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Syngas from steam gasification of polyethylene in a conical spouted bed reactor

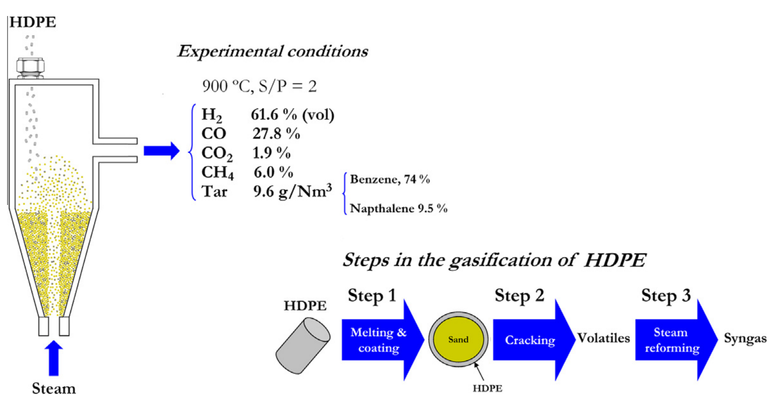
Aitziber Erkiaga, Gartzen Lopez, Maider Amutio, Javier Bilbao, Martin Olazar *

Department of Chemical Engineering, University of the Basque Country UPV/EHU, P.O. Box 644, E48080 Bilbao, Spain

HIGHLIGHTS

- The spouted bed reactor performs well with carbon efficiency being above 90%.
- The 850–900 °C range is suitable for a high yield of H_2 and a low yield of tar.
- Steam/plastic ratio increases process efficiency, H_2 yield and favours tar cracking.
- Tar yield is low (6%) and made up of monoaromatic hydrocarbons.
- The syngas ratio ($H_2/CO = 2.2$) is suitable for hydrocarbon or DME synthesis.

GRAPHICAL ABSTRACT



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ABSTRACT

The steam gasification of high density polyethylene in continuous mode has been carried out in a conical spouted bed reactor. The effect of temperature (in the 800–900 °C range) and steam/plastic mass ratio (between 0 and 2) on the distribution of products (gas and tar) and their composition has been studied. In order to reduce tar formation, two catalysts have been used in situ, namely, olivine and γ-Al_2O_3. The spouted bed reactor has an excellent performance between 850 and 900 °C, and an increase in the steam/plastic ratio from 1 to 2 only improves slightly both carbon conversion efficiency (to 93.6% with steam/plastic ratio = 2) and hydrogen concentration (61.6%). The use of olivine and γ-Al_2O_3 instead of sand gives way to a moderate reduction in the tar formation, whose yield is 4.8% with olivine. The syngas obtained has a H_2/CO ratio of 2.2, with a low tar content whose composition (monoaromatics, mainly benzene) augurs well for the use of the syngas in DME synthesis.

1. Introduction

The world's overall consumption of plastics in 2010 was 230 million tones and the predictions are for an upward trend of 3% annual in developed countries and 10% in developing countries. Consequently, the development of recycling processes at industrial scale is urgent to avoid the environmental problems related to waste plastic landfill and contribute to intensifying the upgrading of oil, of which 8% is used in the production of plastics [1]. Amongst waste plastic valorisation routes, thermochemical processes have best perspectives and they have been developed to pilot and demonstration scale [2]. Pyrolysis is an interesting option for the treatment of polyolefins to obtain fuels and monomers [3,4]. Gasification is another alternative, given that it is a flexible process that allows operating with a wide range of plastics, mixed plastics and even combining different wastes, such as biomass [5,6] and coal [7,8]. Furthermore, depending on the gasification agent used, it is possible to direct the process towards the production of a gas fuel with low (using air) or high (using pure oxygen) heating

* Corresponding author. Tel.: +34 946 012 527; fax: +34 946 013 500.
E-mail address: martin.olazar@ehu.es (M. Olazar).

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value or a hydrogen rich syngas (using steam). The syngas produced is suitable for energy conversion systems such as combined cycle turbines and engines, thus improving electricity generation efficiency [9] and avoiding the emission of harmful and toxic gases formed in the combustion of waste plastics [8]. Furthermore, the syngas obtained from residues (plastics, tyres, lignocellulosic biomass) is an alternative raw material for the production of fuels (hydrocarbons and oxygenates). Currently, single-step dimethyl ether synthesis is gaining attention due to its thermodynamic advantages compared to methanol synthesis, which favours CO_2 cofeeding together with the syngas [10–12].

Arena has recently carried out an in-depth review of the technologies and solutions applied to the gasification of municipal solid wastes [13]. Moreover, Consonni and Vigani have studied the present scenario by comparing the alternative options of gasification and combustion for the treatment of solid wastes [14]. Different technologies have been reported in the literature for waste plastic gasification, with the gasifying agent being air or steam [5,7,9,15–19] and reforming catalysts been used to increase H_2 yield [20–24]. Wu and Williams have proposed a two-step pyrolysis and gasification reactor, with and without catalyst, in order to intensify H_2 production by means of steam reforming [25–27]. Similarly, Kriz and Bicakova studied a two-step process with coal and waste plastic mixtures in the feed [8]. Fluidized bed reactors are suitable for the gasification of waste plastics, given that they are isothermal, versatile concerning operating parameters and can operate with continuous feed [5,7,9,15–19].

This paper addresses the steam gasification of HDPE in a continuous bench-scale plant provided with a conical spouted bed reactor. Studies have been carried out both on the effect of temperature and the steam/plastic ratio and on the performance of in situ catalysts (olivine and γ-Al_2O_3) for minimising tar formation.

The interest of the spouted bed reactor for the gasification process lies in its features related to the solid circulation pattern for gas–solid contact, which make it especially suitable for the gasification of low-rank coals, as reported by Mendes et al. [28] and Bernocco et al. [29]. Therefore, spouted beds are suitable for mitigating defluidization problems [30], which are a serious limitation for fluidized beds in the pyrolysis, combustion and gasification of wastes [31–34].

The conical spouted bed reactor has been successfully applied to the pyrolysis of different waste plastics and other residues whose treatment involves difficulties in fluidized bed reactors due to agglomeration and defluidization problems [35–38]. The high heat transfer rates [39] together with the vigorous solid flow pattern characteristic of spouted beds [40] ensure almost immediate melting, sand particle coating with fused plastic, pyrolysis and subsequent gasification of the plastic, thus minimising the formation of undesired tar and solid residue. Furthermore, the conical spouted bed is of easy design [41], given that it does not require distributor plate, has low pressure drop [42] and its throughput by reactor volume unit is much higher than that of fluidized beds due to the lower amount of sand required for fluidization. The low segregation is another interesting feature of conical spouted beds [43] for the operation with catalysts in situ for tar cracking or reforming.

Moreover, the conical spouted bed reactor is suitable for continuous operation, which is especially interesting for the implementation of the large-scale process. Accordingly, improvements have been carried, such as the use of internal devices, to increase bed stability (controlled spout geometry and fountain height) and reduce gas flow rate requirements [44,45]. In fact, this technology has been scaled up, and a biomass pyrolysis pilot plant (25 kg/h) is currently operative [39,44]. The main challenge for the industrial development of a waste plastic gasification process is energy integration in a highly endothermic process. In order to overcome this problem of heat supply to the reactor, two solutions are considered: (i) operating with a dual spouted bed reactor (gasifier and combustor), which is a similar concept to that applied in the steam gasification of biomass [46–48]; (ii) co-feeding a mixture of steam and oxygen to balance the energy required in the process, although this reduces hydrogen content in the syngas produced [49].

2. Experimental section

2.1. HDPE properties

The high density polyethylene (HDPE) was provided by Dow Chemical (Tarragona, Spain) in the form of chippings (4 mm), with the following properties: average molecular weight, 46.2 kg mol^{-1}; polydispersity, 2.89; and density, 940 kg m^{-3}. The higher heating value, 43 MJ kg^{-1}, has been determined by differential scanning calorimetry (Setaram TG-DSC-111) and isoperibolic bomb calorimetry (Parr 1356).

2.2. Catalytic materials

The γ-Al_2O_3 has been provided by Alfa Aesar, Karlsruhe (Germany) and the olivine by Minelco, Lulea (Sweden). Both materials have been ground and sieved to the desired particle diameter, 0.4–0.8 mm in the case of γ-Al_2O_3 and 0.35–0.4 mm in that of olivine. Olivine has been calcined at 900 °C for 10 h prior to use in the gasification reaction to enhance its reactivity in the tar cracking reaction. The surface properties (BET surface area) have been measured by N_2 adsorption–desorption (Micromeritics ASAP 2010). Calcined olivine has a limited porosity, with a surface are of only 0.18 m^2 g^{-1}. However, γ-Al_2O_3 has a much higher porous development, reaching a surface area of 159 m^2 g^{-1}.

2.3. Equipment

Steam gasification runs have been carried out in a bench scale plant whose scheme is shown in Fig. 1. The main element of the plant is the conical spouted bed reactor whose design is based on previous hydrodynamic studies [43] and on the application of this technology to the pyrolysis of different solid wastes, such as biomass [36,50], plastics [37,51] and waste tyres [35,52].

The reactor is located within an oven which is in turn placed in a forced convection oven maintained at 270 °C to avoid the condensation of steam and tars before the condensation system. This forced convention oven contains a high-efficiency cyclone and a sintered steel filter (5 μm) for retaining the fine sand particles entrained from the bed and the soot or char particles formed in the gasification process.

The plant is provided with a system for feeding plastic, which allows operating under continuous regime. The system for solid feeding consists of a vessel equipped with a vertical shaft connected to a piston placed below the material bed. The plastic is fed into the reactor by raising the piston at the same time as the whole system is vibrated by an electric engine. A very small nitrogen flow rate introduced into the vessel stops the volatile stream entering the feeding vessel. The plastic feed rate can be varied from 0.2 to 5 g min^{-1}. The pipe that connects the feeding system with the reactor is cooled with tap water to avoid the plastic melting and blocking the system.

Water has been fed by means of a Gibson 307 pump that allows a precise measuring of the flow rate. The water stream has been vaporized by means of an electric cartridge (not plotted in Fig. 1) placed inside the forced convection oven and prior to the entrance of the reactor. Moreover, N_2 is used as fluidizing agent during the heating process and its flow rate is controlled by a mass flow