Abstract The process of producing synthetic gas from waste plastics by steam reforming was investigated. To evaluate this process, the steam reforming of the oils derived from low-density polyethylene and polystyrene were carried out using a laboratory-scale fluidized bed of Ni–Al₂O₃ catalysts. The performance of gasification in terms of carbon conversion, gas yield, and gas compositions was examined. Although oils derived from plastics contain many kinds of heavy hydrocarbons and aromatics, they were well gasified at temperatures above 1023 K with a steam/carbon ratio of 3.5 and a weight hourly space velocity of 1 h⁻¹. The hydrogen content of the product gas was very high at approximately 72 vol% for polyethylene-derived oil and 68 vol% for polystyrene-derived oil. These compositions agreed well with the values calculated from chemical equilibrium.

Key words Steam reforming · Waste plastics · Hydrogen · Coking · Catalyst

Introduction

Various plastic recycling processes have been developed in Japan, based on the Package Recycling Law passed in 2000. Among these processes, the gasification of waste plastics was considered to be a promising method for feedstock recycling, and two large commercial recycling plants were constructed and are running successfully at full operation.

However, this conventional gasification process requires large-scale facilities such as an oxygen plant because the process is based on partial combustion and it requires a large quantity of pure oxygen to keep the reaction temperature very high. The development of smaller and more efficient processes is desirable because the collection of a large amount of waste plastics is very difficult, except in areas of high population density. Therefore, we have been studying the process of gasification of waste plastics by steam reforming, which occurs at relatively low temperatures and does not require pure oxygen. The production of gas by reacting hydrocarbons with steam in the presence of a catalyst is a well-known process that was established in the 1930s. A vast number of studies have focused on the steam reforming of natural gas, naphtha, and other hydrocarbons; however, the steam reforming of the oil derived from waste plastics has not been reported so far. The authors first studied the performance of the steam reforming of oils derived from low-density polyethylene and polystyrene by using a small tubular reactor. These oils were well gasified with very high carbon conversions and low coking rates at temperatures above 973 K, despite the high molecular weight of the constituents of these oils. This article reports a study using a laboratory-scale fluidized-bed reactor.

Steam reforming of waste plastics

The process we developed to produce synthetic gas from waste plastics by steam reforming is composed of two steps (Fig. 1): the first step is the liquefaction of waste plastics and the second step is the steam reforming of the light oil from the first thermal decomposition step. As steam reforming is a strong endothermic reaction, the heat of reaction is provided by the combustion of some fraction of the heavy oil arising from the first stage. In this way, the energy efficiency of the whole system becomes very high. The primary chemical reactions relating to steam reforming are described as follows:

\[ \frac{1}{m} C_mH_n + H_2O \rightarrow CO + \left( \frac{n}{2m} + 1 \right) H_2 \]  
\[ CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H = -41.13 \text{kJ/mol} \]  
\[ CO + 3H_2 \rightarrow CH_4 + H_2O \quad \Delta H = -205.7 \text{kJ/mol} \]
Equation 1 expresses the steam reforming reaction where $C_mH_n$ represents a component of the plastic oils. The value of $n/m$ is nearly 2 for PE oil and 1 for PS oil.\(^1\) Equation 2 is a water gas shift reaction and Eq. 3 is the reverse reaction of Eq. 1.

**Materials**

Plastic oils

To investigate the steam reforming of plastic-derived oils, the plastic oils were produced by thermal decomposition from virgin pellets of low-density polyethylene (J2522, Ube Industries, Ube, Japan) and polystyrene (G8102 K, A&M Styrene, Tokyo, Japan) in the temperature range 650–700 K. The polyethylene oil (PE oil) produced contained primarily paraffins and 1-olefins from around C5 to C25, whereas the polystyrene oil (PS oil) contained primarily styrene monomer with some dimers and trimers. Table 2 shows the elemental analyses of the plastic oils. The hydrogen/carbon molar ratio (H/C ratio) of PE oil was 2.00, which is the same as the ratio for polyethylene, whereas, the H/C ratio of PS oil was 1.07, which is larger than that of styrene because PS oil contains some saturated fragments such as toluene and ethyl benzene. More details of these oils can be found elsewhere.\(^3,4\)

Catalyst

The catalysts used in this experiment were commercial Ni–Al$_2$O$_3$ catalysts (C11NK, C11N, SÜD-Chemie, München, Germany) which were designed for the steam reforming of naphtha (Table 2). C11NK and C11N have a cylindrical shape (17 mm × 17 mm) with a single hole. The catalysts were crushed to form particles and sieved with screens for use in a fluidized bed. The average diameter of the particles was determined to be around 0.25 mm to satisfy the requirement for the gas velocity to be greater than twice the minimum fluidizing velocity. The catalyst was prereduced in a hydrogen stream for 3 h at a temperature of 873 K.

**Experimental**

Figure 2 shows a schematic of the experimental apparatus for steam reforming and the apparatus used to produce the plastic oils. The reactor for steam reforming was a laboratory-scale fluidized bed made of stainless steel with an inside diameter of 52 mm and a height of 600 mm. A perforated stainless steel disk was used as the gas distributor. A total of 80 g of catalyst was loaded as the bed material. The reactor was heated by a tubular electric heater from the outside. The feed rate of the plastic oils was fixed at about a weight hourly space velocity of 1 h$^{-1}$. The steam carbon ratio, $S/C$, which is defined in Eq. 4, was set at about 3.5. The reaction temperature was in the range 873–1073 K.

\[
S/C = \frac{\text{moles of steam}}{\text{moles of carbon in feedstock oil}} \tag{4}
\]

The product gas was cooled in a condenser and separated from water. The gas was sampled with a Teflon bag at a given time and at fixed intervals. The volume of gas and its components were measured by a gas meter and by gas chromatography.

**Results and discussion**

Figure 3 shows the temperature dependence of gas yield and carbon conversion (CC), which is defined as:

\[
CC = \frac{\text{atoms of carbon in product gas}}{\text{atoms of carbon in feedstock oil}} \tag{5}
\]