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Pyrolysis of waste tyres in an atmospheric static-bed batch reactor: Analysis of the gases obtained

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Abstract

Scrap tyre pyrolysis was studied under nitrogen atmospheric pressure in order to analyse temperature influence on the global yields and the gas composition. A static-bed batch reactor was used to pyrolyse 300 g of shredded scrap tyres at temperatures from 400 to 700 °C.

The reactor was externally heated by means of electrical resistances, the heating rate being approximately 12 K min^{-1}. Once the required system temperature was reached and stabilised, it was maintained for 4 h. The residence time of the gas in the reactor was calculated, with values falling between 1 and 1.5 min.

Three phases were obtained after pyrolysis: solid (char), liquid (water and oils) and gas (light hydrocarbons, H_2, CO and CO_2). The product distribution and composition were studied as a function of the thermal treatment. Global yields were determined as follows: char, 47–63 wt.%, oils, 30–43 wt.%, and gas, 2.4–4.4 wt.%. It was observed that the liquid yield increases with temperature from 400 to 500 °C. However, from 500 °C on, this parameter remained almost constant. The solid yield followed an inverse trend to that observed for the liquid yield. On the other hand, the gas yield showed a slight continuous growth with temperatures ranging from 400 °C (2.4 wt.%) to 700 °C (4.4 wt.%).

The gas phase was analysed off-line by gas chromatography. The main gases produced from the pyrolysis process were H_2, CO, CO_2 and hydrocarbons: CH_4, C_2H_4, C_3H_6 and C_4H_8. It was observed that the fraction of light gases (H_2, CO, CO_2 and CH_4) was greater at higher temperatures.

Keywords: Used tyre; Pyrolysis; Static-bed reactor; Gas analysis

1. Introduction

The worldwide generation of waste tyres amounts to 5×10^6 ton per year, representing 2% of total annual solid waste [1–4]. The European Union produces over 2.5×10^6 tonnes of used tyres per year, with a very similar figure for the United States. In the developed world as a whole, approximately one used tyre is produced per capita per year. Most of these tyres (65.5%) are simply dumped in the open or in landfills [5], a disadvantageous ''solution'' in terms of high-added value materials loss and environmental impact. Scrap tyres pose a special challenge for their disposal or reuse because of their size, shape and physicochemical nature [6].

Alternative treatments to landfill absorb almost 25% of solid waste [2]. However, because of their structural characteristics, waste tyres are hard to recycle in the conventional ways used for other waste such as glass, paper and plastics. Thermal treatments directed towards product and energy recovery could provide a promising alternative to landfilling. It is well known that scrap tyres possess high-volatile and low-ash contents, with a heating value greater than that of coal and biomass. These properties make it an ideal material for combustion, pyrolysis and also for gasification. Tyre pyrolysis is currently receiving renewed attention and leads to the production of a solid carbon residue, a condensable fraction and gases. The solid residue contains the mineral matter initially present in the tyre, and

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Table 1
Tyre pyrolysis gas yields for different authors and experimental systems

Authors	Gas (%)	Temperature (°C)	Experimental system
Conesa et al. [6]	6–37	600–800	Fluidized bed reactor
Chang [23]	30–53	200–600	–
Williams et al. [15]	10	300–720	Static batch reactor
Laresgoiti et al. [9]	7–9	400–700	Autoclave reactor
Bouvier et al. [17]	6	372–525	Retort reactor
Lucchesi and Maschuo [18]	15–30	400–700	Bench scale moving bed
Mastral and Murillo [22]	5–12	450–950	Fixed bed reactor
Cunliffe and Williams [7]	5–9	450–600	Static batch reactor
Leung and Wang [12]	5–23	500–1000	Tubular reactor (high-heating rate)

this solid char may be used either as smokeless fuel, carbon black or activated carbon [7,8]. The liquid by-products of tyre pyrolysis consist of a very complex mixture of organic compounds of 5–20 carbons with a very high proportion of aromatics [9]. Thus, the derived oils may be used directly as fuels or as petroleum refinery feedstock. They may also be an important source of refined chemicals (e.g. limonene). Finally, the gas fraction, which could also be useful as fuel, is composed mainly of CO, CO_2, H_2 and light hydrocarbons [7]. Fraction yields and compositions depend on the reaction conditions and the experimental system [10,11].

From different experimental studies carried out in thermogravimetry systems, it has been concluded that thermal degradation of tyre material starts at approximately 200 °C and finishes at around 500 °C. A typical DTG shows three decomposition steps: between 200 and 325 °C, corresponding to the decomposition of oils, plasticizers and additives, between 325 and 400 °C, where natural rubber decomposition occurs, and between 400 and 500 °C where polybutadiene and polybutadiene–styrene (SBR) react [12,13].

A number of studies have been conducted to investigate the pyrolysis of waste tyres in both laboratory and industrial scale, under either inert or partial oxidizing atmosphere. Kaminsky [14] pyrolyzed scrap tyre in a laboratory scale and a pilot scale fluidized bed at a temperature range of 700–800 °C and obtained a gas rich in methane and ethylene. The volume percentage of methane showed a maximum value in the process. Williams et al. [15] pyrolyzed waste tyre in nitrogen atmosphere using a static batch reactor with pyrolysis temperatures between 300 and 720 °C and heating rates between 5 and 50 °C min^{-1}. The maximum conversion of tyre (approximately 55% oil, 10% gas and 35% char) occurred at a temperature of 600 °C. Laresgoiti et al. [9], using an autoclave in a nitrogen atmosphere at temperatures between 400 and 700 °C, found that the pyrolyzed gases consisted of CO, CO_2, H_2S and hydrocarbons (such as CH_4, C_2H_4, C_3H_6 and C_4H_8, and their unsaturated derivatives). They found that temperature poses no significant influence on the char and gas yields over 500 °C. However, temperature variation did influence the gas composition. Roy et al. [16] obtained gases by vacuum pyrolysis, mainly composed of H_2, CO, CO_2 and a few hydrocarbon gases. Bouvier et al. [17], using a 100 l externally heated retort reactor, obtained char (38%), oil (39%) and gas (6%) at a temperature range of 327–525 °C. Lucchesi and Maschio [18] conducted experiments in a bench scale moving bed at a temperature range of 400–700 °C in a nitrogen atmosphere and found that 38–49 wt.% of scrap tyre was converted into oil, 15–30% into gas and 36–38% into solid. The gas product contained mainly CH_4, H_2, CO, CO_2 and light hydrocarbons.

As can be observed, the yields obtained in the tyre pyrolysis process depend on the specific characteristics of the system used (temperature, pressure, heating rate, particle size, heat exchange system, processing capacity, etc.). However, in general two main fractions are obtained: solid residue and liquid fraction. Each fraction amounts to approximately 40–50 wt.%. The general trend is an increase of the yields to liquid and gas as the temperature increases. At high temperatures, the yield to liquids shows a maximum followed by a decrease in this yield and an increase in the gas fraction due to the cracking of the liquids [7,19,20]. In some cases, an increase of the yield to solids has been observed at high temperatures, which is assumed to be due to carbonaceous deposits generated during aromatization reactions [21]. As can be observed in Table 1, the yield to the gas fraction obtained in different experimental systems shows important variations: from 5% [7,12,22] up to 53% [23].

Some of the numerous works carried out on tyre pyrolysis are focussed on the generation of liquid fuel while others are more concerned with investigating the properties of the carbonaceous residue or carbon black produced. Only a few concentrate on the gaseous product. This fact, together with the gas yield differences mentioned above, has prompted the study presented here to determine the yield to the gas fraction in a fixed bed reactor, using material samples of a representative size. As a second objective, a more detailed study was made into the gas composition.

2. Experimental

2.1. Feedstock

The virgin material used for pyrolysis was obtained from a used tyre type Michelin Radial X (165/170 R1379T), cut into 20 mm × 20 mm pieces, including the metallic grid and