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Waste tire recycling process for production of steam activated carbon in a pilot plant

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ABSTRACT

This work is focused on the production of activated carbon from waste tires by means of a two-steps process: steam gasification of starting material followed by steam activation of char. In particular the evaluation of the most appropriate hold time value for the activation step, in terms of quality and amount of activated carbons produced, and the energy balance of the overall process were performed. The hold time was choose as the best compromise between a high surface area of final product and a not excessively low burn-off value. Investigations were carried out through seven experimental tests on a pilot plant based on a rotary kiln reactor. Studies performed pointed out that, when other process parameters were kept constant (in steam gasification: temperature is 850 °C, steam to feed ratio is 1, mean residence time of material is 6 min, carrier flowrate of N_2 is 0.9 Nm^3h^{-1}; in steam activation: temperature is 920 °C, steam to char ratio is 2, carrier flowrate of N_2 is 1 Nm^3h^{-1}), a hold time in activation step set to 3 h is the best choice, resulting in a surface area of 786 $m^2 \cdot g^{-1}$ and a burn-off value equal to 78.4%. Moreover, the energy balance of the overall process which goes from waste tires to activated carbon was performed: if 1 $kg \cdot h^{-1}$ of waste tires are gasified and activated for three hours, an input power of 3.5 kW is requested. After the experimental tests, a theoretical model was developed, based on the Arrhenius equation whose parameters were determined from a sigmoidal regression of the experimental data. The theoretical model showed results in good agreement with the experimental data, especially for hold times greater than 2 h, and can represent a useful tool to make decision choices.

1. Introduction

Europe produces about 355 million of tires per year, corresponding to 24% of the total world production (ETRMA, 2011), of which the end of life tires (ELTs) became about 2.6 million tons subtracting the re-used, exported and reconstructed amounts (about 5%, 4% and 9% respectively). ELTs represent a relevant problem within the waste management strategy of the European Community and, despite the attempts of repurposing waste tires in many different ways, a relevant fraction (nearly 13%), is still landfilled.

Apart from this, Europe is also one of the most active areas in the world for the recovery of ELTs (about 95%, even if Italy and the Czech Republic are still between 70% and 90%) (ETRMA, 2014). Thermal

treatment technologies such as pyrolysis and gasification, are some of the proven solutions for high-efficiency material and energy recovery from ELTs (Antoniou et al., 2014; Choi et al., 2014; Karatas et al., 2012; Donatelli et al., 2010; Kandasamy and Gokalp, 2015; Portofino et al., 2011; Portofino et al., 2013; Sainz-Diaz and Griffiths, 2000). In particular, the sustainability of the whole process, on both pilot and industrial scales, is guaranteed if a valuable exploitation of the solid by-products is implemented.

More in detail, gasification is a partial oxidation of feedstock, normally performed at higher temperatures than pyrolysis which instead occurs in inert conditions. These technologies convert the intrinsic chemical energy of a carbon-rich material into intermediate products: syngas (a fuel gas), oil and solid residue (char). Types and yields of

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Nomenclature

c_p	Specific heat (kJ·kg^{-1}·K^{-1})	T	Temperature (°C)
D	Diameter of the kiln (m)	X_c	Moles of carbon (moles)
E	Activation energy (kJ·mol^{-1})		
G	Mass-flow rate (kg·h^{-1})	*Greek symbols*	
k^I	Surface reaction rate constant (s^{-1})		
L	Length of the kiln (m)	β	Kiln slope (°)
m	Reaction order	Δt	Hold time (min)
M	Mass (kg)	θ	Angle of repose (°)
MRT	Mean residence time (min)		
n	Rotational speed (min^{-1})	*Subscript*	
HHV	Higher heating value (kJ·kg^{-1})		
LHV	Latent heating vaporization (kJ·kg^{-1})	a	Activation
$\dot{Q}$	Thermal power (kW)	ac	Activated carbon
R	Molar constant gas (J·mol^{-1}·K^{-1})	c	Condensable
$S(X_c)$	Transient specific surface area (m^2·g^{-1})	g	Gasification
SCR	Steam to char ratio (h^{-1})	in	Input
SFR	Steam to feed ratio	out	Output
		sg	Syngas
		st	Scrap tires

these products can be adjusted by changing the operating parameters (Portofino et al., 2013). The char, containing 85 wt% carbon, can be valuable as raw material both as a filler for reuse in the rubber industry or in the asphalt. As filler, the results showed that the char has similar properties to a semi-reinforcing filler with prospects for manufacturing process of the new tire (Shah et al., 2006; Martınez et al., 2013).

Other major application can be its use as activated carbon. Many researchers studied activated carbon deriving from char tire pyrolysis with BET surface areas up to 1000 m^2·g^{-1} under well-established process conditions (Ariyadejwanich et al., 2003; Mui et al., 2004; Saleh and Danmaliki, 2016). Usually, the whole process consists of two steps: thermal pyrolysis at a relatively low temperature (400–700 °C) under nitrogen or helium gas and followed by activation with an oxidizing agent at 800–1000 °C. Gonzalez et al. (Gonzalez et al., 2006) prepared activated carbons with surface areas of 1317 and 496 m^2·g^{-1} by activation of pyrolytic tire char at 900 and 850 °C in a steam/N_2 mixture and CO_2, respectively. The activation time and the nature of the oxidizing agent affected the porosity and the surface area of the activated carbons while the raising of the temperature had a lower effect. Many procedures are described in the literature for activating waste tires (Mui et al., 2004) which suggest that the steps consist of a first micropores formation, followed by pores enlargement until to crash of the carbonaceous structure. Moreover, using steam as activating agent, the activated carbons show higher total micropore volumes and BET surface areas than those produced using CO_2; so the steam activation shows best results in terms of the external surface areas but the process is energy consuming growing when the activation time increases (Mui et al., 2004; Gonzalez et al., 2006). On the other hand, the porosity of the produced activated carbons usually enhances when burn off increases and the carbonaceous adsorbent yield reduces. Higher activation temperatures and longer hold times should give a lower activated carbon yield, but leads to higher BET surface area, higher volume and larger pore sizes (Hadi et al., 2016).

So, it is mainly important to understand the char activation development and in particular the reaction kinetics and pore structure evolution. Few researchers studied the kinetics of tires char activation and some suggested models were considered useful to understand the gas–solid reaction kinetics between activating gas and char (Mui et al., 2004; Guo and Lua, 2001).

Physical activation using CO_2 or steam as oxidizing agents are the most commonly used processes in the production of tyre carbons but the aim of our research is to get good results in terms of the external surface areas of the carbons assessing also energy consuming of the process. Moreover, even if the production of activated carbons from

waste tires by means of thermal treatments (gasification) has been widely studied and experimented, few experimental activities on pilot or preindustrial scale are available in Literature. The novelty of our work is the optimization of the activated carbon production from waste tires on a pilot plant, in view of industrial exploitation. In particular, the main target of our experimental activities is to study how hold time affects the BET surface area and the burn-off of activated carbon produced from waste tires, when other process parameters (mainly temperatures and steam-on-char ratio) were kept constant, in order to find the best compromise between the surface activity and the amount of activated carbon obtained. The experimental data help us to propose a kinetic model for the theoretical study of carbon activation process. Moreover, with regard to the best compromise found, an energy balance of the process as a whole (gasification and activation steps) is performed.

2. Materials and apparatus

2.1. Feedstock matrix

The chosen feedstock for experiments have been rubber grain derived from waste tires, already employed in previous experimental works (Donatelli et al., 2010; Portofino et al., 2011; Portofino et al., 2013). The reinforced fibers and the steel belts have been extracted and removed from waste tires, and then samples have been shredded to 1–2 cm particle size diameter by a cold mechanical grinding. Then, the rubber grains have been stored under dry conditions before the experimental tests.

Samples of rubber grain were characterized by an elementary analyzer EA 1110 CHNS-O (ThermoQuest) which was used to determine the mass fraction of the carbon, hydrogen, nitrogen, sulfur and oxygen (in weight%) in agreement with ASTM D5373-08 and ASTM D5016-08. The material was exposed to a temperature of 1000 °C under an oxygen atmosphere. The produced gases (CO_2, SO_2, N_2 and H_2O) were separated in chromatography columns and then measured by selective infrared (IR) and thermal conductivity detectors (TCD). Proximate analysis was investigated with a thermo-balance 2950 (TA Instruments) which was used to determine the fixed carbon and volatile organic matter (in dry weight%) in agreement with ASTM D3175-77, while the moisture content and ash were determined in agreement with ASTM D3173-11 and ASTM D2866-11. The higher heating value of the waste tires was investigated by a calorimetric bomb IKA C5000: it determines the heat produced by the combustion of the sample under examination, and absorbed by a known mass of water where temperature rise is