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## Styrene recovery from polystyrene by flash pyrolysis in a conical spouted bed reactor

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### ABSTRACT

Continuous pyrolysis of polystyrene has been studied in a conical spouted bed reactor with the main aim of enhancing styrene monomer recovery. Thermal degradation in a thermogravimetric analyser was conducted as a preliminary study in order to apply this information in the pyrolysis in the conical spouted bed reactor. The effects of temperature and gas flow rate in the conical spouted bed reactor on product yield and composition have been determined in the 450–600 °C range by using a spouting velocity from 1.25 to 3.5 times the minimum one. Styrene yield is strongly influenced by both temperature and gas flow rate, with the maximum yield being 70.6 wt% at 500 °C and a gas velocity twice the minimum one.

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### 1. Introduction

Commodity plastics reached a global production of 288 million tons in 2012, from which 25.2 million tons of post-consumer plastic wastes have been recovered in the EU (Zhuo and Levendis, 2014). This means a serious environmental issue given that 38% of this stream is disposed in landfills and 35% is used for energy (Plastics, 2015). Feedstock or tertiary recycling by means of flash pyrolysis has been considered as the most attractive recycling method. In fact, waste plastics are a valuable source of liquid or gas fuels, chemicals, polymer monomers and char that may be upgraded to activated carbon (Al-Salem et al., 2009, 2010). Furthermore, flash pyrolysis can be performed at large scale using equipment that have reached an adequate technological development (Butler et al., 2011; Kumar et al., 2011; Chen et al., 2014).

Flash pyrolysis involves significant advantages compared to other valorisation routes for waste plastics: (i) plastics of different composition can be valorised jointly with other wastes (biomass, tires) contained in the municipal solid waste, which reduces separation costs; (ii) emissions are lower than in other alternatives, such as incineration, because temperatures are lower and no oxygen is required.

The high monomer (styrene) recovery rates that may be attained evidence that flash pyrolysis is especially interesting for

the valorisation of polystyrene (PS), whose consumption in the EU accounts for 6% of the total (Al-Salem et al., 2010). In fact, thermal pyrolysis of PS has been extensively studied, especially for monomer recovery (Aguado et al., 2003; Park et al., 2003; Kaminsky et al., 2004; Undri et al., 2014; Mo et al., 2014; Achilias et al., 2007). Thermal degradation of PS takes place by radical formation, in which three steps are distinguished (Marczewski et al., 2013): (i) initiation; (ii) depolymerising propagation; (iii) radical coupling, whose development in a DTG run evolves with temperature.

The effect of pyrolysis conditions on the styrene yield was studied by Mo et al. (2014). The variables studied are as follows: temperature, heating rate, reaction time and the interactions among these factors. These authors have determined that the optimum temperature is between 470 and 505 °C, the increase in heating rate enhances styrene yield and the gas yield must be in a given range in order to avoid secondary reactions.

The CSBR is of simple design (essential to reduce the investment costs related to industrial or recycling treatments) and especially suitable for the pyrolysis of waste plastics due to the absence of segregation problems (thanks to the cyclic movement of the solid, Fig. 1), and therefore less defluidisation problems than in fluidised beds (Aguado et al., 2005; Elordi et al., 2011). Moreover, the heat transfer rate is higher than in fluidised beds, with wall-to-bed and bed-to-particle heat transfer coefficients being 170 and 220 W m<sup>-2</sup> K<sup>-1</sup>, respectively (Makibar

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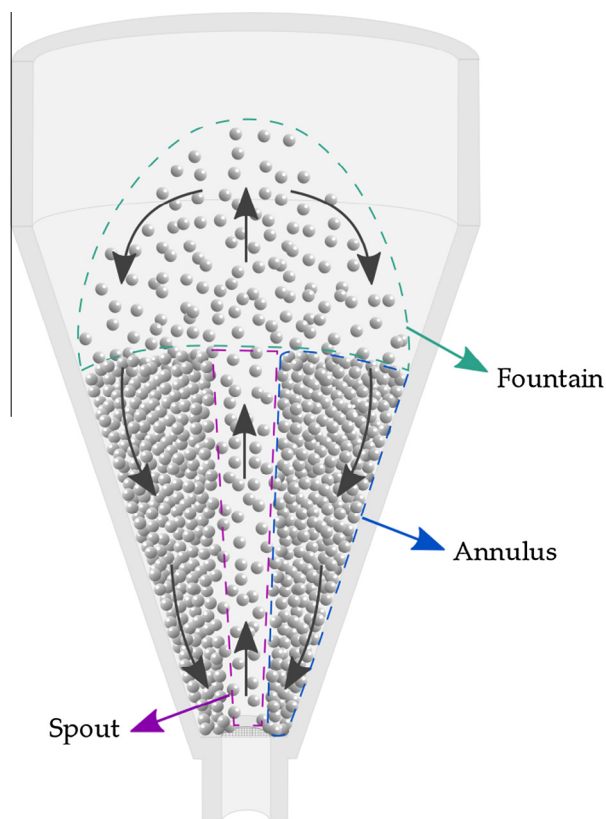


Fig. 1. Scheme of the solid cyclic movement in a conical spouted bed reactor (CSBR) for moderate gas flow rates.

et al., 2011), which allows for attaining heating rates in the order of  $10^4\text{ }^\circ\text{C s}^{-1}$ . These are crucial features bearing in mind process endothermicity and the poor thermal conductivity of PS and other plastics. In a previous study, the CSBR was proven to have an excellent performance for the flash pyrolysis of PS in batch regime, with styrene yield being 64.5 wt% in the 450–500 °C temperature range (Aguado et al., 2003).

The CSBR has been successfully used for the continuous pyrolysis of numerous plastics (Lopez et al., 2010a; Artetxe et al., 2010, 2012b; Elordi et al., 2011). Furthermore, this reactor has also successfully been scaled up to  $25\text{ kg h}^{-1}$  for biomass pyrolysis process (Fernandez-Akarregi et al., 2013), which reinforces the possibility to develop this process at full scale. In the spouted beds, the gas is introduced through a central nozzle located at the bottom of the reactor and forms a central jet causing the particles to circulate upwards in a uniform way along a spout zone (see Fig. 1), in which the gas and solid velocities are high and the residence time of the volatiles is very short (<100 ms), although it may be varied in a wide range. However, the gas and descending particles are in counter-current flow in the annulus, with the residence time in this region being an order of magnitude higher. The objective of this study is to enhance styrene yield in the flash pyrolysis of PS carried out in a conical spouted bed reactor (CSBR) with continuous PS feed. The aims pursued in this study are: (i) to confirm the good performance of this technology operating by continuously feeding PS (which is highly interesting for the applicability of the results at large scale); (ii) to determine suitable pyrolysis conditions (temperature and gas flow rate) in order to guarantee the depolymerisation selectivity, with the aim being the improvement of styrene recovery; (iii) to quantify by-product yields under different conditions, bearing in mind their potential interest as fuel or raw material.

## 2. Experimental

### 2.1. The polymer

The PS has been supplied by Dow Chemical Company (Tarragona, Spain) in the form of cylindrical pellets (3.5 mm length  $\times$  2 mm diameter). Its most significant features are as follows: molecular weight,  $311.6\text{ g mol}^{-1}$ ; polydispersity, 2.39; density,  $1030\text{ kg m}^{-3}$  and higher heating value,  $40\text{ MJ kg}^{-1}$ . The higher heating value has been measured by differential scanning calorimetry (Setaram TG-DSC 111) and isoperibolic bomb calorimetry (Parr 1356) and the remaining properties have been provided by the supplier.

### 2.2. Pyrolysis kinetic study

A preliminary kinetic study has been carried out based on thermogravimetry in a TGA Q5000 thermobalance. The experimental method consists in degrading the PS sample (approximately 6 mg) from room temperature to 800 °C under inert atmosphere using different heating rates (from 2.5 to  $20\text{ }^\circ\text{C min}^{-1}$ ). The gas flow rate was  $100\text{ ml min}^{-1}$  in all the experiments. In order to avoid the entrance of oxygen traces that may disturb the results, a slight overpressure was generated inside the reaction chamber by means of a valve located at the thermogravimetric analyzer gas outlet.

### 2.3. Equipment and facilities

Fig. 2 shows the bench-scale plant used in this study. The design of the experimental unit is based on the knowledge acquired in the continuous pyrolysis and gasification of different types of plastics (Erkiaga et al., 2013; Artetxe et al., 2012a), biomass (Alvarez et al., 2014; Erkiaga et al., 2014) and waste tyres (Lopez et al., 2009, 2010b). The solid feeding 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 reactor by raising the piston while the whole system is vibrated by an electric motor. The pipe that connects the plastic feeding system with the reactor is cooled by tap water in order to avoid plastic melting and system blockage.

The dimensions of the CSBR have been established based on previous hydrodynamic studies (Olazar et al., 1993, 1992) and they are as follows: total height of the reactor, 34 cm; conical section height, 20.5 cm; angle,  $28^\circ$ ; diameter of the cylindrical section, 12.3 cm; bottom diameter, 2 cm, and gas inlet diameter, 1 cm.  $\text{N}_2$  is used as fluidising agent and heated to the reaction temperature by means of a preheater.

The volatiles formed in the reactor circulate through a gas cleaning system, which consists of a high efficiency cyclone and a  $25\text{ }\mu\text{m}$  sintered steel filter in order to retain the particles contained in the gas stream. Both are placed inside a forced convection oven maintained at 280 °C in order to avoid the condensation of heavy compounds prior to the chromatographic analysis. The condensation system consists of a double-shell tube condenser cooled with tap water and coalescence filters, which ensure that permanent gases are cleaned before their analysis by chromatographic techniques.

The product stream leaving the gas cleaning system has been analysed by an on-line Agilent 7890 chromatograph. The sample is driven to this equipment through a line thermostated at 280 °C to avoid the condensation of any heavy product. Cyclohexane (not formed in the process) has been used as an internal standard to validate the mass balance closure. This compound has been fed into the product stream at the outlet of the sintered steel filter.

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