ABSTRACT 05

Conversion of waste tires into activated carbon through pyrolysis and physical activation with CO_2

Isaac Meza, Alicia Guevara & Ernesto de la Torre

DEMEX/Facultad de Ingeniería Química y Agroindustria/EPN, Ecuador.

ABSTRACT 05

A particular environmental problem is the growing generation and the difficulties in the disposal of waste tires. The European Union, USA, and Japan produce around 6 million tons of scrap tires per year; while in the entire world generate 1 billion of waste tires. Tires are an environmental passive produced by several sectors from the industry and human activity. The mining industry is closely related with the disposal of ELTs of high tonnage, yet, this sector has not proposed a possible solution to treat this type of waste. Commonly, landfill zones are the primary destiny of tires, where they represents hazards such diseases and accidental fires.

Actual treatments such as energy recovery in cement kilns and recycling process do not offer an integral way to benefit the end life tires (ELT). However, pyrolysis has shown to be an alternative treatment, and an attractive way to recover valuable products such as combustible gases, fuel and carbon. The last one is of interest in this research because it is the precursor in the production of activated carbon. This treatment proposes a possible solution to take profit of waste tires of mining industry.

The main purpose of the present work was to prepare activated carbon from waste tires, which is suitable as an adsorbent of relatively large molecules. Small pieces of rubber (2-3 cm) from the sidewall of tires were used into the experimentation. The pyrolysis tests were developed into laboratory and pilot scales under temperatures between 450-550 °C. The physical activation of the char was carried under CO2 atmosphere and temperatures between 850-900 °C. The methods of iodine index, blue-methylene adsorption, and sugar index were used to determinate the specific area, and the adsorption capacity of activated carbon.

Pyrolysis results demonstrated that residence times superior to 45 min were necessary to get a char with a high content of fixed carbon with an overall weight loss constant of 67%. Activated carbon with specific area over 800 m2/g has been produced under certain conditions. The activation with CO2 shown a linear relation between time residence and specific surface for burnoff less to 70%.

Keywords: End life tires (ELT), pyrolysis, burnoff, physical activation.

INTRODUCTION

The tires are made up of four groups of raw materials: elastomers, textile, additives and steel wires. The proportion of these materials varies depending on the use, size, design and purpose of the product (Castro, 2008). The natural or synthetic rubber is obviously the essential element of the tire. The tire industry used close to the 70% of the world natural rubber production, which indicates the importance of the latex in the automotive industry (Carrasco et al, 2003). About 1.4 billion tires are sold around the world each year and subsequently just as many fall into the category of end of life tires. (ETRMA, 2010)

All around the world, and particularly in Chile, a disturbing case are the high tonnage tires generated by the copper mining, which are being accumulated increasingly, becoming an environmental liability that occupies large tracts of land. Each tire used by the great mining weighs between 2 and 3 tons. Actually just in Quito, more than 0.8 million of ELT are disposed per year, whereas landfill and unknown location accumulated at least 3 million of scrap tires.

Several solutions to reduce landfill disposal have been developed or are under consideration yet. Tire recycling practices as retreading, grinding and the use of tires as an additive to asphalt roads have been made. However, they all have significant disadvantages or limitations. The calorific value of tires is around 28-37 MJ / kg, which is comparable to high rank coals, so thermal processes, such as combustion, pyrolysis and gasification have been considered as attractive methods for recovery of energy and raw materials from scrap tires. (Aranda et al., 2007)

Pyrolysis of scrap tires is one of the most reasonable alternatives in terms of environmental protection. This method consists in a series of thermal decomposition reactions, which take place in the absence of air, in a chemical inactive and reducing atmosphere. The ELTs are transformed into liquid hydrocarbons known as tar, gaseous components and a solid residue called char, composed mostly of carbon. (Bascones, & Jimenez, 2003)

Previous investigations have demonstrated that the tar produced can be used directly as fuel oil. The gas can be used as fuel gas or reinserted as tail gas into the fuel stream that feeds the pyrolysis furnace, while the char can be employed as carbon black in gasification processes and as a raw material for the production of activated carbon. (Alvarez el at., 2008)

After the production of char through the pyrolysis stage. The modification of specific surface of carbon takes place. The use of a gasifying agent such as carbon dioxide is necessary in this process to develop the porosity all the active points located in the particle. These agents extract carbon atoms from the structure of the porous char according to the following stoichiometric equations. (Marsh & Rodriguez, 2006)

$$C + CO_2 = 2CO \tag{1}$$

METHODOLOGY

The present work examined the behaviour of scrap tires through the actions of pyrolysis and physical activation in order to perform the operational requirements of the overall process.

Physical and chemical characterization

The physical characterization analysed the following characteristics: moisture, volatile material, ashes and fixed carbon contents, real and apparent density. Elemental analysis of the chemical components from ELTs was performed using scanning electron microscopy (SEM-EDX Tescan with QUANTAX X-ray analyser Bruker).

Size reduction method

This manual process consisted in divided the tire zones with metal content from the parts free of metallic cord. For this reason, the sidewall section was chosen. During this stage, the tires were cut using various instruments until reaching smaller fraction (2-3 cm).

Pyrolysis process

Pyrolysis experiments were carried out on a laboratory scale in an electric muffle (Linderberg-Blue M) using two temperatures (450 and 550 °C) and four different residence times (30, 60, 90 and 120 min) with a sample mass of 50 g. These tests were used to determine the best residence time and the best working temperature to provide a product with the highest content of fixed carbon. Pilot scale essay took place in a single-hearth oven under reducing atmosphere (lambda <1) at 550 °C, with a sample mass of 500 g of ELTs.

Physical activation process

Carbon activation tests at laboratory scale were conducted under inert atmosphere of CO2 in a tubular furnace (Thermolyne Tube Furnace-21100) with a sample weight of 1 g of char. The best working conditions were determined by varying the temperature (850 and 900 °C) and the residence time (30, 60, 90 and 120 min). With the best activation temperature, testing was performed in a single-hearth oven (Nichols-Herreshoff), under reducing atmosphere (lambda <1) and with 1 kg of sample mass.

The characterization of activated carbon properties was performed by using techniques such as iodine number, discoloration of sugar, methylene blue index and scanning electron microscopy. The present work studied the behaviour of scrap tires through the stages of pyrolysis and physical activation in order to accomplish the best operational conditions of over hall process.

RESULTS AND DISCUSSION

Physical and chemical characterization

Table 1 Physical characterization

δ real (g/ml) (powder sample)	1.07
δ apparent (g/ml) (pieces 2-3 cm)	0.43

Table 2 Proximate analysis

Property	Content (%)
Moisture	0.86
Volatile	66.29
Ashes	1.98
Fixed carbon*	31.73

* calculated by difference

Table 3 Chemical characterization (SEM-EDX)

C (%)	O (%)	S (%)
90,69	8,23	1,09

Tables 1, 2 and 3 show the physical and chemical characteristics of rubber samples obtain from the sidewall of car ELT.

Pyrolysis process

Laboratory scale

Figure 1 shows the effect produced by the temperature into the pyrolysis stage. For lower temperatures, the transformation process of rubber into char is slower than for higher temperatures where the process ends after 50 min of time residence with a fixed carbon content close to 90 % and an overall weight loss of 67%.

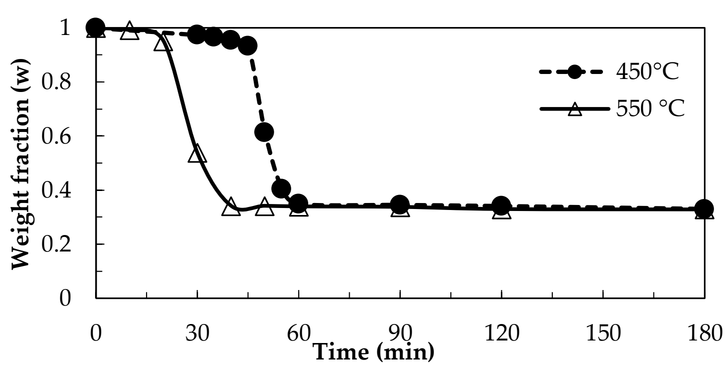

Figure 1 Weight loss of ELT's samples during the pyrolysis stage

During this second stage, working temperature were tested, to obtain a char product with the highest content of fixed carbon and the lowest presence of ashes into his composition. A temperature of 550 °C and a residence time of 50 min showed to be the most suitable conditions to achieve the optimal conditions.

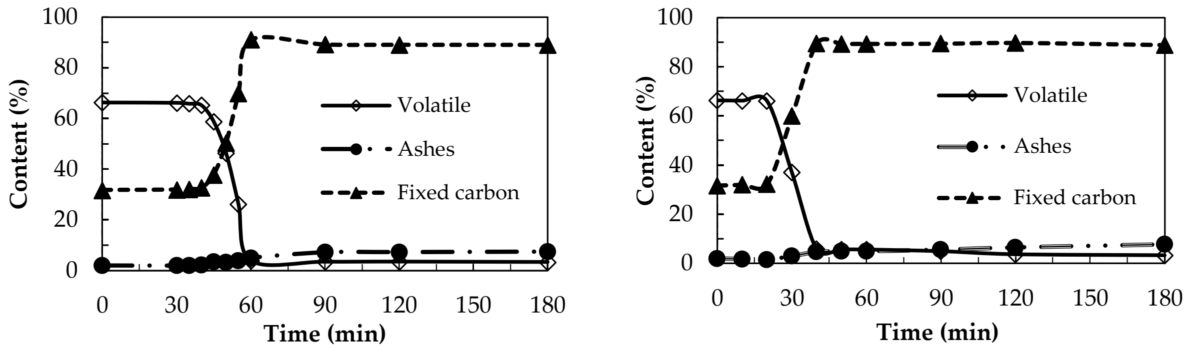

Figure 2 Variation of volatile, ashes and fixed carbon content as function of residence time, in pyrolysis process at laboratory scale tests A. (T=450 °C) B. (T=550 °C)

Figure 2-A and 2-B, allow to view the effect caused by the rise of temperature over the ashes, and fixed carbon contents in char, with respect to residence time. For the zone of high temperatures, the volatile matter presents in the rubber samples is quickly transformed into condensable and non-condensable gases given, a char product with high fixed carbon content. For lower temperatures, the final product also has a fixed carbon content over 90%; due to the rate of volatile material transformation is slower.

Pilot scale

The tests developed under pilot scale condition has displayed similar results concern to time and carbon fixed content as well as laboratory scale essays for a working temperature of 550 °C. This procedure give as results that a temperature of 550 °C and a residence superior to 45 min is required to obtain a desirable product.

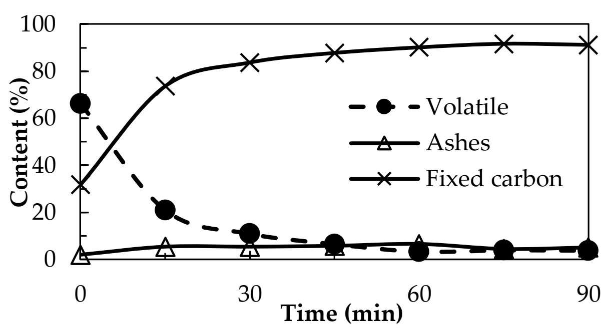

Figure 3 Variation of volatile, ashes and fixed carbon content as function of residence time, in pyrolysis process at pilot scale tests (T=550 °C)

Activation process

The development of the specific area has a close relation with the increase of the temperature. In the figure 4 for the activation temperature of 850 °C and a residence time of 6 h the iodine number reached is 845 m²/g, while, for 900 °C and a residence time less than 4 h the specific surface achieved is superior to 1000 m²/g.

According to Figure 5, the burnoff and residence time show a linear relation. The increase of temperature rises the rate of gasification in the process of activation.

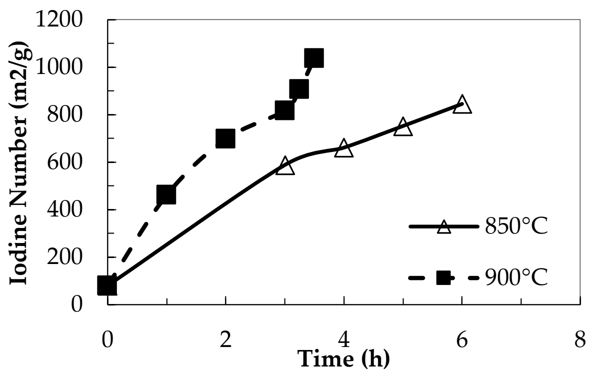

Figure 4 Specific surface development trough time residence in laboratory scale

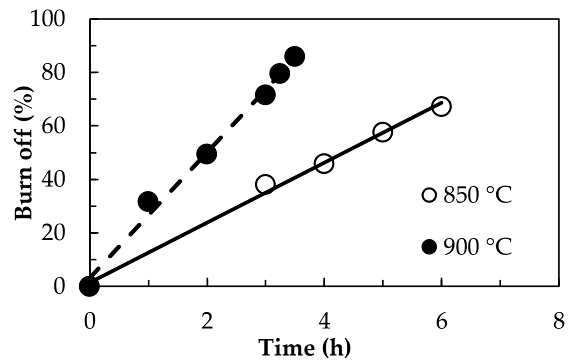

Figure 5 Gasification of char at different activation condition in laboratory scale

After the temperature of activation was defined at 900 °C. A pilot scale essay was performed to find the optimal residence time for the activation process. To reach a specific surface of 523 m²/g at list 8 h were required, as it is shown in the Figure 6. This occurs due to the rise of the carbon from 1g to 1 kg, and the decrease in the concentration of CO_2 into the activation atmosphere.

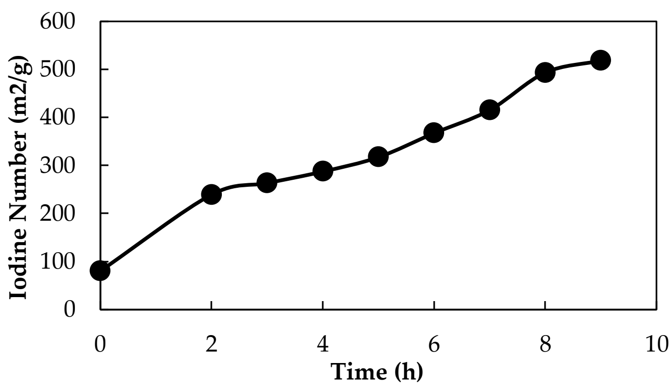

Figure 6 Specific surface development trough time residence in pilot scale

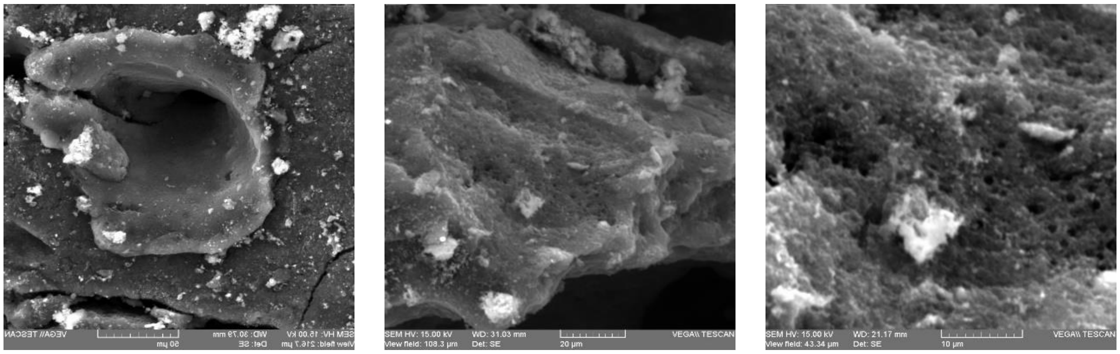

Figure 7 SEM photos of activated carbon pores and structure

A small activated carbon plant, with and total production of 10 t/month is proposed as result of this study. A rotary kiln with and diameter/length relation 10/1 and with the operating conditions established by the results achieved (t_r= 8,5 h and T_f=900 °C) was designed. Considering that the sale price of activated carbon produced is $ 1.50/kg, annual sales over $ 180,000 were estimated. An estimation of 10-year horizon were selected for the plant operation. Based on the above was prepared annual cash flow to calculate economic indicators: IRR and NPV. The results presented is shown in table 4.

Table 4 Economic indicators for a plant of powder activate carbon of 10 t/month

IRR	18 %
NPV	$ 22000,26

According to Table 4 the project can be profitable. The initial capital with which these values were calculated is 125,000 USD.

CONCLUSION

The residence time necessary to obtain pyrolytic carbon with a fixed carbon content higher than 90% and an overall weight loss constant of 67 % in the pyrolysis process is 50 min. This process requires a reducing atmosphere and a working temperature of 550 °C.

The pyrolysis of scrap tires is an endothermic process, which is total dependently of working temperature. As we can see at higher zone of temperatures, the rate of transformation has been favored.

The specific area into the activation stage has a linear dependence with the residence time for the first 3 h in laboratory scale tests at 850 °C.

The gasification rate will be favored with the rise of the temperature; at 900 °C, the specific area achieved for a residence time of 3.5 h is 1036 m2/g.

In physical activation process and with CO_2 as an activating agent, the gasification rate and the residence time maintain a linear relation for burn-off lower than 70 %.

The activation in pilot scale test shows a slow gasification rate due to the lower concentration of CO_2 into the exhausted gases stream. The final specific area achieved was 513 m2/g, which results in a product with a lower specific surface than the results obtained from laboratory scale tests.

The pyrolysis and activation processes propose to be suitable treatments to take advantage of ELTs produced by the mining industry. A powder active carbon plant of 10 t/month displays an IRR of 18% and a NPV of 22000,26 USD with an initial investment close to 125000 USD.

ACKNOWLEDGEMENTS

We acknowledge the Escuela Politécnica Nacional as well the Departamento de Metalurgía Extractiva, for supporting this study and authorizing the publication of this information.

NOMENCLATURE

Lambda (λ)	Ratio of air fed to the burner and the stoichiometric air required for complete combustion of the LPG. Therefore, $\lambda > 1$ implies an operation in an oxidizing atmosphere, while between $0.4 < \lambda < 1$ corresponds to an operation in a reducing atmosphere.
t_r	Time of residence
T_f	Temperature of kiln

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