Thermal and Catalytic Degradation of Polystyrene with a Novel Catalyst

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Abstract—Waste polymer recycling has received a great attention due to increasing amounts of waste polymers generate enormous environmental problems. The pyrolysis of polystyrene was examined as an effective way to recycle this polymer and recover its monomer styrene. In this paper, thermal and catalytic degradation of polystyrene at the atmospheric pressure was investigated. Various conditions of temperature and catalyst/Polystyrene mass ratio were considered to determine the product composition and effects of catalyst/Polystyrene mass ratio and temperature on conversion. The results showed that with increasing the temperature, the conversion increased. The products of the degradation mostly consist of liquid, less gas and solid residue. The AIT100s catalyst showed good catalytic performance for the degradation of PS with selectivity to aromatics more than 99%.

Keywords—Catalytic degradation, polystyrene, monomer, AIT100s

1. Introduction

Nowadays, polymer composite productions are used widely over the last few decades [1, 2]. It has been estimated that 100 million tonnes of plastics are produced world-wide each year [3]. Polystyrene is broadly used for many purposes such as packaging, consumer goods, etc., but this widely use brings lots of wastes and causes environmental pollution because of their non-degradable nature. Therefore, recycling, reuse and making them biodegradable by various means will prevent this problem [4-7].

Among them polymers containing semiconductor particles play a significant role, especially for the manufacturing of electronic devices. Inorganic–organic polymer composites have attracted wide interest, because the addition of inorganic particles to polymers can enhance conductivity. Until now four different methods has been developed which include: [1, 2, 8] Primary recycling, referring to “in plant” recycling of scrap material [9]; Mechanical Recycling, in which polymer separation is done by melt extrusion or other techniques [10]; Chemical or feedstock recycling where depolymerization to the monomers is performed; Energy recovery, an effective way to reduce the volume of organic materials by incineration [8]. Solid acids and base are the most commonly used catalysts [11-14]. PS (polystyrene) can be thermally depolymerized to monomer styrene with a high selectivity in contrast to polyethylene and polypropylene [7].

In this field Zhang et al. reached a styrene yield of 70 wt. % at degradation temperature of 350 °C using a semi-batch reactor with a continuous flow of nitrogen [15]. While, Audisio et al. used solid acids such as silica –alumina and HY or REY zeolites at 350 °C and showed a very low selectivity (less than 5 wt.%) to the styrene in PS [16]. Ukei et al. employed solid bases, especially BaO and reported better selectivity of styrene monomer in comparison to solid acids at 350 °C [17].

The main objective of this work is to study the production of liquid fuels by thermal and catalytic degradation of polystyrene using AIT100s as catalysts. Also the effects of temperature and catalyst on degradation are presented in this paper.

2. Experimental

2.1. Material and catalysts

PS employed in this work, was granules form, supplied by TAITA Chemical Company from Taiwan. The properties of polystyrene are described in Table 1.
The catalytic and thermal degradation of PS was carried out in a semi-batch reactor. A mixture of PS and catalyst was loaded inside a Pyrex vessel of 1000 ml. The reactor was pressurized and purged with nitrogen two times to ensure an oxygen-free medium. The polymer and catalyst mixture was heated at a rate of 20 °C/min to reach the desired temperature. The reaction temperature was measured by a thermocouple that was in direct contact with the reaction mixture. The oil and gases exiting the reactor were condensed in the condenser system which consisted of a water-cooled condenser illustrated in Figure 1, then volatile hydrocarbons is separated into gases and liquids. The condenser system was weighed before and after the experiment to determine the total oil yield.

### Table 1. Polymer Properties.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Nominal Value</th>
<th>Unit</th>
<th>Test Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Gravity</td>
<td>1.04 g/cm³</td>
<td>ASITM D792</td>
<td></td>
</tr>
<tr>
<td>Melt Mass-Flow Rate (200°C, 5 kg)</td>
<td>7.0 g/10 min</td>
<td>ASTM D1238</td>
<td></td>
</tr>
<tr>
<td>Tensile Strength (22°C, 3.18 mm)</td>
<td>15.1 MPa</td>
<td>ASTM D638</td>
<td></td>
</tr>
<tr>
<td>Tensile Elongation (Room, 23°C)</td>
<td>2.0 %</td>
<td>ASTM D638</td>
<td></td>
</tr>
<tr>
<td>Notched Izod Impact (23°C)</td>
<td>14.1 kJ</td>
<td>ASTM D256A</td>
<td></td>
</tr>
<tr>
<td>Vicat Softening Temperature</td>
<td>100 °C</td>
<td>ASTM D1525</td>
<td></td>
</tr>
<tr>
<td>Flammability (1.59 mm)</td>
<td>HR</td>
<td>UL 94</td>
<td></td>
</tr>
<tr>
<td>Haze (2000 μm)</td>
<td>0.16 %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Residual Monomer - SM</td>
<td>&lt; 200 ppm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 2. Physical properties of the catalysts used in the experiments

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Typical</th>
<th>Min.</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>Wt. %</td>
<td>43.5</td>
<td>38.5</td>
<td>48.2</td>
</tr>
<tr>
<td>Pt</td>
<td>Wt. %</td>
<td>0.001</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total SA</td>
<td>m²/g</td>
<td>40</td>
<td>38</td>
<td>42</td>
</tr>
<tr>
<td>BET surface area</td>
<td>m²/g</td>
<td>101.16</td>
<td>99.37</td>
<td>300.37</td>
</tr>
<tr>
<td>Attrition Index</td>
<td>Wt. %</td>
<td>1.5</td>
<td>-</td>
<td>5.3</td>
</tr>
<tr>
<td>ABD</td>
<td>g/ml</td>
<td>0.4</td>
<td>.38</td>
<td>.42</td>
</tr>
</tbody>
</table>

### 3. Results and discussion

Figure 2 shows the product yields obtained from the pyrolysis of polystyrene. It illustrate the results for the absence of a catalyst, and in presence of AIT100s catalyst in relation to catalyst temperature, respectively.

According to the Figure 3 by increasing the temperature, conversion was increased. It can be seen from this table that adding AIT100s catalyst led to an increase in pyrolysis conversion in lower temperature. As it is clear from this Figure, an increase in catalytic reaction temperature caused the conversion to increase from 65% from to approximately 99%.

Figure 3. Effect of temperature on catalytic degradation of PS.

2.2. Characterization of catalyst

In this study a novel catalyst was used, named AIT100s, which properties were shown in Table 2.
Figure 4 shows the influence of the catalyst/polystyrene ratio for the AIT100s catalyst. Data presented in this table showed the pyrolysis of 100 (gr) of polystyrene in relation to the mass of the AIT100s. As the mass of catalyst increased, reduction in the yield of conversion was observed.

![Figure 4](image)

**Figure 4.** Effect of catalyst on degradation of PS.

### 3.1. Product yield

PS with catalyst AIT100s in the reactor, was degraded at various temperatures (350, 370, 390 and 410 °C) and different catalyst: plastic ratio. Figure 5 illustrates the gases, liquids and residues on the catalyst from the degradation experiment. The amount of gases products was calculated by subtracting the sum of weights for liquids and residues, from the total weight of PS sample and fresh catalyst initially loaded to the reactor. Carbonaceous compounds adhering to the reactor wall were dissolved in n-hexane and were measured as degradation residues. In all cases, the liquid oils were main products.

![Figure 5](image)

**Figure 5.** Product yield from the catalytic pyrolysis of PS

It can be figured out from Figure 5 that the amount of liquid products increased with temperature, while the residues decrease with temperature. At low temperatures, the amount of residues for AIT100s catalyst was high, 31 and 18 wt. % for 350 and 370 °C, respectively. However, their amounts were very small at higher temperatures. This indicates that the competitive cross-linking reactions take place first, especially at low temperatures; therefore, the cracking of the resulting cross-linked polymer becomes more difficult.

#### 1.1.1. Effect of catalyst: plastic ratio on product yield

Figure 6 shows the effect of the catalyst: polystyrene ratio on degradation product for the AIT100s catalyst. As the mass of catalyst increased, a reduction in liquid yield was observed. Increase of this ratio also showed an increase in gas yield and carbon formation on the catalyst surface.

![Figure 6](image)

**Figure 6.** Effect of catalyst ratio on product yield.

After the catalytic cracking, the residue remaining within the reactor showed a black solid, which completely covered the reaction zone. However, this black residue was not observed in thermal cracking experiments, which indicates that the acid catalysts promoted the cross-linking reactions. The main product of thermal and catalytic degradation of polystyrene is liquid. By increasing the temperature, the amount of liquid product was increased. The reason is that at higher temperature, more bonds will break. Styrene monomer and dimer were the main components in the oils obtained by solid acid. Since cracking of hydrocarbons on solid acids has been explained in terms of β-scission of C–C bonds [13], these were probably produced by β-scission of C–C bonds in the PS main chains as shown in Figure 7.
The mechanism of acid catalyzed cracking is categorized as carbenium nature which is shown in Figure 8. The most likely reaction pathway involves the attack of a proton associated with a Brønsted acid site to the aromatic rings of PS, due to the reactivity of its side phenyl groups towards electrophilic reagents. The resulting carbocations may undergo \( \beta \)-scission followed by an inter/intramolecular hydrogen transfer, leading to different products (benzene, ethylbenzene, cumene, etc.). Alternatively, the protonated polymer backbone may proceed through cross-linking reactions among adjacent polymeric chains or even inside the same polymer [13].

### References


[8] Dimitris S. Achilias, Iliana Kanellopoulou,


