Influence of process conditions on syngas production from the thermal processing of waste high density polyethylene☆

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ABSTRACT

A range of process conditions, including the type of reactor, the reacting atmosphere and the presence of catalyst, and their influence on the production of syngas, i.e. hydrogen and carbon monoxide, from the thermal processing of waste high density polyethylene (HDPE) has been investigated. Pyrolysis in the presence of nitrogen and in the presence of carbon dioxide, two-stage pyrolysis-steam reforming and carbon dioxide/catalysis process conditions were investigated in relation to gas composition and particularly hydrogen and carbon monoxide yield. The influence of addition of a Ni–Mg–Al catalyst in the second reactor was also investigated. It was found that a two-stage pyrolysis at 500 °C, followed by second stage reaction at 800 °C resulted in a significant increase in hydrogen production. With the addition of carbon dioxide, the two stage process also increased carbon monoxide yield in addition to hydrogen. Addition of steam into the second stage reactor with the carbon dioxide produced a further increase in hydrogen production. Also, the presence of a Ni–Mg–Al catalyst in the second reactor increased the amount of hydrogen and carbon monoxide produced.

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1. Introduction

There is current interest in the production of syngas from waste materials and in particular from waste plastics [1–5]. Pyrolysis and gasification of waste plastics is a promising route to produce high yields of a hydrogen-rich syngas. Pyrolysis of plastics produces low yields of hydrogen [6,7]. However, two-stage processing of waste plastics which combines thermal degradation of the plastic in a first stage pyrolysis step followed by gasification/reforming in a second stage, usually in the presence of catalysts generates high yields of hydrogen [8–10]. The gasification process produces reactions of the volatile products that are released from the pyrolysis process and recombines them to produce synthesis gas. The addition of steam via steam reforming of the waste plastic is recognised to be effective for hydrogen production through promotion of the water gas shift reaction [11]. Compared with steam reforming, studies on carbon dioxide reforming, also known as dry reforming, are limited especially on waste plastic.

The use of carbon dioxide for hydrocarbon reformation is of current interest because carbon dioxide is known to be a cost effective, recyclable and a toxic-free carbon source. In addition, the concerns around the increasing levels of carbon dioxide in the atmosphere particularly arising from anthropogenic activities has resulted in research into carbon capture schemes which are likely to generate large quantities of carbon dioxide which has the potential for use, rather than sequestration [12].

Widespread studies have been made specifically on methane dry reforming with carbon dioxide to synthesis gas [13–16]. One of the reasons for such interest is because methane reforming with carbon dioxide produces synthesis gas with a ratio close to unity, i.e. $H_2/CO = 1$ which has been suggested to be beneficial for the production of Fischer–Tropsch liquid hydrocarbon and oxygenate [17–19]. Tsang et al. [16] reported that the dry reforming of methane is more endothermic than steam reforming because it is thermodynamically favoured above 913 K. Bulushev [20] also suggested that the dry reforming process has to be performed at high temperature and low pressure to achieve maximum conversion because of the highly endothermic nature of the reaction.

In this paper, the influence of process parameters on the yield of syngas, i.e. hydrogen and carbon monoxide from waste high density polyethylene has been investigated. The yield of syngas from pyrolysis in nitrogen and carbon dioxide are compared, followed by comparison with two-stage pyrolysis–gasification/reforming. Further investigations on syngas production from carbon dioxide reforming of high-density polyethylene using the two-stage reactor with the addition of steam and Ni–Mg–Al catalysts were also carried out. A Ni–Mg–Al catalyst was used in this research since this

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catalyst has been shown to be effective, with good catalytic and stability results during our previous work on the steam reforming of waste plastics to produce a hydrogen-rich syngas [8,21,22].

2. Materials and methods

2.1. Materials

High-density polyethylene (HDPE) was obtained as 2 mm waste polymer pellets provided by Regain Polymers Limited, UK.

The Ni–Mg–Al catalyst with molar ratio of 1:1:1 was prepared by the rising-pH technique according to the method reported by Garcia et al. [1]. $Ni(NO_3)_2 6H_2O$, $Mg(NO_3)_2 H_2O$ and $Al(NO_3)_3 9H_2O$ were dissolved in 200 ml deionised water with moderate stirring at 40 °C. Ammonium solution was then added to the aqueous solution until the pH value of 8.3 was reached. The solution was filtered, dried overnight at 105 °C and calcined at 750 °C with a heating rate of 10 °C min^{-1} for 3 h. The catalyst was ground using a mortar and pestle and finally sieved to produce a particle size of 50–200 μm.

2.2. Experimental reactors

Two types of reactor were used as shown in Figs. 1 and 2. Fig. 1 shows a one-stage fixed bed reactor used for the pyrolysis of the waste HDPE under two different types of reaction atmosphere, nitrogen (N_2) or carbon dioxide (CO_2). The reactor was 250 mm in length by 30 mm internal diameter and was externally heated by an electrical tube furnace (1.2 kW). 2 g of waste HDPE was placed in the sample crucible boat. The pyrolysis temperature was increased from ambient to 500 °C at a heating rate of 10 °C min^{-1} and maintained at 500 °C for 30 min. Nitrogen or carbon dioxide was used as the carrier gas with a flow rate of 200 ml min^{-1}. The oils were condensed in a three stage dry ice condenser system and the gases were collected in a Tedlar^{TM} gas sample bag.

For two-stage pyrolysis–gasification/reforming experiments a two-stage fixed bed reactor was used as shown in Fig. 2. The reactor was constructed of stainless steel and electrically heated by two separate furnaces. The experimental procedure involved heating the second stage gasification/reforming reactor which contained 1 g of the Ni–Mg–Al catalyst to the desired temperature of 800 °C. 2 g of waste HDPE was placed in the 1st stage reactor and heated from ambient temperature to 500 °C at a heat-
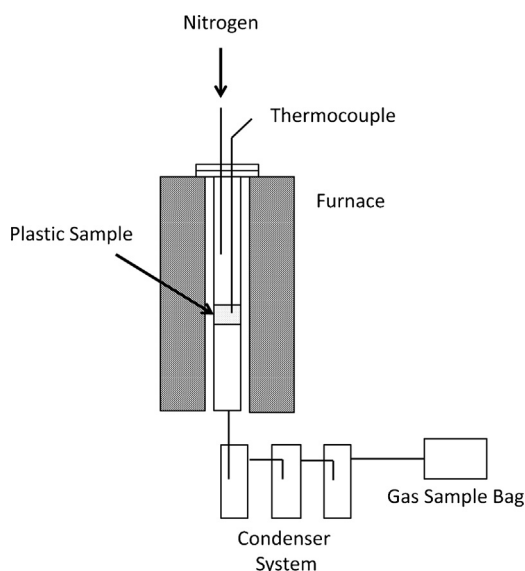

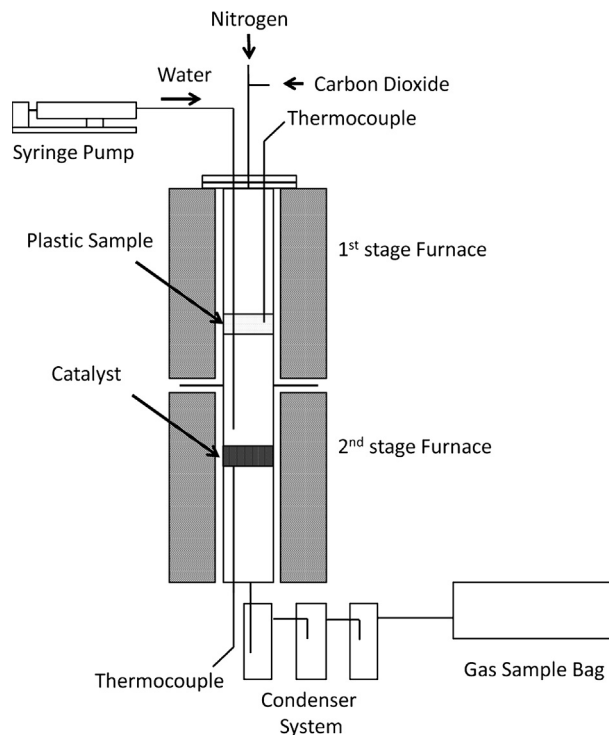Fig. 2. Schematic diagram of two-stage fixed bed reactor.

ing rate of 10 °C min^{-1}. The volatile pyrolysis products passed directly to the 2nd stage reactor maintained at 800 °C, where further gasification/reforming reactions took place. Sand was used as the substitute when the experiment was carried out without the Ni–Mg–Al catalyst. N_2 or a mixture of N_2 and CO_2 were injected as the feed gases into the top of the 1st stage reactor. The flow rate of the nitrogen was fixed to 200 ml min^{-1}. Where steam was used, this was added to the second stage and used a syringe pump to deliver the water.

2.3. Gas analysis

The gases collected in the sample bag were analysed by gas chromatography (GC). Hydrocarbons (C_1–C_4) were analysed using a Varian 3380 GC with a flame ionisation detector, with a 80–100 mesh Hysep column in a nitrogen carrier gas flow. Hydrogen, oxygen, carbon monoxide and nitrogen (H_2, O_2, CO and N_2) were analysed using a different Varian 3380 GC with a 60–80 mesh molecular sieve column while carbon dioxide (CO_2) was analysed with a 80–100 mesh Hysep column, both in argon carrier gas.

In this work, the carbon dioxide conversion was calculated according to the formula reported by several researchers; Albarazi et al., Asencios et al. and Oyama et al. [23–25].

CO_2 conversion

$$= (mols CO_2 input - mols CO_2 output)/mols CO_2 input$$

2.4. Characterisation of reacted catalyst

The properties of the carbonaceous coke deposited on the reacted catalysts were determined by temperature-programmed oxidation (TPO) experiments. TPO experiments were carried out using a thermogravimetric analyser (TGA-50 Shimadzu). About 8 mg of reacted catalyst was heated in an atmosphere of air with

Fig. 1. Schematic diagram of one-stage fixed bed reactor.