VALORIZATION OF WASTE TIRES BY PYROLYSIS IN A CONICAL SPOUTED BED REACTOR

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Abstract

The pyrolysis of waste tires in continuous mode has been studied in a bench scale plant provided with a conical spouted bed reactor, in the 425-600 ºC range. The properties of the pyrolysis products have been characterized using different techniques for both the volatile and solid fraction. Continuous operation in the 425–600 ºC range gives way to a yield of 1.8–6.8 wt % of gases, 44.5–55.0 wt % of liquid fraction (C_5–C_{10} range hydrocarbons, with a maximum yield of limonene of 19.3 wt % at 425 ºC), 9.2–11.5 wt % of tar and 33.9–35.8 wt % of char. The high yield of limonene, the flexibility in the operating conditions and the capacity for a continuous removal of the residual carbon black from the reactor are the advantages of conical spouted bed technology.

Keywords: *waste tire, pyrolysis, spouted bed, waste management, tire valorization*

1. Introduction

The world generation of used tires in 2005 was over 2.5 million tones in North America, 2.5 million tones in Europe and 0.5–1.0 million tones in Japan, which means 6 kg (the approximate weight of a tire) per inhabitant and year [1]. Given that they are considered a hazardous waste and there are regulations that forbid their landfill, considerable attention has been paid to waste tire management.

Pyrolysis (heating to moderate temperatures in an oxygen free atmosphere) has good perspectives for upgrading waste tires. Different technologies have been applied to the tire pyrolysis process (apart from thermogravimetric analysers and fast heating microreactors used for kinetic studies), such as fixed bed reactors [2], rotatory kilns, circulating fluid beds, bubbling fluid beds [3], and vacuum moving beds. A conical spouted bed reactor (CSBR) has been used in this study for tire pyrolysis. This reactor is an alternative technology to classical fluid beds for handling sticky and irregular materials. Certain features of the CSBR that make it suitable for scrap tire pyrolysis are: cyclic particle movement characteristic to spouted beds, bed isothermicity, with a high heat transfer between phases, which is essential for the treatment of a low conductivity material such as rubber and finally short residence time of volatiles, which minimizes secondary reactions and allows high yields of sensitive products, such as limonene.

2. Materials and Methods

The tire material used in this work is a rubber free of steel and other tire carcass elements and has been provided by Jenecan S.L. Its main components are: natural rubber (SMR 5CV), 29.59 wt %; styrene-butadiene rubber (SBR 1507), 29.59 wt %; carbon black (ISAF N220), 29.59 wt %. The materials have been ground to a particle size below 1mmafter been frozen in liquid nitrogen. The low heating value is 38.8 MJ kg^{-1}.

A bench scale plant provided with a conical spouted bed reactor has been used to study the pyrolysis of waste tires in the 425 to 600 ºC temperature range. For operating under continuous conditions, the plant has a system for feeding scrap tires, which is pneumatically actuated and is able to feed up to 300 g h^{-1} of tire. Prior to entering the reactor, it is heated to the reaction temperature by means of a preheater. The reactor is the unit's main component, being a spouted bed of conical geometry with a cylindrical upper section. The volatile products leave the reactor together with the inert gas and the finest carbon black particles. These particles are retained in a high efficiency cyclone followed by a sintered steel filter. The gases leaving this filter circulate through a volatile condensation system consisting of a condenser and a coalescence filter.

In order to quantify volatile stream components, samples have been taken at the reactor outlet and analyzed online by means of a GC Agilent 6890 (HP-Pona column). Furthermore, identification and quantification of noncondensable components has been carried out by taking samples at the outlet of the condensation system and sending them to a micro GC connected to a mass spectrometer (Agilent 5975B). In order to identify the components of the condensable fraction, the liquid obtained by product stream condensation has been analyzed by GC/MS (Shimadzu UP-2010S provided with a HP-Pona column).

3. Results and Discussion

In order make easier the interpretation of the results, the pyrolysis products have been grouped into five fractions: Gas (C_1–C_4 hydrocarbons), non-aromatic liquid fraction (non-aromatic C_5–C_{10} hydrocarbons), aromatic liquid fraction (single-ring C_{10}- aromatic hydrocarbons), tar (which includes C_{11}+ hydrocarbons, independently of their aromatic or non-aromatic nature) and char or residual carbon black. Figure 1 shows the evolution of the yields of the different fractions with temperature in the range studied. As observed, there are some clear trends, such as the increase in C_1–C_4 gas fraction with temperature as a result of more severe thermal cracking at high temperatures. The yields of gases obtained in a spouted bed reactor are similar to those obtained by other authors in fluid bed reactors [3]. The gases comprise mainly methane and C_2–C_4 olefins.

A significant increase in C_{10}- aromatic compounds with temperature has been obtained, from 13.1 wt % at 425 ºC to 22.9 wt % at 600 ºC. This behaviour of C_{10}- aromatic fraction is due to Diels–Alder reactions that promote the formation of aromatic compounds from olefins. The gaseous and C_{10}- aromatic fractions increase with temperature and the yield of non-aromatic C_5–C_{10} fraction decreases, which is due to thermal cracking and secondary reactions at high temperatures.

The heavy fraction, or tar, made up of C_{11}+ components, has no clear trend in the temperature range studied. The amount of liquid fraction is almost constant up to a temperature of 500 ºC and then decreases at 600 ºC.

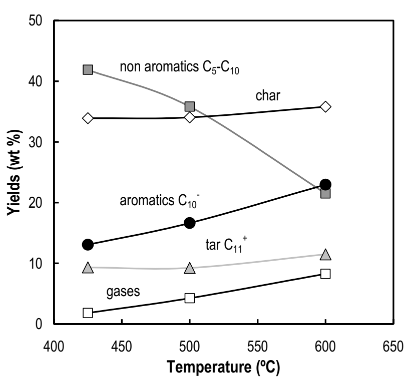

Fig. 1. Effect of temperature on the yield of the different lumps in the 425-600 ºC range.

The CSBR is a suitable technology for obtaining high yields of liquid due its excellent performance. Thus, one of the features of this reactor is the high heat transfer between phases that allows for a high heating rate of the tire particle. Moreover, the residence time of the volatile products in the reactor is very short (of the order or milliseconds). Consequently, the cracking reactions in gas phase are largely avoided resulting in a low yield of gaseous products compared to other technologies. Another difference involves the properties of the liquid fraction. Thus, the liquid obtained using this technology is lighter than other ones due to the reduction in repolymerization reactions as a consequence of the short residence time of the pyrolysis primary products in the reactor.

It is noteworthy the high limonene yields obtained in this process, the maximum yields have been obtained operating at 425 ºC, reaching a yield of 20.4 wt %. Limonene is an interesting chemical with numerous industrial applications, such as the production of industrial solvents, resins and adhesives, as well as in cosmetics.

The residual carbon black is made up mainly of carbon, hydrogen, and sulfur, with the sulfur content being around 3 wt %. This content corresponds to half of the sulfur contained in the tire. This sulfur content may limit the applications of residual carbon blacks. The surface area of the residual carbon black shows a clear trend to increase with temperature, which gives way to a carbon black with 116.3 $m^2 g^{-1}$ at 600ºC.

4. Conclusions

The CSBR is suitable for obtaining high yields of liquid at moderate temperatures. Temperature has an important effect on product distribution by increasing the aromatization of the volatile fraction and the gas yield. Moreover, the quality of the solid fraction (adulterated carbon black) is improved by operating at high temperatures. The liquid fraction is of suitable quality for its use as fuel or it can be an interesting feedstock for a refinery, especially for the hydrocracking process. Pyrolysis oil contains interesting products in high concentrations depending on the operating conditions, such as limonene.

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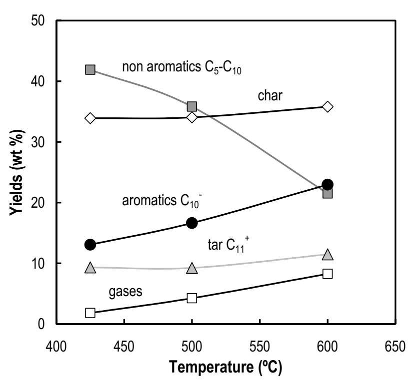

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plastic materials are chemically resistant against acids, basics and alcohols. Mixtures, Table 2, have been obtained mixing polyethylene pellets and wastes of the same material with 25, 50 and 75 wt%. The stagnant bed heights studied are in the range 0.05 - 0.35 m.

Table 1. Properties of the materials.

Material	ρ_s (kg/m^3)	size range (mm)	$\overline{d}_S$ (mm)	ϕ	ε_0
LDPE pellets	923	2.7-5	3.5	0.95	0.34
HDPE pellets	940	2.7-5	3.5	0.92	0.36
LDPE wastes (4 LDPE)	923	10x12x0.5-14x18x0.5	5.3	0.24	0.35
LDPE wastes (2 HDPE)	940	10x12x0.5-14x18x0.5	5.3	0.24	0.35

Table 2. Properties of the mixtures.

Material	ρ_s (kg/m^3)	weight percent (wt%)	$\overline{d}_{S\ mixture}$ (mm)
LDPE mixtures	923	25, 50, 75	3.8 4.2 4.7
HDPE mixtures	940	25, 50, 75	3.8 4.2 4.7

3. Results and Discussion

The stable operating conditions of beds of polyethylene wastes in spouted beds have been delimited in diagrams of stagnant bed height, H_o, against gas velocity, u.

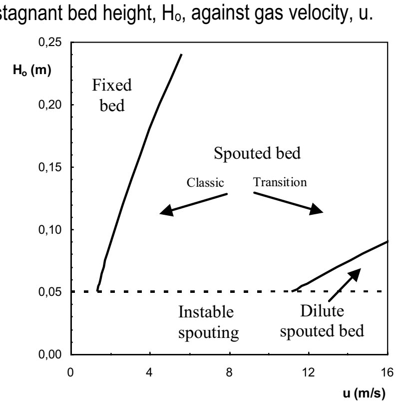

Fig. 2. Operating regimes in conical contactors. Experimental conditions: γ = 36°; D_o = 0.04 m and HDPE of $\overline{d}_S$ = 5.3 mm.

In Figure 2, the results plotted as an example correspond to a spouted bed contactor geometry (γ= 36º; D_o= 0.04 m) and for a bed consisting of HDPE of 3.5 mm of particle diameter and for different values of the stagnant bed height. The borders between the regimes, drawn with solid lines, have been obtained experimentally for each stagnant bed height. As it is observed, as gas velocity is increased bed passes from fixed bed to spouted bed regime. It is noteworthy that the HDPE has an instability region for low stagnant bed heights.

The experimental value of minimum spouting velocity is determined from the values of pressure drop by decreasing slowly gas flow as the point when the pressure drop levels off and it increases as stagnant bed height is increased and.

4. Conclusions

Gas inlet diameter and height of conical spouted bed reactor have been obtained for thermal treatment of polyethylene pellets, wastes and their mixtures, in a wide range of gas flow rate. Furthermore, it is determined that mixtures improve bed performance in the transition regime between conventional spouted bed and dilute spouted bed regimes.

These results predict good perspectives for polyethylene wastes recycling by this technology.

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