Recycling of Waste Polyethylene Terephthalate (PET) into Feedstock Monomers
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ABSTRACT
Polyethylene terephthalate (PET) is one of the polymers with the most growing market with an estimated expansion rate of 8-10%. With increasing PET consumption, its recycling has received worldwide attention for the preservation of resources and the protection of the environment. Saudi Arabia is one of the major producers of plastic in the world with total production capacity of around six million metric tons per year. It is assumed that the chemical recycling through depolymerization of PET into its monomer will be an ideal recycling method for Saudi Arabian waste PET because it could be recycled permanently. Several chemical degradation methods of PET were carried out in our laboratory under various conditions. Excellent feedstock monomers were obtained.

Keywords: PET, degradation, pyrolysis, recycling, waste management

1 INTRODUCTION
The amount of polyethylene terephthalate (PET) products alone has been rising each year, used for producing fibers, textiles, film base for audio and video recording, packaging and containers, etc. USA, Europe and Japan generate about 50 million tons of post consumer plastic waste material. In Europe, only 7% of the waste plastics are recycled to produce low grade plastic products, and the rest is land filled or incinerated. Among the different polymers, around 7.6 wt. % of these plastics is based on PET [1]. Polyethylene terephthalate (PET) is a polymer in widespread use in the production of bottles and containers of water and carbonated drinks. It is predicted that about 80 and 45% of all water and carbonated drink containers, respectively, will be made of PET by 2006 [2]. As a consequence of this increase and the short life of the containers, the presence of PET in municipal waste has also increased. Various processes have been developed for recycling plastic waste, including mechanical, energy recovery and chemical processes.

Several chemical recycling processes for PET depolymerization have been put forward with different depolymerizing agents and operation conditions [3, 4]. Saudi Arabia is one of the major producers of plastic in the world with total production capacity of around six million metric tons per year [5]. The amount of plastic wastes in Saudi Arabia is about 15 wt% in the composition of domestic municipality waste. SABIC produced 103,000 tons of PET, which was used in polyester fiber production and in the manufacture of soft drink bottles, food containers and other injection molded consumer product containers [6].

2 EXPERIMENTAL
Pyrolysis reaction of PET
The pyrolysis reactions were carried out in a Parr Micro Reactor No. 4593 M. The reactor system consists of stainless steel vessel with 100-cm³ capacity and equipped with precise temperature control and motorized stirrer with RPM control. The reactor utilized in this work was a batch pressurized autoclave reactor, the schematic diagrams of which are shown in Figures 1. The reaction vessel was stirred using a Parr Instrument Co. magnetic drive. About 2-8 g of sample was used in each experiment.

Fig. 1: Schematic diagram of Reactor outer parts of system
The liquid and solid fractions were analyzed by solvent fractionation, using a series of solvents as shown in Fig 2. IR analysis was performed on hexane soluble fractions which are representatives of fuel oils. The boiling range distribution of the hexane soluble fractions was determined by simulated distillation using the ASTM D2887 method and a dedicated Varian 3800 gas chromatograph equipped with RTX-2887 DMP capillary column from Restek Corporation.

RESULTS AND DISCUSSION

The experiments were conducted to establish the solubility of the unreacted PET in polar and non-polar solvents. The solvents used for extraction analyses were HPLC grade hexane, toluene and tetrahydrofuran (THF). Table 1 shows the solubility behavior of PET produced by SABIC, Saudi Arabia. PET polymer was found to be highly insoluble in THF and n-hexane and slightly (>1%) soluble in toluene solvents.

Table 1: Percent distribution of the products obtained from the pyrolysis of PET

<table>
<thead>
<tr>
<th>Plastic</th>
<th>Sample</th>
<th>Gases</th>
<th>Hxs</th>
<th>THFs</th>
<th>IOM Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET 2 H</td>
<td>P1</td>
<td>43</td>
<td>36.6</td>
<td>29.8</td>
<td>7.2</td>
</tr>
<tr>
<td>PET 4 H</td>
<td>P2</td>
<td>3.6</td>
<td>42.0</td>
<td>31.5</td>
<td>7.4</td>
</tr>
<tr>
<td>PET Bottle, 3 H</td>
<td>PW1</td>
<td>7.8</td>
<td>31.3</td>
<td>29.0</td>
<td>7.0</td>
</tr>
<tr>
<td>PET Bottle, 4 H</td>
<td>PW2</td>
<td>4.6</td>
<td>39.8</td>
<td>29.6</td>
<td>7.5</td>
</tr>
<tr>
<td>PET Bottle, 2 H</td>
<td>PW3</td>
<td>4.7</td>
<td>33.0</td>
<td>31.8</td>
<td>7.4</td>
</tr>
<tr>
<td>PET, AIBN 5%, 3 H</td>
<td>P4</td>
<td>3.6</td>
<td>43.8</td>
<td>35.0</td>
<td>7.7</td>
</tr>
<tr>
<td>PET, AIBN 10%, 3 H</td>
<td>P5</td>
<td>2.6</td>
<td>47.3</td>
<td>38.5</td>
<td>7.9</td>
</tr>
<tr>
<td>PET Bottle, AIBN 5%, 3 H</td>
<td>PW6</td>
<td>2.2</td>
<td>42.0</td>
<td>35.3</td>
<td>7.5</td>
</tr>
<tr>
<td>PET Bottle, AIBN 10%, 3 H</td>
<td>PW7</td>
<td>5.4</td>
<td>45.5</td>
<td>35.9</td>
<td>7.7</td>
</tr>
</tbody>
</table>

A summary of prominent peaks observed in the IR spectra of P2H hexane solubles are given below:

- Broad and strong peak at 2828 due symmetrical –CH₂ stretching
- Broad and strong peaks at 2665, 2547 and 1915 and 1785 are due to some overtones
- Strong and strong peak at 1674 is due to carbonyl stretching which may be due to α,β unsaturated aldehydes and ketones.
- Medium peak at 1601 is due to C=C stretch
- Sharp and strong peaks at 1414, 1279 may be due to C-O-H and C-O stretching
- Medium and sharp peak at 1175 may be due to C-CO-C stretch and bending.
- Medium peak at 925 may be due to O-H out of plane bending
- Weak peak at 802 may be due to para substituted aromatic ring.

The SIM results show a general decrease in IBP recovery temperature for the PET plastic and waste PET bottles as shown in Figure 3. Initially PET has a relatively lower boiling point around 235°C and waste PET bottle has a little high boiling point around 245°C and therefore the HXs produced from the pyrolysis of these two had high boiling point. Boiling point goes down because of the addition of lighter hydrocarbons.

CONCLUSION

Pyrolysis reactions of PET afforded approximately 78-95% conversion into gases and liquid fuel products under different set of operating conditions. Addition of AIBN initiator in pyrolysis reactions afforded higher conversions of PET into liquid fuels. The results of this study, if implemented, can help in managing clean environmental and minimizing waste disposal problems of PET.

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REFERENCES