20 % PET + PS	450	54	72.5
4	30 % PET + PS	450	30.4	50.8

To give an illustrating The thermal degradation of PET lead to thermally degradable more oxygen atoms release and that has an effect on polystyrene degradation and produce more non-condensable gases when the temperature increase from 400°C to 450°C in case of 30% PET + PS.

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), Buekens [17] reported the same notice.

**Figure 6.** Effect of temperature on the products produced from thermal pyrolysis

3-3. GC-MS analysis

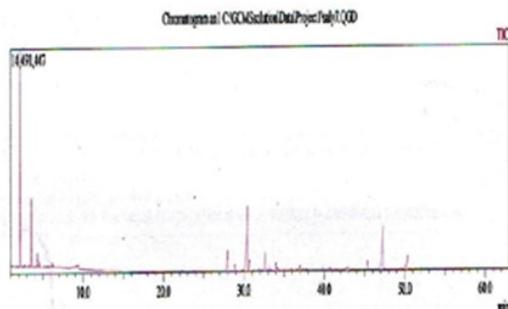
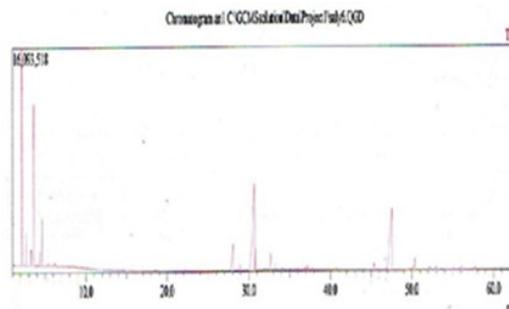
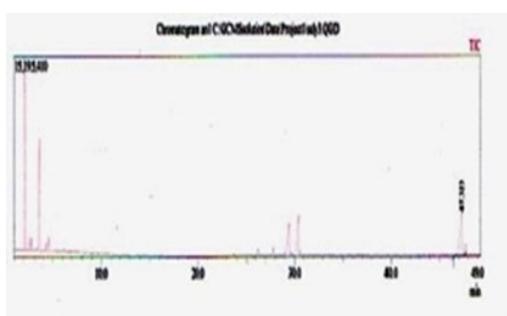
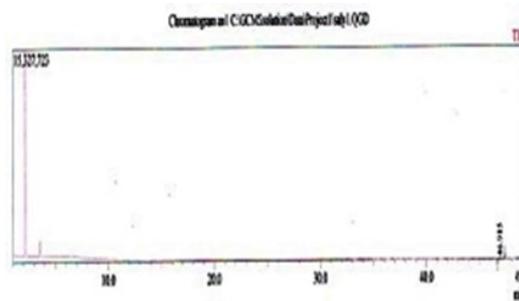
The liquid product obtained from the thermal pyrolysis of polystyrene (PS), and polyethylene terephthalate (XPET), optimized conditions were specified by GC_MS. Figures 7,8,9,10 show the GC-MS spectra of the liquid products derived from PS and PS+XPET. The liquid product gained from the pyrolysis of waste PS, and XPET+PS gave mainly aromatic hydrocarbons. The analysis aimed to study the effect of temperature on the main components distribution. Table (4) gives the main component appear in GC-MS analysis for the liquid produced from thermal pyrolysis of PS and XPET+PS.

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 which is the same as that found with 100% PS because the PET percentage is low therefore the effect of PET on PS degradation is low.

From GC-MS analysis new chemical compounds appeared in liquid produced from thermal 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.

Table4. The major component appear in GC-MS analysis for the liquid produced from thermal pyrolysis of PS and XPET+PS

PS	10%PET+ PS	20%PET+ PS	30%PET+PS
styrene (C ₈ H ₈)	styrene (C ₈ H ₈)	styrene (C ₈ H ₈)	styrene (C ₈ H ₈)
toluene(C ₇ H ₈)	toluene(C ₇ H ₈)	toluene(C ₇ H ₈)	toluene(C ₇ H ₈)
ethylbenzene (C ₈ H ₁₀)	ethylbenzene (C ₈ H ₁₀)	ethylbenzene (C ₈ H ₁₀)	ethylbenzene (C ₈ H ₁₀)
1,3 Diphenylpropane (C ₁₅ H ₁₆)	1,3 Diphenylpropane (C ₁₅ H ₁₆)	1,3 Diphenylpropane (C ₁₅ H ₁₆)	1,3 Diphenylpropane (C ₁₅ H ₁₆)
α- methylstyrene (C ₉ H ₁₀)	α- methylstyrene (C ₉ H ₁₀)	α- methylstyrene (C ₉ H ₁₀)	α- methylstyrene (C ₉ H ₁₀)
4-phenyl-1 butene (C ₁₀ H ₁₂)	4-phenyl-1 butene (C ₁₀ H ₁₂)	4-phenyl-1 butene (C ₁₀ H ₁₂)	4-phenyl-1 butene (C ₁₀ H ₁₂)
-----	-----	Benzaldehyde (C ₇ H ₆ O)	Benzaldehyde (C ₇ H ₆ O)
-----	-----	1-Phenylnaphthalene (C ₁₆ H ₁₂),	1-Phenylnaphthalene (C ₁₆ H ₁₂),
-----	-----	1,3-Diphenyl-1-butene (C ₁₆ H ₁₆),	1,3-Diphenyl-1-butene (C ₁₆ H ₁₆),
-----	-----	1,4-Diphenylbenzene (C ₁₈ H ₁₄)	1,4-Diphenylbenzene (C ₁₈ H ₁₄)

**Figure7.** GC-MS of liquid produced from Thermal pyrolysis of PS at 450°C.**Figure 8.** GC-MS of liquid produced from Thermal pyrolysis of 10%PET+PS at 450°C**Figure 9.** GC-MS of liquid produced from thermal pyrolysis of 20%PET+PS at 450°C.**Figure 10.** GC-MS of liquid produced from thermal pyrolysis of 30%PET+PS at 450°C.

4. Conclusions

The maximum liquid yields from thermal 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.

Mostly, the liquids yield products decreased with the increase in the amount of polyethylene 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 (C₁₂-C₂₄) and due to increasing of polyethylene terephthalate percentage many new oxygenated hydrocarbons is formed. The physical property of the produced liquid was closely to gas oil specifications.

Acknowledgements

This study was carried out on the chemical engineering department- university of technology, GC-MS analysis has been done at ministry of science and technology.

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