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VALORISATION OF WASTE TIRES

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A CONICAL SPOUTED BED REACTOR FOR THE VALORISATION OF WASTE TIRES

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ABSTRACT

A pilot plant provided with a conical spouted bed reactor has been used for the valorisation of waste tires by thermal pyrolysis in continuous mode. The effect of pyrolysis temperature on product distribution and properties has been studied in the temperature range from 425 to 600 °C. This variable has proven to have an important effect on product distribution. Thus, pyrolysis oil yield was reduced from 64.3 wt% at 425 °C to 55.9 wt% at 600 °C. However, the quality of carbon black was improved operating at high temperatures (increasing BET surface area values). High yields of certain interesting chemicals have been obtained in the liquid fraction, such as limonene (19.3 wt%), isoprene (5.7 wt%) and styrene (6.1 wt%).

INTRODUCTION

Waste tires are a serious environmental problem due to the potential risk involved in their stockpiling. Furthermore, stockpiling is not a suitable solution due mainly to the volume of waste, which according to estimations will continue increasing at an even higher rate over the coming decades. The world generation of used tires in 2005 was over 2.5 million tonnes in North America, 2.5 million tonnes in Europe and 0.5-1.0 million tonnes in Japan, which means 6 kg (the approximate weight of a tire) per inhabitant and year (1). According to these estimations, this figure will increase to above 17 million tonnes per year (approximately 1.4 billion tires) by 2012, given that the national gross product in developing countries encourages car demand and tire substitution as a measure for safe driving. These trends are not offset by the measures adopted for prolonging tire life (2,3).

Different technologies are reported in the literature for tire pyrolysis. Fixed bed reactors have commonly been used (4-8) but the problem related to this technology is the poor heat transfer and efficiency. Another technology applied to tire pyrolysis process is that based on a rotary kiln (9,10). Fluid bed reactors have been extensively used for the pyrolysis of polymeric material since the 70s due to their high heat transfer and bed isothermicity. Several studies in the literature approach tire pyrolysis on fluidised bed reactors (11-14). The main problem of fluid beds for that process is the need for grinding the tire material to a small particle diameter. This process requires high amounts of energy, especially if cryogenic methods are used for grinding.

The conical spouted bed reactor (CSBR) has been successfully used for the pyrolysis of other solid residues, such as biomass (15) and plastics (16). The conical spouted bed reactor has interesting features for waste tire pyrolysis, such as small pressure drop, simple design or the capacity for handling coarse particles. The latter is especially interesting because it allows using this technology with tire particles

whose size is of the order of centimetres, which avoids fine grinding of the tire rubber. In addition, the conical spouted bed reactor is highly versatile for operating with high gas velocities and, consequently, a vigorous gas solid contact is generated, which enhances heat and mass transfer between phases, increases the heating rate of the solid and avoids bed defluidization by agglomeration of particles, even under severe conditions involving very sticky particles (17). Moreover, operation can be carried out with short gas residence times (as low as milliseconds) in the dilute spouted bed (18). Consequently, the secondary reactions of the volatiles formed in the reactor are reduced.

EXPERIMENTAL EQUIPMENT

A continuous pyrolysis unit for tire processing has been set up and fine-tuned based on hydrodynamics studies conducted in a cold unit (19) and under reaction conditions (20), and finally on the experience acquired in the pyrolysis of other types of wastes (15,16,21-23). The elements of the bench scale pyrolysis plant are shown in Figure 1. The main element of the plant is the reactor, which is a spouted bed of conical geometry with a cylindrical upper section. A scheme of the reactor is shown in Figure 2. The total height of the reactor is 34 cm, the height of the conical section is 20.5 cm, and the angle of the conical section is 28°. The diameter of the cylindrical section is 12.3 cm, the bottom diameter is 2 cm and the gas inlet diameter is 1 cm. These dimensions guarantee the bed stability in a wide range of operating conditions, given that it may operate from the regime of spouted bed to a vigorous regime of dilute spouted bed.

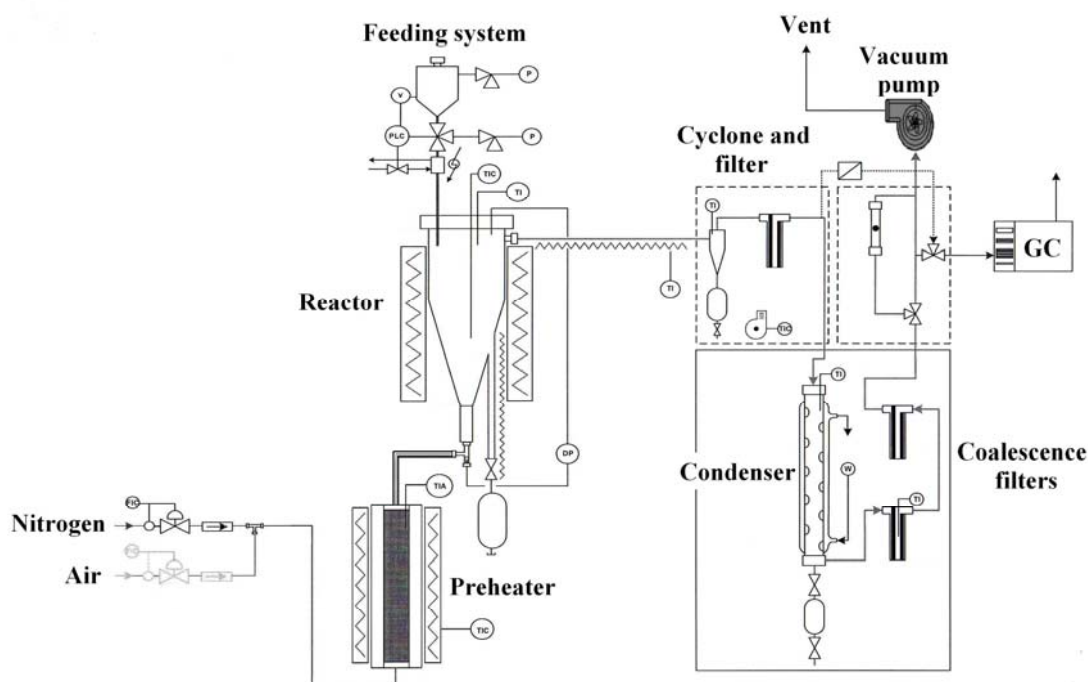


Figure 1. Scheme of the pyrolysis pilot plant unit provided with a conical spouted bed reactor

The feeding system is pneumatically actuated and consists of a ball valve and a hopper. The feed rate can be controlled by varying the number of load-unload cycles

in the valve, which allows for feeding up to 5 g min^{-1} of tire. The nitrogen flowrate is controlled by a mass flow controller that allows feeding up to 30 L min^{-1} . Prior to entering the reactor, it is heated to the reaction temperature by means of a preheater. 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 $25 \mu\text{m}$ sintered steel filter. Both elements are placed at the outlet of the reactor and inside a forced convection oven maintained at $280 \text{ }^\circ\text{C}$ to avoid the condensation of heavy hydrocarbons. The gases leaving this filter circulate through a volatile condensation system consisting of a condenser and a coalescence filter. The coalescence filter ensures total condensation of volatile hydrocarbons. The condenser is a double shell tube cooled by tap water.

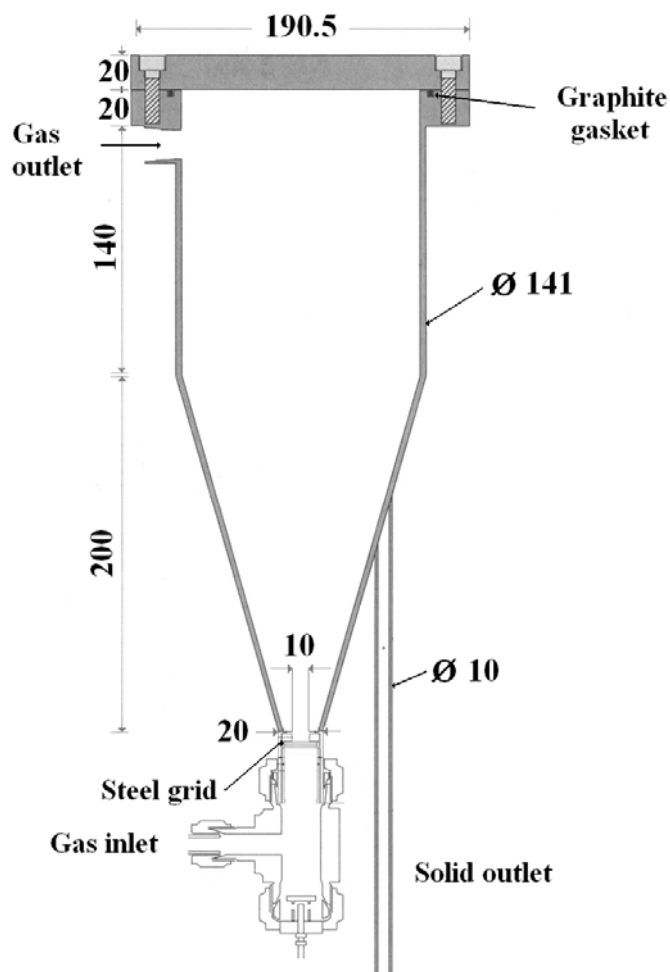


Figure 2. Scheme of the reactor and its main dimensions.

The tire material used 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% and other less important additives.

A bed of 35 g of sand (particle diameter range 0.63-1 mm) has been used to guarantee a good heat transfer and isothermicity during the continuous pyrolysis

operation. In order to ensure stable spouting, the nitrogen flowrate has been set at 1.2 times minimum spouting velocity. The nitrogen flowrate was 9.5 NI min^{-1} at $500 \text{ }^\circ\text{C}$ and this value varies slightly with temperature, increasing at $425 \text{ }^\circ\text{C}$ and decreasing at $600 \text{ }^\circ\text{C}$. Continuous operation has been carried out by feeding 3 g min^{-1} of scrap tire and each run lasts for around 30 min. The CSBR allows for continuous operation by selectively removing the carbon black from the bed, which avoids its accumulation throughout the pyrolysis process. The fountain region of the CSBR is characterized by the segregation of different density materials. In this region, the solids of lower density (carbon black particles) describe higher trajectories, whereas the heavier particles (sand and unreacted tire) record lower heights. Based on this segregation, the removal of carbon black from the reactor is carried out through a lateral pipe placed higher than the bed surface (Figure 2). The product stream collected at the outlet of the system has been analysed on-line by means of a GC Agilent 6890. The line to the chromatograph is heated to a temperature of $250 \text{ }^\circ\text{C}$ in order to avoid condensation of heavy hydrocarbon compounds and make possible a complete analysis of the volatile products formed in the tire pyrolysis process.

The liquid collected has also been analysed by GC/MS Shimadzu UP-2010S in order to identify individual compounds in the reactor outlet stream. Non-condensed gases have also been identified by means of the same equipment (GC/MS Shimadzu UP-2010S), given that it is provided with a port for gas injection. Once a continuous run has been completed (100g of tire fed), the char collected by the lateral outlet and retained in the cyclone and filter was weighed and the liquid was also collected for weighing and subsequent analysis.

RESULTS

The effect of temperature on product distribution has been studied in the $425\text{-}600 \text{ }^\circ\text{C}$ temperature range. To make easier the interpretation of the results the products have been grouped into five lumps: Gas ($\text{C}_1\text{-C}_4$ hydrocarbons), non-aromatic liquid fraction (non-aromatic $\text{C}_5\text{-C}_{10}$ 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 (solid residue).

Figure 3 shows the evolution of the yields of the different lumps with temperature in the range studied. The main effect of temperature is the increase of aromatic liquid fraction and gases and the reduction of the non-aromatic $\text{C}_5\text{-C}_{10}$ fraction. The yield of the gas fraction increases with temperature as a result of more severe thermal cracking at high temperatures. This trend has also been observed by other authors (6,9-13,24). The yields of gases obtained in a spouted bed reactor are similar to those obtained by other authors in fluid bed reactors (12,13), but lower than those obtained operating in devices with low heating rates (25). These differences are explained by the longer residence time of the volatile fraction inside the reactor for low heating rate devices compared to fluid beds and spouted bed reactors.

The gases are mainly methane and $\text{C}_2\text{-C}_4$ olefins and, given that their yield is low in the temperature range studied, always below 10 wt%, their recovery is not viable. Consequently, it is best burnt to produce energy for the pyrolysis process. A significant increase in C_{10} -aromatic compounds with temperature has been observed, from 13.1 wt% at $425 \text{ }^\circ\text{C}$ to 22.9 wt% at $600 \text{ }^\circ\text{C}$. This behaviour of C_{10} -

aromatic fraction is due to Diels-Alder reactions that promote the formation of aromatic compounds from olefins (26).

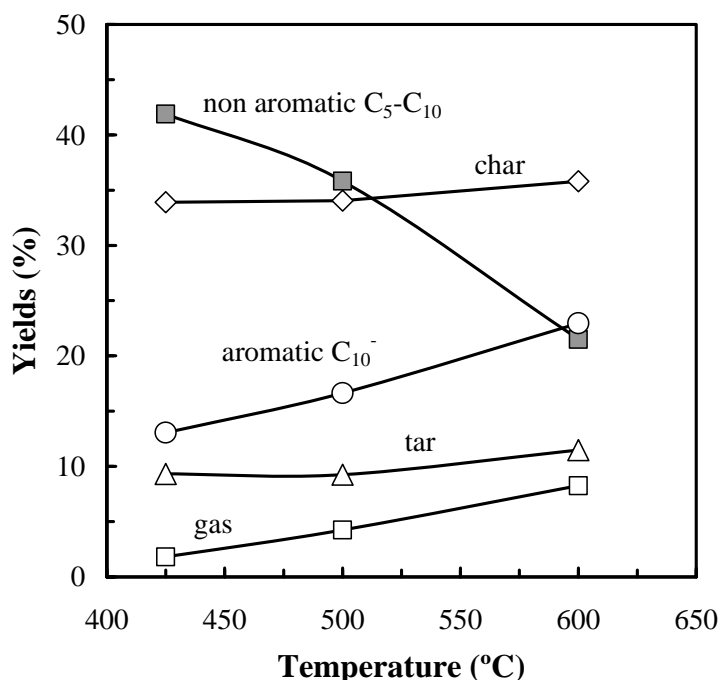


Figure 3. Evolution of the yield of different lumps in the pyrolysis of tires in the 425-600 °C temperature range

The gaseous and C₁₀- aromatic fractions increase with temperature and the yield of the non-aromatic C₅-C₁₀ fraction decreases, which is due to thermal cracking and secondary reactions at high temperatures.

The heavy fraction, or tar, made up of C₁₁+ components, has no clear trend in the temperature range studied. The maximum yield of the tar fraction is obtained at 600 °C, which accounts for 11.5 wt%, and the yields obtained at 425 and 500 °C are very similar (9.2 and 9.3 wt%, respectively). This complex behaviour of the tar fraction with temperature is a result of two opposite processes; on the one hand, the thermal cracking of tar to yield gases at high temperatures and, on the other, the condensation of aromatic rings to yield heavy aromatic hydrocarbons (24).

Operation under relatively low temperatures and short residence times, as in this case, gives way to a high yield of liquid fraction. The amount of liquid fraction is almost constant up to a temperature of 500 °C and then decreases at 600 °C. Studies in the literature report a decrease in the liquid yield working under fast heating conditions, using technologies such as fluid beds, rotary kilns and microreactors (10,11,14) However, other authors have not found any significant effect of temperature on the liquid yield in the 500-700 °C temperature range, operating under low heating rates (6,7).

The yield of char or solid residue increases in the temperature range studied from 33.9 wt% at 425 °C to 35.8 wt% at 600 °C. The char is mainly the original carbon black and the effect of temperature is to increase hydrocarbons deposition on its surface, which causes a slight increase in the mass of solid residue obtained. It

should be noted that char by itself has a catalytic activity that contributes to the condensation of polyaromatic compounds. Other authors have also observed limited variations in the char yield in the 400-600 °C temperature range (6,9).

The residual carbon blacks from waste tires have high sulphur contents, which is a serious problem for the use of this solid for tire manufacturing (26), so a desulphuration process is required for carbon black recycling. The sulphur content is around 3 %, which is similar to that obtained by other authors in the thermal pyrolysis of tires (9,25,27). Another outstanding fact revealed by elemental analysis is that most of the original tire sulphur is retained in the solid residue. In fact, few sulphur compounds are found in the volatile fraction and their concentration is very low. The adulterated carbon black obtained is of limited quality, given that it has a relatively low surface area (below 120 m²/g). In order to use this solid residue as active carbon, an activation process with steam or carbon dioxide is required. This process is carried out at temperatures of around 900 °C and active carbons of commercial quality are obtained (28,29).

Some interesting chemicals are obtained in the liquid fraction, the yield of isoprene remains between 5.7 and 4.5 wt% in the temperature range studied. This component is produced by the pyrolysis of natural rubber. Other interesting compounds obtained in the tire pyrolysis process are those of the BTXE fraction. Thus, xylene demand is growing in the plastic industry and indene is used to produce resins of indene/cumarone for the manufacturing of adhesives and paints. The yield of BTXE fraction increases with temperature by enhancing the Diels-Alder condensation and dehydrogenation reactions.

The content of aromatics and olefins in the liquid is rather high, which may limit its direct application as fuel, particularly in the case of the liquids obtained at 600 °C, in which the amount of aromatic and polyaromatic compounds is considerably high. The liquid fraction may be processed in a refinery by feeding the pyrolysis liquid to hydrocracking units for reducing aromatic and olefin content.

The main individual component in the liquid fraction is limonene, which reaches its maximum yield of 19.3 wt% at 425 °C. Given that a high heat transfer rate and a short residence time in the reactor are factors that promote a high limonene yield (30), the conical spouted bed reactor is a suitable for obtaining high yields of this component (31). Limonene is very unstable at high temperatures and, operating under these conditions, its yield undergoes a sharp reduction to less than 1 wt% at 600 °C. The limonene yields obtained in batch operation are higher than in continuous (a maximum yield of 24 wt% at 425 °C) and their decrease with temperature is less pronounced [30].

CONCLUSIONS

The conical spouted bed reactor is a suitable technology for tire fast pyrolysis in continuous mode. Continuous operation gives way to higher yields of gases and both aromatic and non-aromatic C₅-C₁₀ compounds, but lower yields of C₁₁+ fraction. Temperature has an important effect on product distribution by increasing the aromatisation 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, isoprene and BTX fraction. The adulterated carbon black has enough BET surface area for its recycling, but a desulphuration process is needed for this purpose. Furthermore, commercial quality active carbons can be obtained from residual carbon black by means of an activation process.

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