Catalytic steam reforming of waste plastics for production of hydrogen

Yeongsu Park, Kayoko Aoki, Tomoaki Namioka, Kunio Yoshikawa

Department of Environmental Science and Technology, Tokyo Institute of Technology, Tokyo, Japan

Abstract: Catalytic steam reforming is used to produce hydrogen-rich gas from waste plastics by the following two reaction steps: pyrolysis of plastics and catalytic steam reforming of pyrolysis gases. In this study, the gas fraction of polyethylene terephthalate (PET) generated from pyrolysis was catalytically reforming in the temperature range of 773 ~ 973 K, in the steam to carbon ratio (S/C) range of 1.1~3.3 and in the weight hourly space velocity (WHSV) range of 0.3~0.8 h⁻¹ employing the ruthenium-based (Ru/Al₂O₃) catalyst. This catalyst is more active than the Ni catalyst and can suppress carbon deposition at the low S/C ratio. The carbon conversion rate and the yield of hydrogen increased with raising the temperature and decreasing WHSV. On the other hand, the change of the S/C ratio little affected the steam reforming of PET, which is caused by the strong chemical reaction with the oxygen contained in PET instead of the weak chemical reaction with steam. In the experiment performed at 973 K, S/C=1.1 and WHSV=0.38 h⁻¹, the results were that the hydrogen yield was 25 mmol/g-sample and the hydrogen concentration in the produced gas was 43 %. The cold gas efficiency of this process at 973 K can reach to as high as 78.8 % if we ignore the thermal loss.

Keywords: Catalytic steam reforming, Waste Plastics, PET, Ruthenium Catalyst, Hydrogen

1. INTRODUCTION

In the plastic pyrolysis, the polymeric materials are heated in the absence of oxygen, so their macromolecular structures are broken down into smaller molecules and a wide spectrum of hydrocarbons are formed. The products of pyrolysis may be used as a chemical feedstock or fuel. But PET pyrolysis has some problems. Generally, no liquids are obtained at the exit of the condenser while yellowy powders are formed which stick to the walls of the pipelines, making it impossible to collect them and quantify the pyrolysis products[1]. Therefore PET is a difficult material to be pyrolyzed.

For that reason, we propose an alternative process which is the catalytic steam reforming process to produce hydrogen from PET. The steam reforming process transforms hydrocarbons into gaseous mixtures constituted of carbon dioxide (CO₂), carbon monoxide (CO), methane (CH₄) and hydrogen (H₂). The main reactions that take place are the following ones[2].

\[
\text{CnHm} + n\text{H}_2\text{O} \rightarrow n\text{CO} + (n+\frac{m}{2})\text{H}_2 \quad \Delta H<0 \quad (1)
\]

\[
\text{CO} + 3\text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O} \quad \Delta H = -206 \text{kJ/mol} \quad (2)
\]

\[
\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H = -41.2 \text{kJ/mol} \quad (3)
\]

In this process, PET is pyrolyzed in an externally heated pyrolyzer and the pyrolysis gas flows into the reformer. In the reformer, the pyrolysis gas is reformed by the steam reforming reaction under the existence of the Ru/Al₂O₃ catalyst (Fig. 1).

Generally, the carbon deposition takes place on the catalysts when the pyrolysis gases were streamed on them. But it is reported by Okada et al., that a Ru/Al₂O₃ catalyst is very effective for preventing the carbon deposition during the steam reforming of hydrocarbons[3-5]. This catalyst is more active than the Ni catalyst at a low S/C ratio.

The reaction product composition is determined by the thermodynamic equilibrium between gaseous species according to operation conditions[2]. Therefore we have tested at the optimum temperature, S/C and WHSV conditions employing Ru/Al₂O₃ catalyst for increasing the concentration of H₂. The test results are reported in this paper.

2. EXPERIMENTAL

2.1 Catalyst

The Catalyst, used at this study, is commercial catalyst (AP4002) provided by N.E. CHEMACT Co. in japan. This is 0.5 % Ru catalyst supported on Al₂O₃ and is cylindrical form(approximately 3.2 mm² × 5 mm). Specific surface area is 90~110 m²/g and fill density is 900~1100 g/l.

2.2 Experimental apparatus and method

A schematic diagram of the experimental setup is shown in Fig. 1.

Corresponding author: H. Kimura, isets07@esi.nagoya-u.ac.jp

Fig. 1 Schematic diagram of apparatus
This apparatus mainly consists of a pyrolyzer (210 mm$^2 \times 430$ mm), a reformer (120 mm$^2 \times 350$ mm), a steam generator, a condenser and the gas analyzer.

At first, totally 400 g of PET samples were put in the pyrolizer and they were pyrolyzed in the externally heated pyrolizer. Then the pyrolysis gas flowed into the reformer. In the reformer, the pyrolysis gas is reformed into light gases by the reaction with preheated steam (773 K) under the existence of the Ru/Al$_2$O$_3$ catalyst. The reformed gas was cooled down by passing through the condenser and the deposits is separated here. In the gas/oil separator, the reformed gas is separated into gases and oils. The tar and moisture were trapped in the tar/moisture collector and the purified gas was analyzed by a gas chromatograph, which can measure volume concentrations of H$_2$, O$_2$, N$_2$, CH$_4$, CO, CO$_2$, ethylene (C$_2$H$_4$), ethane (C$_2$H$_6$) and propane (C$_3$H$_8$).

Experimental conditions are summarized in Table 1.

Table 1 Experimental condition

<table>
<thead>
<tr>
<th></th>
<th>Pyrolysis</th>
<th>Catalytic steam reforming</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supplied sample [g]</td>
<td>400</td>
<td>400</td>
</tr>
<tr>
<td>Pyrolyzer temperature [K]</td>
<td>653</td>
<td>653</td>
</tr>
<tr>
<td>Reformer temperature [K]</td>
<td>593</td>
<td>773–973</td>
</tr>
<tr>
<td>Steam temperature [K]</td>
<td>-</td>
<td>773</td>
</tr>
<tr>
<td>S/C [-]</td>
<td>-</td>
<td>1.1–3.3</td>
</tr>
<tr>
<td>WHSV [1/h]</td>
<td>-</td>
<td>0.3–0.8</td>
</tr>
</tbody>
</table>

Steam to carbon ratio and the weight hourly space velocity is defined as follows.

\[
S/C = \frac{\text{Steam supply speed [mol/min]}}{\text{Carbon supply speed in the reformed gas [mol/min]}} [-] (4)
\]

\[
\text{WHSV} = \frac{\text{Supply speed of the reformed gas[g/h]}}{\text{Weight of catalyst[g]}} [1/h] (5)
\]

3. RESULTS AND DISCUSSION

3.1 Comparison of pyrolysis and catalytic steam reforming

The carbon conversion rate and the composition of products after the pyrolysis and the catalytic steam reforming of PET are shown in Fig. 2a and b, respectively.

For the pyrolysis, the carbon conversion rate of gas was only 19.1 % and the primary components of the gas were CO and CO$_2$. In contrast to the pyrolysis, by carrying out the catalytic steam reforming at the pyrolyzer temperature of 653 K and the reformer temperature of 973 K the carbon conversion rate of the gas increased up to 72.3 % and the primary gas components became H$_2$ and CO.

In the case of the pyrolysis, the formation of the deposit was remarkable and caused blockage of the gas piping. This is the main problem of the thermal recycling of PET material by pyrolysis. However, in the case of the catalytic steam reforming, the deposit products were not formed.

3.2 Effect of the reformer temperature

The product gas yields in the catalytic steam reforming of PET at different temperatures are shown in Fig. 3. The product consists mainly of H$_2$, CO and CO$_2$. As the temperature increased from 773 K to 973 K, the yield of H$_2$ and CO in the gas products increased (form 8 to 25 mmol/g-sample and from 5 to 21 mmol/g-sample for H$_2$ and CO, respectively), while that of CO$_2$ slightly decreased from 10 to 9 mmol/g-sample. The increase in the CO yield should be expected as a result of the thermodynamic equilibrium of the water-gas shift reaction as shown in Eq (3), which is an exothermic reaction and the temperature increase should cause the formation of much CO[6].

3.3 Effect of WHSV

![Fig. 3 Effect of the reformer temperature on the gas yield](image)
The WHSV is the indicator showing how many abundant materials can be processed at unit catalyst weight.

Figure 4 shows the effect of the WHSV on the yield of gases. As the WHSV increased from 0.3 to 0.8 h⁻¹, the yield of H₂ and CO in the gas products decreased (from 25 to 13 mmol/g-sample and from 21 to 10 mmol/g-sample for H₂ and CO, respectively). Especially, the yield of CO decreased significantly between 0.5 and 0.8 h⁻¹.

4. CONCLUSIONS
Steam reforming with Ru/Al₂O₃ catalyst is effective to reform the deposits produced from pyrolysis of PET material.

In the experiment performed at 973 K, S/C=1.1 and WHSV=0.3 h⁻¹, the results were that 25 mmol/g-sample for H₂ yield and 43 % for the concentration of H₂ in the produced gas were achieved. Assuming we ignore the thermal loss, we can estimate that the cold gas efficiency of this system will reach to 78.8 %.

3.4 Effect of S/C
Figure 5 shows the effect of S/C on the yield of gases. As the S/C increased from 1.1 to 3.3, the yield of H₂ and CO₂ in the gas products slightly increased (from 25 to 30 mmol/g-sample and from 9 to 18 mmol/g-sample for H₂ and CO₂, respectively), and that of CO slightly decreased from 21 to 16 mmol/g-sample.

The carbon conversion rate and the yield of H₂ increased with increasing temperature and decreasing the WHSV. On the other hand, the change of S/C ratio little affected the steam reforming of PET, which is caused by the strong chemical reaction with the oxygen contained in PET instead of the weak chemical reaction with steam.

3.5 Energy balance evaluation of the total system
Figure 6 shows the energy balance of the total system in case of PET material. The cold gas efficiency of this process at 973 K, WHSV=0.5 h⁻¹ and S/C=3.3 can reach to as high as 78.8 % if we ignore the thermal loss.

REFERENCES