



Production of activated carbon by waste tire thermochemical degradation with CO₂

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ABSTRACT

The thermochemical degradation of waste tires in a CO₂ atmosphere without previous treatment of devolatilization (pyrolysis) in order to obtain activated carbons with good textural properties such as surface area and porosity was studied. The operating variables studied were CO₂ flow rate (50 and 150 mL/min), temperature (800 and 900 °C) and reaction time (1, 1.5, 2, 2.5 and 3 h). Results show a considerable effect of the temperature and the reaction time in the porosity development. Kinetic measurements showed that the reactions involved in the thermochemical degradation of waste tire with CO₂, are similar to those developed in the pyrolysis process carried out under N₂ atmosphere and temperatures below 760 °C, for particles sizes of 500 μm and heating rate of 5 °C/min. For temperatures higher than 760 °C the CO₂ starts to oxidize the remaining carbon black. Activated carbon with a 414-m²/g surface area at 900 °C of temperature, 150 mL/min of CO₂ volumetric flow and 180 min of reaction time was obtained. In this work it is considering the no reactivity of CO₂ for devolatilization of the tires (up to 760 °C), and also the partial oxidation of residual char at high temperature for activation (>760 °C). It is confirmed that there are two consecutive stages (devolatilization and activation) developed from the same process.

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1. Introduction

Nowadays in the world, the use of materials and/or products that have reached their useful life, takes an increasing importance. In this sense and considering the large increase in the use of vehicles, more than 330 million waste tires are disposed each year in the world [1]. For example, in 2007 for the Valle de Aburrá Metropolitan Area (AMVA) in Medellín, Colombia, an annual generation of used tire units around 1,290,000, approximately equivalent to 34,659 tons [2], was reported. Most of these tires generated are disposed in illegal and not permitted sites, as well as open burning for the steel extraction, creating a serious problem of environmental pollution.

Tires are designed to be extremely resistant to physical, chemical and biological degradation, being difficult to apply techniques for their recycling and/or further processing. Also, storing represents a high risk of fire that would cause serious difficulties for their extinction, besides the great environmental impact on the atmosphere, soil and groundwater.

At present, there are few alternatives for the waste tire valorization. Processes such as pyrolysis, gasification and combustion, have been extensively studied for the energy recovery and for the pro-

duction of materials with high commercial value such as activated carbon among others. In this sense, the process usually developed for the production of activated carbon from waste tires, has been developed usually in two stages: the first, considered a step of devolatilization in an inert atmosphere (pyrolysis), which yields a carbonaceous material (char), as well as oil and gas that is used to provide the energy for the process. The second stage, in a different process, allows for the porosity development in the carbon matrix obtained in the pyrolysis stage through physical activation with CO₂ and/or steam.

However, other researchers [3,4] have reported the possibility of obtaining a carbon matrix with good characteristics of porosity from waste tire without a previous stage of devolatilization. This procedure presents a greater chance of being implemented on an industrial scale, given the fewer stages of the process compared with the conventionally studied. Researches with previous stage of devolatilization (pyrolysis) had reported surface areas of 432 m²/g [5] for temperatures around 970 °C, residence times between 120 and 150 min and H₂O, CO₂ and N₂ gas mixture. Also González et al. [1], with temperatures of 850 °C, 180 min of residence time and CO₂ atmosphere, reported surface area of 496 m²/g. Studies of directly activation without a previous pyrolysis stage, have reported activated carbons with surface area of 1260 m²/g [3] using steam as an oxidizing gas and a temperature around 900 °C. Also, Lehmann et al. [4], reported surface area of 690 m²/g at 900 °C, 120 min of reaction time and water steam oxidizing atmosphere.

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Considering that there are few works on the subject, this work studies the thermochemical degradation of waste tires in a CO₂ atmosphere, without previous treatment of devolatilization (pyrolysis) in order to obtain activated carbons with good textural properties such as surface area and porosity; taking into account the process parameters (CO₂ gas flow, temperature and reaction time) effect in the final carbon material characteristics.

2. Materials and methods

The raw material used to activated carbon production was the product of the tire scraping process of waste tires. Steel and textile netting was previously eliminated. The ultimate analysis of waste tire (in dry basis), was developed in a Carlo Erba EA 1108 elemental analyzer. The carbon, hydrogen, nitrogen and sulfur percentages were 87.14%, 7.46%, 0.51% and 1.47%, respectively. The proximate analysis (on dry basis), was performed according to ASTM standards (D-3175-77, D 2866-83) and showed a 65.60% for the volatile matter, 30% for the fixed carbon, 3.60% for the ash and 0.8% for the moisture. The higher heating value (HHV), on dry basis was obtained in a calorimeter automatic bomb (IKA, model C5000) according to ASTM D5865, and a value of 38.8 MJ/kg was found.

Kinetic information was obtained in a thermogravimetric balance (NETZSCH STA, model 409). The instrument had a feeding system and N₂ flow regulation coupled to the thermobalance, as well as an electronic data acquisition system. 10 mg of sample were taken and placed inside the furnace which is the reaction chamber. N₂ was circulated for 5 min at 100 mL/min in order to purge the system. Finally, the heating rate (5 °C/min) and the temperature set point were adjusted keeping in all cases, the flow and inert atmosphere inside the reaction chamber.

The particle size distribution of the waste tire, was accomplished through a vibrating action device (GILSON, model 55-15), in order to obtain particle size waste tires retained in mesh 30 that gives a 600 μm (according to ASTM E11). In the classification some steel particles were removed. According to González et al. [6], this granulometry allows that the phenomena involved in the thermochemical transformation process be dominated mostly by the chemical reaction, without significant effects of the mass and energy transfer phenomena.

The activated carbons were prepared in a fixed bed reactor which has a stainless steel sampler of 40 mm diameter and 90 mm of height. The process consisted in placing 3.5 g of waste tire inside, leaving the sample in direct contact with the CO₂ flow (50 or 150 mL/min) for 30 min. Subsequently the heating rate (15 °C/min) and the reaction temperature (800 or 900 °C) were adjusted. Based on the operating conditions implemented, the reaction time was fixed to (1, 1.5, 2, 2.5 and 3 h) after reaching the desired temperature. Once reaction time was over and the temperature inside the reactor was close to the ambient, the gas supply was closed. The CO₂ came from the top of the reactor. The gases produced during the activation were condensed in a cold impingers system. The energy required to achieve the thermochemical degradation was provided by an electric resistance furnace with PID control temperature. The experimental error associated with this installation was calculated by performing five identical experiments under the same conditions. The standard deviation was calculated and turn out to be 4%.

The mass loss was calculated by using Eq. (1), where w_1 is the initial mass (tire on a dry ash free basis) and w_2 is the final mass after the activation on dry ash free basis:

$$\% \text{ conversion} = \frac{w_1 - w_2}{w_1} \times 100 \quad (1)$$

The samples were characterized from N₂ adsorption isotherms using a Nova 3200 (Quantachrome) equipment, as well as the

Autosorb program in order to establish the corresponding correlations. Surface area and pore size distribution calculations, were calculated by using the Multipoint BET method and BJH equation, respectively.

The samples were also subjected to Mercury porosimetry in a Pore Master equipment (Quantachrome), and to scanning electronic microscopy in a SEM-EDX Hitachi S-3400N microscope.

3. Results and discussion

The results were mainly discussed based on studies of activated carbons obtained from waste tire with a previous pyrolysis stage and post-physical activation [1–9] as well as in researches that did not considered the stage of devolatilization [3,4,10].

3.1. Thermogravimetric analysis

This analysis aimed to identify the principal temperature values at which waste tire reacts under two different conditions: oxidant (CO₂) and inert (N₂). In addition, mass changes in the waste tire sample was analyzed. Fig. 1a, shows that regardless the carrier gas used with a constant flow rate of 100 mL/min in both cases, the waste tire degradation takes place primarily at 430 °C obtaining a constant weight loss about 65% until a temperature around 760 °C.

Also, Fig. 1 shows the reaction rate evolution with temperature. It was observed that for both working conditions, three main zones were identified according to the most representative peaks. The first zone is in the temperature range between 100 and 270 °C, the second zone between 270 and 350 °C, and a third area between 350 and 450 °C. According to Murillo et al. [11], the first zone is associated with drying of the particles and additives degradation. The second zone shows the breakdown of natural rubber tire and the third zone may be due to the decomposition of the mixture of styrene–butadiene rubber and butadiene rubber. However, only when CO₂ is used as carrier gas, a fourth zone is identified in the temperature range between 760 and 950 °C. From these results, it is obvious that at temperatures higher than 760 °C the CO₂ starts to oxidize the remaining carbon black, with the corresponding mass loss (see Fig. 1) and reaction rate increase. This new zone has no peak shape because the thermobalance could not be operated at temperatures above 975 °C and during the heating up period not all the char was gasified. Moreover, the high activation energy of the carbon and CO₂ reaction makes that although this is a very slow reaction, the reaction rate increases considerably in the studied temperature interval.

Considering the N₂ inert nature as well as the similarity of results for the two gases worked (until 760 °C and 10,000 s of reac-

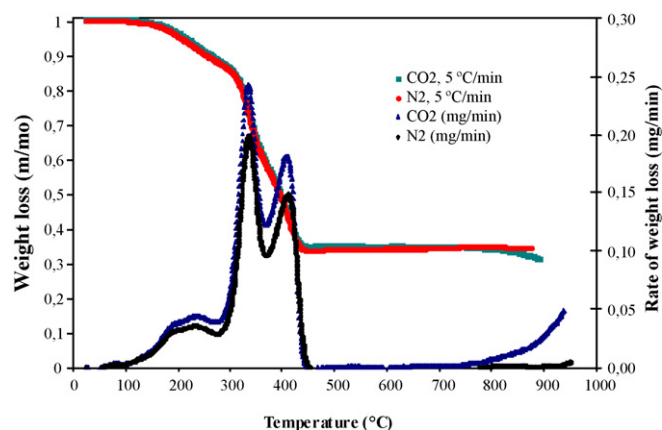


Fig. 1. Reaction rate vs. temperature and weight loss vs. reaction time.

Table 1
Products and activated carbon textural properties.

Sample	CO ₂ flow (mL/min)	Temp. (°C)	Reaction time (min)	Solid (%)	Liquid (%)	Gas ^a (%)	Surface area (m ² /g)	Pore volume (cm ³ /g)
Tire							0.96	0.00
1			60	36.4	46.8	16.8	74.46	0.12
2			90	34.9	47.0	18.1	72.6	0.12
3	50	800	120	34.5	47.0	18.5	78.91	0.12
4			150	34.0	47.9	18.1	81.11	0.14
5			180	34.0	48.6	17.4	87.55	0.13
6			60	32.9	56.9	10.2	82.18	0.14
7			90	32.1	51.3	16.6	79.63	0.13
8	50	900	120	30.3	48.5	21.2	77.78	0.13
9			150	29.9	48.5	21.6	101.30	0.15
10			180	29.0	49.1	21.89	87.99	0.14
11			60	35.1	45.6	19.3	117.76	0.17
12			90	33.9	45.6	20.5	128.15	0.16
13	150	800	120	33.4	45.6	20.9	196.74	0.02
14			150	33.7	51.3	15.0	225.45	0.02
15			180	34.7	42.8	22.5	278.86	0.25
16			60	30.5	45.6	23.9	139.61	0.18
17			90	29.1	42.8	28.1	218.56	0.22
18	150	900	120	28.0	48.5	23.5	225.00	0.22
19			150	27.5	51.3	21.2	266.74	0.25
20			180	25.6	48.5	26.0	414.50	0.33

^a By difference.

tion), it is possible to affirm that for the particle size (500 μm) and the process heating rate (5 °C/min) used, the reactions involved in the thermochemical degradation of waste tire with CO₂, are similar to those developed in the pyrolysis process carried out under N₂ atmosphere. Therefore all the conversion results shown in this paper together with the morphological characteristics of the produced activated carbons can be compared, not only with the results obtained in one stage process but also with all the results obtained according the two-stage process.

3.2. Product distribution in the activation process

In the thermochemical degradation three products were obtained: gas, liquid and activated carbon. The results for the different experimental conditions implemented in this work were presented in Table 1. In the first instance, it was observed that the higher the temperature, the lower the solid production and similar conclusions to those found from the thermobalance experiments could be extracted: the pyrolysis stage was not affected by the final temperature because the tire devolatilization ends before this temperature was reached and the activation stage was very sensitive to this variable due to the high activation energy for the development of the reaction involved [3,10,12,13].

Fig. 2 shows the activated carbon yield vs. reaction time tendency (once the temperature was reached). The results at 800 °C did not show the same trend as those obtained at 900 °C. In the last experiments, it was evident the decline in the activated carbon yield with reaction time and the CO₂ volumetric flow. This could be attributed to the short reaction time and CO₂ low reactivity at 800 °C, as evidenced in the TG analysis. According to González et al. [1] and Leung et al. [14], high temperature in thermochemical treatments of tires in an inert atmosphere (pyrolysis) promotes the gas fraction production while the solid (char) and oils (tars) fractions decrease. The authors justify this, in the light hydrocarbons thermal cracking and in the char reduction reaction with the CO₂ produced in the same process.

Regarding to the oil yield, it was observed that similar values were found in all the runs, regardless the final process temperature or flow rate. Oils were only produced in the first steps of the degradation reaction when the rubber depolymerization occurs.

3.3. Temperature, reaction time and volumetric flow rate effect in the process

The temperature and reaction time influence with respect to the activated carbon conversion grade is shown in Fig. 3. The results suggest a growing linear relationship between the conversion and the activation time for both flow rates at the same temperature. Trend line extrapolations showed no interceptions in the origin. According to Cunliffe and Williams [7], Li et al. [8] and Murillo et al. [15], this behavior may indicate that two stages arise in the tire char activation: a fast mass loss at low conversions, and the tendency presented in Fig. 3 where a linear conversion grade is observed from a slow reaction rate phase. According to Li et al. [8], it is very likely that the fast mass loss is due to the so-called “weak carbon” conversion, which has a structure less organized and more reactive than the “carbon black” present in the fixed carbon. This may explain the behavior found in this work, since the implemented procedure did not consider a previous pyrolysis stage, char collection and/or possible char conditioning. Therefore, the weakest organic components formed as byproducts at the beginning of the pyrolysis process will remain in the char in the temperature interval

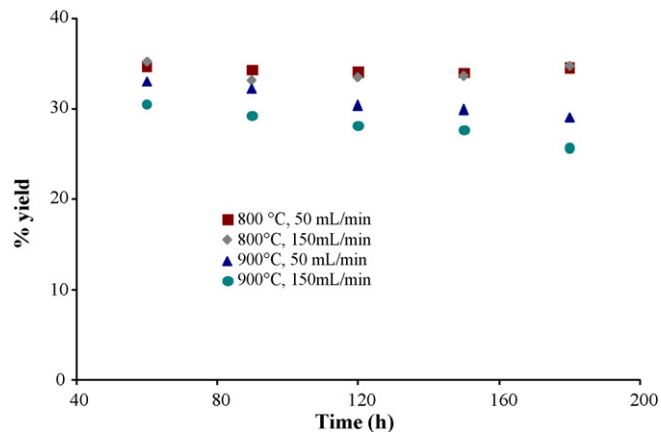


Fig. 2. Activated carbon production vs. reaction time.

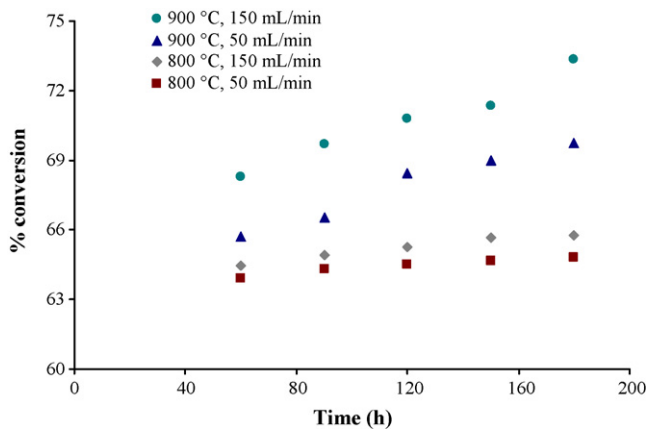


Fig. 3. Temperature and reaction time influence compared to the conversion grade.

between 450 and 750 °C and later be gasified when the CO₂ starts to be active.

Fig. 3 shows that conversions obtained at 900 °C variations with the CO₂ volumetric flow. The maximum conversion reached (73%) took place at 180 min of activation time and 150 mL/min of CO₂ volumetric flow. This value is similar to the reported by Cunliffe and Williams [7] in physical activation experiments with a previous pyrolysis stage: 72% conversion at 134 mL/min of CO₂, and 935 °C of reaction temperature.

According to pyrolysis experiments conducted by González et al. [6], the gas flow affects the residence time of volatile compounds produced in the thermochemical process. High flow rates allow the products fast transport far from the reaction zone, minimizing the secondary reactions such as cracking and the char formation. However, in the experiments reported in this paper, two different effects are shown. First, it is observed that regardless the flow rate and final temperature, the differences found in the oil yields are within the experimental error. Therefore, in the low temperature range (when the temperature is below 750 °C) it seems to be that the flow rate does not affect to the waste tire degradation or product distribution or the influence is not significant enough to compensate for the experimental errors. On the other hand, it is observed that at temperatures higher than 750 °C, when the CO₂ starts to gasify the remaining char, the flow rate affects to the final conversion. Fig. 3 shows that the higher the flow rate, the higher the conversion. Probably, high flow rates are improving the mass transfer from the gas phase to the char particle surface, increasing the reaction rate and eventually the final conversion.

The temperature shows a direct influence in the reaction rate. In this sense, various authors have found that high temperatures, in combination with high activation times, allow high tire conversion grade [1,8,15], as shown in Fig. 3. On the other hand, Fig. 4 shows that higher conversion degree allows greater surface area, suggesting a linear growing relationship between these variables. Typical surface areas for conventional activated carbons show values between 400 and 1500 m²/g, showing potential in different adsorption processes. In this work, activated carbons with 73% conversion show surface areas of 414 m²/g.

3.4. Surface area and porosity characteristics of the activated carbons

The results of surface area and pore volume of the samples are shown in Table 1. In the first instance, the input variables considered in the process (temperature, flow rate and reaction time), show significant effects on the porosity development of the obtained solid product. Increases in surface area, were evident from increases in

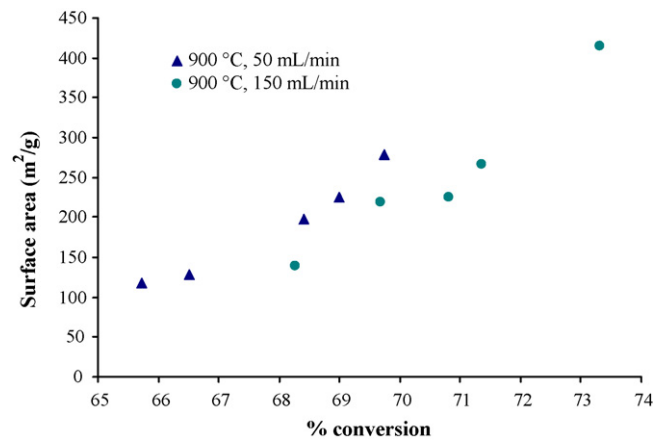


Fig. 4. Conversion grade vs. surface area of activated carbons at 900 °C.

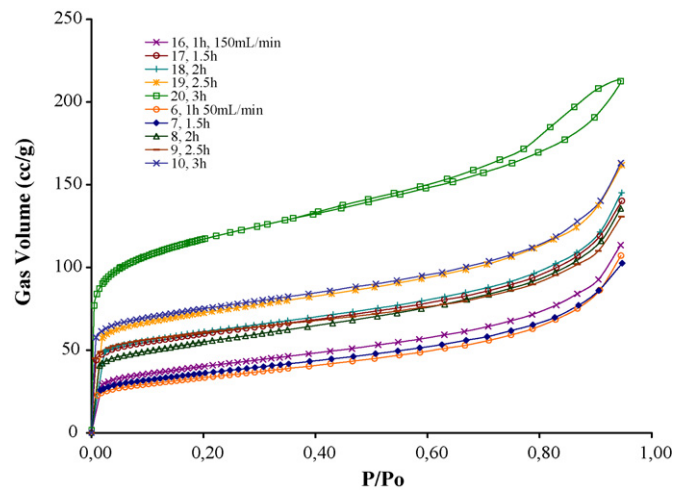


Fig. 5. N₂ adsorption isotherms (77 K) of activated carbons from CO₂ at 900 °C.

temperature, activation time and the CO₂ flow rate. The waste tire activation at low temperature levels, does not favor the porosity development as it was expected from the low conversion achieved. The results show that at 800 °C, the surface area is between 72 and 100 m²/g, similar to several results in used tire pyrolysis experiments without activation stage. In this sense, Lehmann et al. [4], found a value of 89.9 m²/g at 600 °C of temperature and a reaction time of 45 min under N₂ atmosphere; Ariyadejwanich et al.

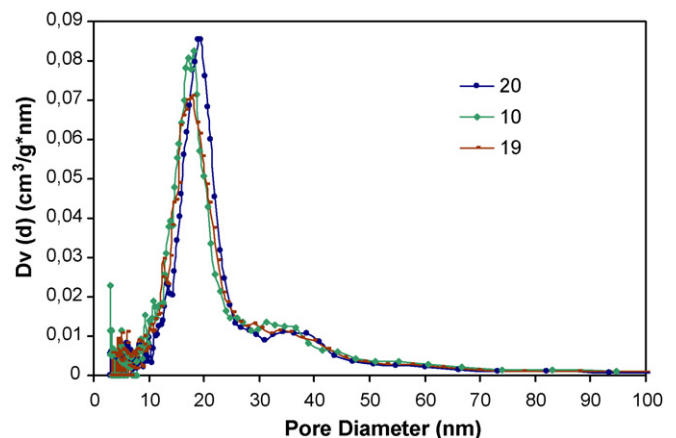


Fig. 6. Pore size distribution obtained from mercury porosimetry.

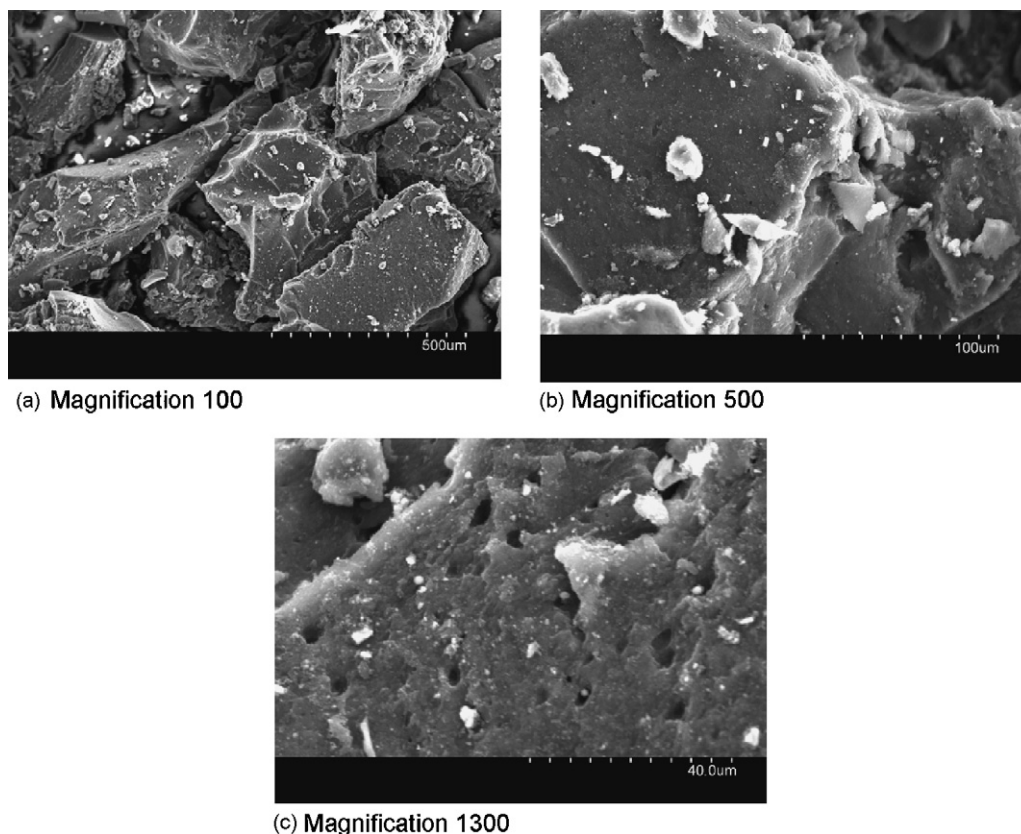


Fig. 7. SEM micrography for the sample 20. (a) Magnification 100; (b) magnification 500; (c) magnification 1300.

[16], reported a value of $89.8 \text{ m}^2/\text{g}$ at 500°C of temperature in 1 h of reaction time under N_2 atmosphere; Cunliffe and Williams [7], working at 600°C and 90 min of reaction time, found a solid carbon residue with a surface area of around $74 \text{ m}^2/\text{g}$.

However, other authors such as González et al. [1] reported surface area values of $146 \text{ m}^2/\text{g}$, submitting the tire at pyrolysis process under conditions of 800°C and 1 h of reaction time with N_2 flow of $100 \text{ mL}/\text{min}$ and subsequently based on the char obtained (with a surface area of $126 \text{ m}^2/\text{g}$), an activation process at 800°C of temperature, $600 \text{ mL}/\text{min}$ of CO_2 and 1 h of reaction time.

The results of this research show lower values of surface area for the lowest values of temperature and CO_2 volumetric flow implemented. In contrast, the samples treated at 900°C , $150 \text{ mL}/\text{min}$ of CO_2 volumetric flow and 180 min of reaction time, yielded an activated carbon with a surface area of $414.5 \text{ m}^2/\text{g}$. Researches with devolatilization stage (pyrolysis), have reported surface areas of $432 \text{ m}^2/\text{g}$ [5] at temperatures around 970°C , residence time between 120 and 150 min and a H_2O , CO_2 and N_2 gaseous mixture. Also [1] reported surface areas around $496 \text{ m}^2/\text{g}$ with 850°C of temperature, 180 min of reaction time and CO_2 volumetric flow of $600 \text{ mL}/\text{min}$.

Fig. 5 shows the N_2 adsorption isotherms (77 K) for the activated carbons obtained with different reaction times and two CO_2 volumetric flows at 900°C . In this sense the results for the sample 20, have a better adsorption capacity due to low relative pressure adsorption, suggesting the presence of a microporous structure [17]. According to San Miguel et al. [18], adsorptions at very low relative pressures ($P/P_0 < 0.1$) are attributed to the presence of microporous structures.

Also, and according to the classification proposed by Brunauer, Deming, Deming and Teller (BDDT), the isotherm forms for samples 17, 20, 9 and 10 presented an intermediate behavior between types I and II, reflecting micropore characteristics, as well as a good

development of mesoporous structures [1]. The other samples can be classified as type II isotherms, which are characteristic of macroporous structures.

In general, adsorption isotherms showed that higher temperatures and reaction times, favor the porosity development. For the same conditions of reaction time and temperature, there is a greater N_2 adsorption capacity with a higher CO_2 flow (Fig. 5).

On the other hand, and considering that the produced activated carbons show evidences of macro- and mesopores existence, mercury porosimetry characterization was performed (see Fig. 6) to the samples that had the best surface area and total pore volume features (samples 10, 19 and 20). It was observed that the average pore diameter was about 20 nm, reflecting a mesoporous considerable presence in the studied samples.

SEM micrographs (three magnifications in the same direction) for the activated carbon that showed higher surface areas (sample 20) are shown in Fig. 7. Microscopy enables to observe a heterogeneous distribution of grain, as well as small size pores (Fig. 7c), attributed to the higher porous structure. Also, Fig. 7 shows the existence of cavities and rough texture, attributed to the organic compound release from the CO_2 reaction at high temperatures.

4. Conclusions

It is possible to obtain an activated carbon with a $414\text{-m}^2/\text{g}$ surface area from waste tires without previous pyrolysis stage and 900°C of temperature, $150 \text{ mL}/\text{min}$ of CO_2 volumetric flow and 180 min of reaction time in a fixed bed reactor. In this sense there is a time and temperature significant effect in the porosity development.

Usually activated carbon from waste tires has been developed in two steps: first a pyrolysis process where volatile matter releases and finally a physical activation process with any oxidizing agent

(carbon dioxide and/or steam) where the porosity and surface area are developed. This work was done without a devolatilization stage, showing that its textural properties can be compared in terms of surface area to the activated carbons produced with a previous pyrolysis stage. In this sense, the process under one stage may be advantageous when its industrial scale implementation is considered, because the investment and operation costs may be reduced in comparison with the two-stage process.

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