Research article

Influence of the conditions for reforming HDPE pyrolysis volatiles on the catalyst deactivation by coke

Itsaso Barbarias, Maite Artetxe*, Gartzen Lopez, Aitor Arregi, Javier Bilbao, Martin Olazar

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

ABSTRACT

Pyrolysis of high density polyethylene (HDPE) has been carried out in a conical spouted bed reactor (500 °C) and the volatiles have been reformed in-line over a Ni commercial catalyst in a fluidized bed reactor. The evolution of reaction indices (conversion, H_2 yield and other gaseous product yields) with time on stream has been studied under the following operating conditions: temperature, 600–700 °C; space-time, 8.3–20.8 g_{cat} min g_{HDPE}^{-1}, and steam/plastic ratio, 3–5. High initial conversion (> 94.5%) and H_2 yields (> 76.7%) are attained under all the operating conditions studied, with HDPE conversion and H_2 yield increasing when the three variables are increased, which is explained by the enhancement of the reforming reaction. However, a significant effect of operating conditions on catalyst stability has been observed. Thus, an increase in temperature, space-time and steam/plastic ratio decreases catalyst deactivation as a consequence of a lower rate of coke deposition on the catalyst due to both a lower C_{5+} coke precursor amount in the reaction medium and a higher gasification rate of the coke deposited.

1. Introduction

World plastic production has increased gradually, reaching 322 million tonnes in 2015 [1]. As consequence, 25.8 million tonnes of plastic wastes have been recovered in Europe in 2014, of which 8 were land filled, 10.2 were used for energy recovery and 7.7 were recycled [1]. Bearing in mind recycling as a first option for sustainable development, mechanical recycling is nowadays the most implemented plastic recycling route. Besides, based on recent studies in which life cycle assessment methodology has been applied to assess the environmental impact of mechanical plastic recycling processes, it has good perspectives for a wider use and reducing the environmental impact caused by plastic wastes [2]. However, mechanical recycling has several drawbacks, such as recycled material poor quality or the need of sorting and cleaning plastic wastes [3]. In light of this, thermo-chemical plastic recycling routes have been considered promising alternatives for plastic waste valorisation at large scale, with the aim being the production of fuels, chemicals, monomers and H_2 [4–7].

Hydrogen is a clean fuel and a raw material for petrochemical industry with an increasing demand, which at present is mainly produced by naphtha or methane steam reforming [8–10]. Although steam gasification is a well-known and feasible technology for obtaining H_2 rich syngas from plastics [11–14] and other materials, such as biomass [15–19], it has the drawback involving the difficult and costly removing of the high tar content produced together with the syngas [20–23]. As an alternative to gasification, plastic pyrolysis-reforming strategy has been proposed for obtaining high quality syngas [24,25] or H_2 [8,26–28]. The interest of this process, made up of two steps in-line, lies in the following points: i) pyrolysis is carried out at a lower temperature than gasification, ii) temperature can be independently optimized in the pyrolysis and reforming steps [29], iii) the impurities of plastic wastes are retained in the pyrolysis reactor, which avoids their contact with the reforming catalyst and its subsequent poisoning [27], iv) highly active reforming catalysts allow for total elimination of tars from the gas product.

The pioneering technology proposed by Czernik and French [6] for this strategy is based on continuous operation by means of two in-line fluidized bed reactors. Barbarias et al. [26] have developed a system composed of a conical spouted bed reactor (CSBR) for the pyrolysis of HDPE and an in-line reforming of the volatiles in a fluidized bed reactor over Ni commercial catalyst. Use of a fluidized bed reactor instead of a fixed bed one in the reforming step, as in the study by Erkiaga et al. [30], allows attaining bed isothermicity and diminishing coke deposition (delaying its formation and enhancing its gasification), and therefore operating for longer reaction times without bed blockage by coke formation.

Furthermore, the CSBR has been used in the pyrolysis of different plastic materials (HDPE, PP, PET, PS and PMMA) [31–34] and has been

proven to perform well for avoiding defluidization problems caused by fused plastic aggregates in fluidized bed reactors. The vigorous cycling movement of the particles characteristic of this reactor leads to a uniform coating of sand by fused plastic, avoiding bed defluidization [35]. Besides, the high heat and mass transfer rates and the low residence times of the volatiles in the reactor, allow obtaining a volatile stream composed of long chain lineal hydrocarbons (suitable for reforming) at low pyrolysis temperatures [30].

The effect of operating conditions in the pyrolysis-reforming of HDPE has been studied in a previous work [26] using a Ni commercial catalyst, and the optimum reforming conditions have been established for a temperature of 700 °C, a space-time of 16.7 g_{cat} min g_{HDPE}^{-1} and steam/plastic ratio of 5. A H_2 yield of 92.5% of the maximum allowable by stoichiometry, which accounts for a H_2 production of 38.1 g per 100 g of HDPE in the feed, has been obtained under the conditions mentioned. The effect operating conditions (temperature, space-time and steam/plastic ratio) have on the catalyst stability and amount of coke deposited have been studied in this work with the aim of establishing the most suitable conditions for minimizing deactivation. Catalytic process viability is always conditioned by catalyst deactivation, and therefore the effect reforming operating conditions have on coke deposition and so on catalyst deactivation is crucial in order to minimize coke deposition.

Knowledge on Ni catalyst deactivation has been acquired in the reforming of hydrocarbons and oxygenates, in which Ni catalysts have been used due to their good activity-cost ratio [36–37]. The mechanism of catalyst deactivation by coke deposition is a complex issue due to the heterogeneous nature of the coke and the influence of coke morphology on catalyst deactivation [38–44]. Therefore, encapsulating coke (the main responsible for catalyst deactivation) stems mainly from the formation of aromatic compounds from the hydrocarbons in the reaction medium, whereas CO and CH_4 (reactants in Boudouard and decomposition reactions, respectively) are the main responsible for the structured coke formation (with progressive filament formation). Catalyst irreversible deactivation by Ni sintering has been widely studied in the literature due to its role as a factor conditioning catalyst reusability. Furthermore, it is known that Ni sintering also affects coke deposition, increasing the coke deposition rate as Ni aggregates are formed and Ni crystal size increases [45–47]. In this study, a Ni commercial catalyst designed for CH_4 steam reforming has been used for the reforming of the volatiles formed in HDPE pyrolysis. Taking into account that the operating conditions used in CH_4 steam reforming are more severe than those in this work, catalyst deactivation by Ni sintering has been considered insignificant compared to the deactivation caused by coke deposition.

2. Experimental section

2.1. Materials

The HDPE was supplied by the Dow Chemical Company (Tarragona, Spain) in the form of cylindrical pellets (4 mm). The plastic used is virgin HDPE and it does not content fillers or additives, with its ultimate analysis being 85.7 wt% of C and 14.3 wt% of H. The properties specified by the supplier are as follows: average molecular weight, 46.2 kg mol^{-1}; polydispersity, 2.89 and density, 940 kg m^{-3}. The higher heating value, 43 kJ kg^{-1}, has been measured by differential scanning calorimetry (Setaram TG-DSC 111) and isoperibolic bomb calorimetry (Parr 1356).

The catalyst has been supplied by Süd Chemie and is a commercial Ni catalyst (G90LDP) used for CH_4 reforming. The provider specified that it has a metallic phase of Ni, supported on Al_2O_3 and doped with Ca, with NiO content being 14 wt%. It has been supplied in the form of perforated rings (19 × 16 mm), and ground and sieved (0.4–0.8 mm) for use in the fluidized bed reactor. Ca is commonly added to the catalyst in order to promote CO_2 adsorption capacity [48,49] which enhances the

displacement of water gas shift reaction and so favours H_2 production [49]. However, Ca is used in this case as a promoter for reducing Al_2O_3 support acidity and attenuating catalyst deactivation [50].

The physical properties of the catalyst have been measured by N_2 adsorption-desorption in a Micromeritics ASAP 2010, and the temperature programmed reduction (TPR) has been carried out in an AutoChem II 2920 Micromeritics. The catalyst is a mesoporous material (average pore diameter of 122 Å) and the values of BET surface area and pore volume are rather low, 19 $m^2 g^{-1}$ and 0.04 $cm^3 g^{-1}$, respectively. The TPR curve shows two peaks, a prevailing one at 550 °C associated with NiO reduction and another one at 700 °C associated with $NiAl_2O_4$. A detailed characterization of the catalyst was reported in previous papers [30,51].

2.2. Experimental equipment and operating conditions

The bench scale plant used in this study has been reported elsewhere [26,52]. It is composed of two reactors in series, namely, a CSBR and a fluidized bed reactor, for pyrolysis and catalytic reforming steps, respectively. The solid feed system consists of a vessel equipped with a vertical shaft connected to a piston placed below the material bed. The plastic is fed into the CSBR by raising the piston while the whole system is vibrated by an electric motor. A very small N_2 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} (1, 0.75 and 0.6 g min^{-1} in this study). The pipe that connects the feeding system with the reactor is cooled with tap water to avoid the plastic melting and clogging the system.

Water is fed by means of a Gilson 307 pump and has been vaporized by an electric cartridge placed inside the convention oven. Water flow rate is 3 mL min^{-1} in all the conditions studied, which corresponds to a steam flow rate of 3.73 NL min^{-1}. Steam acts as fluidizing agent in both reactors (CSBR and fluidized bed reactor), and so its flow rate was kept constant in all runs in order to ensure the same hydrodynamic performance in the runs.

The dimensions of the CSBR used guarantee bed stability in a wide range of operating conditions and they have been chosen based on previous hydrodynamic studies and on the application of this technology in the pyrolysis of different solid wastes, such as biomass [53–55], plastics [31–33] or scrap tires [56]. The CSBR was located inside a radiant oven (1200 W), which allows operating up to 900 °C. The bed was made up of 50 g of silica sand (particle diameter 0.3–0.35 mm), and steam was used as fluidizing agent, whose inert nature at moderate pyrolysis temperatures (500 °C) was proven in a previous work [30]. The product stream obtained by HDPE pyrolysis in the CSBR at 500 °C is mainly composed of waxes and diesel fraction, with its overall yield being 92 wt% [26,30,31]. It is to note that continuous operation allows obtaining a pyrolysis volatile product stream with constant composition, which is essential in order to study properly the effect the second step operating conditions have on catalyst stability. Therefore, steam is an inert in the pyrolysis step and its use instead of N_2 greatly simplifies operation in the pyrolysis-reforming system. Furthermore, steam can be easily separated from the product stream and avoids dilution of reactants in the reforming step with N_2, and therefore decreasing the reforming reaction rate.

The pyrolysis volatiles formed have been fed in-line to the fluidized bed reactor where the reforming catalyst has been placed. The catalytic bed consist of 25 g (sand + catalyst), with the amounts of catalyst being 6.2, 9.4, 12.5 and 15.6 g, corresponding to the values of space-time of 8.3, 12.5, 16.7 and 20.8 g_{cat} min g_{HDPE}^{-1}. The effect of space-time has been studied at 700 °C with a steam/plastic (S/P) mass ratio of 4 (S/C molar ratio of 3.1). The effect catalytic bed temperature has on catalyst stability has been analyzed at 600, 650 and 700 °C, with a space-time of 16.7 g_{cat} min g_{HDPE}^{-1} and an S/P ratio of 4. Besides, S/P ratios of 3, 4 and 5 have been used, which have been attained by keeping the same steam flow rate and changing the plastic feed rate, in