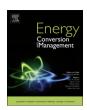
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Syngas production from waste tires using a hybrid filtration reactor under different gasifier agents



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ABSTRACT

This paper investigates the syngas production in a hybrid filtration reactor composed of aleatory waste tires particles and alumina spheres. Parameters as reaction wave temperature, propagation rate and gaseous and solid emissions products were measured as a function of gasifier agents (air and steam) and natural gas presence. Hydrogen and carbon monoxide concentrations in the reaction products were determined by gas chromatography and solid emissions by X-ray spectrometry. Downstream reaction zone propagation was observed in all experiments yielding high reaction temperature $(1,100-1,500\,\mathrm{K})$ responsible of: (1) generating $\mathrm{H_2}$ and CO as main products of the process for different gasifier agents and natural gas presence, and (2) decreased solid particles emissions in comparison with temperatures below $1,100\,\mathrm{K}$. X-ray spectrometry with total reflection was able to detect peaks of Zn and Fe, thought to originate from waste tires particles as well as from reactors insulation material. It was detected that pure air had the best performance as a gasifier agent.

1. Introduction

Worldwide vehicle usage trends have shown a steadily growing behavior in past decades, resulting in an alarming increase of vehiclerelated residues mainly composed of waste tires (WT). In 2011, more than 19 million metric tonnes of new tires were reported to be manufactured worldwide [1], while waste management associations have informed that approximately 17 million metric tonnes are discarded each year [2]. Thus, they pose an environmental issue from the moment that their deposition becomes necessary. Until the 90's most of WT were disposed in landfills or accumulated in stockpiles, which involved a considerable loss of space [1,3] and health issues [4]. Nevertheless, environmental regulations have been introduced in the past 20 years by developed countries like USA, Japan and members from the European Union (EU). They have managed to recycle and reuse more than 80% of their annual WT generation as: energy source, in the form of tire derived fuel (TDF); civil engineering uses like asphalt filling for pavement; or material recovery as raw material for secondary products development such as active carbon and ground rubber [3,5-7]. Additionally, other innovative uses for scrap tires are devulcanization, electric arc furnaces and pyrolysis, the latter being of greater interest, since WT are mainly composed of hydrocarbons with high carbon and volatile material contents, yielding, on average, a higher calorific value than coal [8–10]. Taking these factors into account, WT can be considered as a promising commodity when searching for alternatives to existing energy recovery processes, provided that proper technologies are at hand [11,12].

The processes involved in energy recovery of scrap tires include incineration, pyrolysis and gasification [7,13–17]. Incineration includes the direct combustion of whole or shredded tire material and has been used mostly in cement kilns for the manufacture of clinker [18]. Pyrolysis, a mainly endothermic process, is referred as the thermochemical degradation of organic compounds in absence of oxygen or in partial oxidation combustion conditions, producing carbonaceous materials, oils and gaseous hydrocarbons. On the other hand, traditional gasification processes work mainly as exothermic processes, able of achieving a high performance production of low molecular weight gaseous products such as H₂ and CO through a high-temperature reaction between carbon based materials (tires in this study) and gaseous agents such as air, pure oxygen or steam [19].

In technologies advocated to burn scrap tires, they are usually shredded before being fed to a thermal process, aiming to increase the reactive surface [15], and occasionally mixed with conventional fuels, such as coal or wood pellets, in order to avoid the tendency of rubber to

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become viscous when heated as well as to manage the sulphur content of the blend [20,21], as is the case in the co-combustion in cement kilns [2,22]. In the case of pyrolysis, the researchers have listed the advantages and disadvantages of this process while using WT as pure raw material [9,10] or in blends with biomass [20] or coal [23], its minor environmental impact and the recovery of solid and liquid material being the most remarkable factors. However, an intense temperature control is required to achieve optimal operating conditions. Furthermore, pyrolysis products are considerably more complex than products obtained from incineration or gasification, therefore further processing is needed before reaching an end product. Several authors have conducted research in gasification of WT under different reactor types. such as rotary kilns [13,24], fixed bed, fluidized bed [8] and bubbling fluidized bed (BFB) reactors. The BFB technology is considered to be a proper technology to produce syngas and char at the industrial scale [25]. Advantages of gasification as an energy recovery method for scrap tires are the simplicity of the end-products and a wide operating range, mostly dependent on the equivalence ratio and filtration velocities [13,25]. Nevertheless, market's drive for innovative processes and new approaches to existing technologies require an ample repertoire of alternatives in order to meet most of existing challenges. From this perspective the use of porous media combustion (PMC) turns out to be an interesting option to pair, or to compete, with conventional gasification systems.

The PMC technology involves the interaction between two media, usually a solid and a gas [26]. The two most commonly used design approaches, regarding the flame/reaction zone stabilization in PMC are the stationary and the transient system. The former is widely used in radiative burners because of the high emissivity of the solid media, where the combustion zone is stabilized [27-29] in the finite element of a porous matrix. The latter system based on the excess of enthalpy principle, where the reaction zone is capable of moving freely in an upstream (against the reactants flow) or downstream direction (with the reactants flow), was chosen for this investigation. This operation mode is characterized by its thermal structure, being called normal when the reaction wave propagation rate is faster than the advective transport, resulting in a compact zone where drying, pyrolysis and oxidation occur almost simultaneously. This is also known as a reaction leading combustion regime [30]. On the other hand, when the advective transport and heat transfer acquire a predominant role, a welldefined cascade thermal profile can be identified where drying, pyrolysis and oxidation take place apart from each other, producing a reaction trailing operation mode [30,31]. In the literature PMC is also known as the filtration combustion (FC), when operating with an inert porous matrix, and the hybrid filtration combustion (HFC) when solid fuel is mixed into the porous media [32-41].

In this work, the batch mode-syngas production from the gasification of WT in a fixed, hybrid filtration reactor, composed of aleatory scrap tires particles and alumina spheres under gaseous agent flow (air and steam) and natural gas presence was studied. Solid and gaseous reaction products compositions, reaction wave's temperatures and reaction wave's velocities were analyzed in order to characterize the hybrid filtration reactor performance on the gasification of scrap tires.

2. Methodology

2.1. Experimental apparatus

Experiments on HFC of WT were conducted using the setup shown in Fig. 1. The experimental apparatus consists of four main parts: an atmospheric reactor; thermocouples and data acquisition module; supply and control lines; and finally, the reaction products sampling system.

The reactor displayed in Fig. 1 is a quartz cylinder with an internal diameter of 45.2 mm, a 340 mm length and wall thickness of 2 mm. A layer of ceramic wool (Fiberfrax Fibermax) with a thickness of 4 mm

wrapped its exterior in order to minimize radial heat losses. An inert porous media layer composed of approximately 100 ml of alumina spheres of 5.6 mm in diameter, capable of being chemically inert during the reaction due to fusion temperature greater than 2,300 K, filled the interior of the reactor to a determined level. This inert layer acted as a preheating zone were an efficient heat transfer from the reaction to the premixed gases was achieved through conduction and radiation. A ceramic rod for placing thermocouples, with an external diameter of 5 mm, a length of 460 mm and 6 equally spaced axial bores of 0.8 mm was located coaxially to the reactor. Through the holes of the rod 5 Stype platinum/rhodium thermocouples were installed, as shown in Fig. 1, with the first one (T1) at 60 mm from of the reactor's top, followed by the other four equally distributed at 40 mm intervals. The thermocouples were connected to a data acquisition module (OMB-DAQ-54, OMEGA), where analog voltage signals were converted to digital signals and transferred to a computer for the purpose of visualization and recording (Personal DaqView software was used). A custom manifold was attached at the reactor's bottom, featuring an inlet for the steam line, a bore for the ceramic rod and two more inlets leading to a premix chamber for the air and natural gas lines.

A reciprocating air compressor with an accumulator coupled to a pressure regulator set to 2 barg was used to insure the air supply during experiments. A mass flow controller (MFC) (GFC-37 - Aalborg, Orangeburg, USA) was used to set the air flow required for each experiment. Natural gas (NG) was obtained from the gas line and fed to a MFC (GFC-37 - Aalborg, Orangeburg, USA) used to control the gas flow into the premix chamber. A custom steam boiler was built in order to guarantee a stable steam flow in the range required by the experimental conditions. Its design included an electrical resistance – encased in a sealed steel tank – powered by an AC voltage regulator (VARIAC), a condenser for calibration purposes and a steam supply line attached to the reactor's manifold.

Sampling of gaseous reaction products for chromatographic analysis at the exit of the reactor was achieved by immersing a probe (ceramic rod) into the packed bed to a target depth of 50 mm, in order to ensure a representative syngas production sample from downstream propagation, using a similar procedure as the one reported by [37]. Concentrations of H_2 and CO were directly quantified in a PerkinElmer Gas Chromatograph (GC) Clarus 580 equipped with a thermal conductivity detector (TCD), using a method similar to the one reported in [42].

Solid emissions from gasification of WT were captured by using a fiberglass filter of $1.2\,\mu m$ of porosity and 47 mm of diameter, located in a "volatile collection system" (see Fig. 1). A quartz tube of 93 mm in diameter was immersed in the reactor to a depth of 50 mm and connected to a vacuum system that enabled extraction and saturation of the filter with solid particles. Analysis of the sample was done by X-ray spectrometry, in particular the technique used was X-ray fluorescence, where an XR-100SDD Silicon Drift Detector (SDD) was used.

$2.2.\ Experimental\ procedure$

The aim of this study was mainly focused on analyzing waste tire's gasification under different flows and concentrations of air, steam and natural gas. Therefore, tests were designed to study the effects from varying steam and air flow rate, hybrid matrix composition and presence of natural gas on the syngas production. This resulted in three different experimental sets: (1) Air/Steam; (2) Air/NG/Steam; and (3) Steam. In all the experiments a 50% v/v presence of WT in the porous media was used. Each test was performed in five stages: data logger initialization and flow control set-up; reactor's inert bed ignition and preheating; waste tires/alumina spheres mixture charging into the reactor; gasification products and emissions sampling; and finally, sample analysis by GC and X-ray spectrometry. For the experimental set (1) a base air flow was fixed at 8 lpm (without NG) and 7.74 lpm (with NG at $\phi = 0.3$) was used in (2) test. A fraction of steam flow, ranging from 0% to 60% (or 0–4.8 lpm), was set on every new test. Therefore, for each

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