Activated Carbon from Leather Shaving Waste. Part I. Pyrolysis and Physical Activation

by

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Abstract

Leather industry plays an important role in the world economy. However, the waste generated by this industry can be an environmental problem. Pyrolysis can be an alternative for reusing this waste since it generates useful liquid, gas, and solid fractions. In the present study, leather shaving waste was converted into activated carbon through pyrolysis. The bio-oil produced consisted of over 75% of nitrogenated compounds and 10% of phenols. H_2, CO, CH_4 and CO_2 were detected in the gas produced. The solid fraction (char - a carbonaceous material) was subjected to activation process for a porous structure development. Tests indicated that temperature (700°C and 900°C) had a significant effect on the burn-off and on the surface area. The high temperature tested (900°C) contributed to the development of the highest surface area (241.4 m^2g^{-1}) and the highest pore volume in the pore size region of 40 Å.

Introduction

Leather is an essential material used for the production of footwear, clothing, car seats, and furniture covering, among others. However, leather production generates a large amount of solid and liquid wastes. Over 60% of the initial hide weight in leather production ends up as waste.[1] The solid waste, which is compound mainly of shavings and dusting, corresponds to 20-45% of the hide weight. The production of activated carbon from leather shaving waste is an alternative to the disposal of this material in landfills, which is harmful to the environment, mainly in the case of chrome-tanned leather wastes.

Pyrolysis is a thermo-chemical decomposition process in which organic materials, such as biomass, are converted into a carbon-rich solid and volatile matter by heating in the absence of oxygen.[2] During the pyrolysis process, three phases are formed: solid, liquid and gas. The solid phase is the bio-char, a carbonaceous material that can be activated and used in adsorption processes. The liquid phase is the bio-oil, which has a complex composition derived from the biomass[3] and can be used as a liquid fuel. Finally, the gas phase is the pyrolysis gas, which usually has a high calorific value.

Bio-char can be physically or chemically activated to develop an appropriate porous structure for adsorption processes. Works that evaluated the activation process conditions for different biomasses, mainly cellulosic materials, are found in the literature.[4, 9] According to these works, parameters as activation temperature and time may influence the activated carbon porous structure by developing micro, meso or macropores. Char activation aims at increasing the adsorption efficiency of activated carbon through the formation of a porous structure, preferentially microporous. Furthermore, other characteristics of the activated carbon that must be considered are the surface area, pore volume, and pore size distribution.

In this work, leather shaving waste was converted into activated carbon by a thermo-chemical process. Leather shaving waste pyrolysis was performed in a semi-continuous pilot screw reactor and its products were characterized. The char obtained was physically activated and the effect of time, temperature and particle size on the surface area and pore size distribution were evaluated.

In the second part of this work, [for later publication], carbon activation process will be improved by demineralizing the char and testing different activation times (4 and 6 h), resulting in higher surface areas.

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Materials and Methods

Leather Shaving Waste Characterization

Wet blue leather shaving waste was supplied by Peles Pampas (Brazil). The samples were analyzed for the amounts of total chromium,[10] total sulfur, moisture, ash, fixed carbon, and volatile matter; they were also subjected to ultimate analysis and higher heating value (HHV) determination. The tests were conducted according to ASTM methods.[11-14] Thermogravimetric analysis (TGA/DTG) of the leather shaving waste was carried out using a thermobalance (SHIMADZU, TGA-5050). The analysis was performed by heating the samples from 20°C to 800°C at a heating rate of 10°C/min under nitrogen (N_2) flow of 50 mL min^{-1}. The surface morphology of the samples was observed using a scanning electron microscope (SEM) (SHIMADZU, SSX-550 Super Scam).

Pyrolysis Process and Characterization of the Products

The reactor used in the pyrolysis process was a semi-continuous pilot screw reactor described in details by Ferreira *et al.*[15] In the pyrolysis process, 2.2 kg of dry leather shaving waste were used. A screw conveyor fed the reactor when the temperature reached 450°C. The screw velocity was 0.16 rpm and the residence time of the solid matter inside the reactor was of approximately 30 minutes. The products formed during the pyrolysis (char, oil, and gas) were collected and characterized.

Char yield was calculated according to Equation 1.

$$Y_p = \left(\frac{m}{M}\right) * 100 \quad (1)$$

where Yp is the pyrolysis yield (%); m is the mass of char obtained after pyrolysis reaction (g) and M is the mass of leather shaving waste fed into the reactor (g).

Moisture, ash, volatile matter, fixed carbon, and total chromium content of the char were determined. The char was also subjected to ultimate analysis, TGA, scanning electron microscopy (SEM), and HHV determination. The same methods used for the leather shaving waste characterization were employed for char characterization.

The water present in the oil fraction was removed using a vacuum rotary evaporator (400 mm Hg and 80°C) prior to oil characterization. Then, the bio-oil was diluted in methanol (1:10) and analyzed by gas chromatography-mass spectrometry (HP, GC/MS 6890 / MSD5973) equipped with HP Chemstation software libraries 275 and Wiley 275 libraries. A capillary column HP-5MS (30 m x 250 mm) with film thickness of 0.50 mm (Hewlett Packard, Palo Alto, USA) was used. The analysis conditions were previously described by Simioni *et al.*[16]

The biogas produced during the pyrolysis process was collected 30, 45, and 60 minutes after feeding the reactor. The samples were collected at the outlet of the reactor screw conveyor, before the bio-oil separator. The determination of the non-condensable gases (H_2, CO, CH_4, CO_2) concentration was performed in a gas chromatograph (DANI, Master GC) using a thermal conductivity detector (TCD) and capillary column Supelco Carboxen ™ 1006 (30 m x 0.53 mm).

Production and Characterization of Activated Carbon

Char produced during the pyrolysis was activated in a fixed-bed tubular reactor. The char samples were separated in particle sizes of 10.00, 5.00, and 0.45 mm. The physical activation was performed at 700, 800 and 900°C with a heating rate of 5°C min^{-1} for 30, 45 and 60 minutes under a constant CO_2 flow of 50 ml min^{-1}. After feeding the reactor with 300 g of char, N_2 was used (50 ml min^{-1}) for 20 min to purge the system. When the final temperature was reached, N_2 was replaced by CO_2 to proceed the activation reaction. After the reaction time (30, 45 or 60 minutes), N_2 was used to cool the system to room temperature.

A 2^k factorial experimental design with two replicates in the center point was used to evaluate the influence of the three parameters (temperature, residence time, and particle size) on the process yield and on the activated carbon surface area. The experimental design is presented in Table I.

The process yield was calculated from the burn-off (BO) (Equation 2), which is defined as the decrease in the char mass during the activation process.

$$BO = \frac{m_1 - m_2}{m_1} \times 100 \quad (2)$$

where BO is burning-off (%); m_1 is the initial mass of char fed into the reactor (g), and m_2 is the activated carbon obtained at the end of the reaction.

Table I
Factors and respective levels evaluated in the 2^k factorial experimental design for carbon activation.

Factor code	Corresponding factor	Coded level		
		-1	0	+1
X_1	Temperature (°C)	700	800	900
X_2	Residence time (min)	30	45	60
X_3	Particle size (mm)	0.45	5.00	10.00

Textural Properties of Activated Carbon

The activated carbon was analyzed for its surface area, pore volume, and pore diameter by N_2 adsorption/desorption isotherms at 77.3 K in a surface area and porosimetry analyzer (MICROMERITICS, ASAP 2020). Samples were outgassed under vacuum at 350°C for 20 h prior to testing. The surface area was determined by Brunauer-Emmett-Teller (BET) and pore size distribution by the Barrett-Joyner-Halenda (BJH). Total pore volume ($V_{0.98}$) was determined from the adsorbed amount of nitrogen at $P/P_0 = 0.98$.

Results and Discussion

Characterization of Leather Shaving Waste

Results for the leather shaving waste samples analysis are presented in Table II. High concentration of nitrogen was found in the sample because of its origin: animal hide, which is rich in protein. Sulfur and chromium were derived from the tanning agent used when turning the animal hide into leather. The HHV measured was 18.61 $MJkg^{-1}$, which is a characteristic value for this waste.[17]

The leather shaving waste was characterized according to its thermal behavior and its TGA spectrum under N_2 atmosphere is shown in Figure 1. The weight loss observed at 70°C occurs due to moisture loss. The second region of weight loss, from 300°C to 370°C, is due to the thermal degradation of leather shaving waste. Considering that the pyrolysis process was carried out at 450°C, the weight loss at the end of the process will be around 55%. As observed by Gil *et al.*,[18] leather shaving waste exhibits extensive decomposition between 200°C and 500°C, suggesting that an intensive modification of the biomass structure occurs, accompanied by the formation of condensable compounds and by the emission of gases.

Table II
Properties of leather shaving waste and char obtained after pyrolysis process.

Analysis	Method	Leather waste	Char
Volatile matter (wt.%)	ASTM D-3176	76.78	42.15
Ash (wt.%)	ASTM D-3176	7.59	16.27
Fixed carbon (wt.%)	ASTM D-3176	15.63	41.68
Total chromium (wt.%)	SMEWW	2.92	5.45
Total sulfur (wt.%)	ASTM D-4239	1.98	1.80
Total carbon (wt.%)	ASTM D-5373	42.12	52.62
Hydrogen (wt.%)	ASTM D-5373	5.75	3.29
Nitrogen (wt.%)	ASTM D-5373	16.28	15.05
HHV ($MJkg^{-1}$)	ASTM D-5865	18.61	22.05

Pyrolysis Process

The amounts of char, bio-oil and gas generated during the pyrolysis process in the semi-continuous pilot screw reactor were measured and the values are presented in Table III. The mean yield of char was 0.85 kg, corresponding to 38.5% of the leather shaving waste initial mass (2.20 kg). The fraction of bio-oil corresponded to 0.59 kg, 26.8% of the leather shaving waste initial mass. The gas fraction was determined by difference from the mass balance and corresponded to 34.7% of the final product.

The product yield may differ as observed for the values presented by the different authors. This can be attributed to some parameters used in the pyrolysis process such as the temperature, residence time, particle size, reactor characteristics, etc. Yilmaz *et al.*[19] used a stainless steel fixed bed reactor at 450°C. In those conditions, the authors obtained 44.5% of char. This higher yield results from the low heating rate (5°C min^{-1}) used in the experiments. In this work, biomass was fed just when the desired temperature was reached, in other words, the char yield, in this case, is not influenced by the heating rate. Gil *et al.*[18] carried out the pyrolysis in a horizontal tubular furnace at 750°C and heating rate of 5°C min^{-1}. It resulted in a char yield of 35.4% and liquid yield of 39.7%.

Characterization of the Pyrolysis Products

Char

The char formed in the leather shaving waste pyrolysis was analyzed by proximate and ultimate analysis and the results were previously shown in Table I.

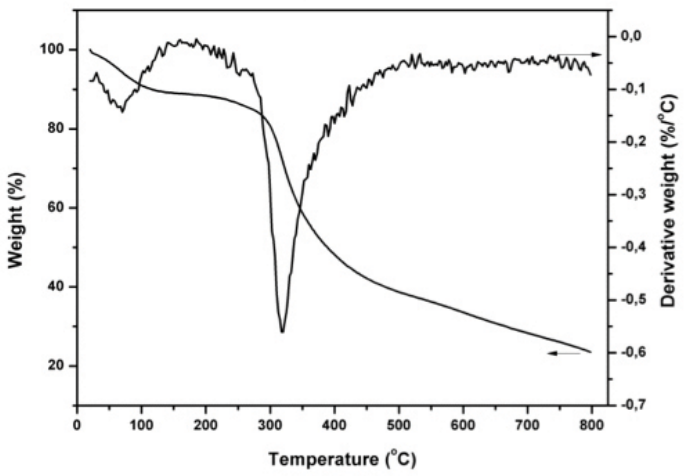

Figure 1. Thermal analysis (TGA) of the leather shaving waste.

The results indicated that char has lower percentage of volatile matter than leather shaving waste. Fixed carbon content increased in the char. According to Oliveira *et al.*,[21] complete pyrolysis of wet-blue leather shaving waste occurs at 630°C. This could explain the low fixed carbon value in the char, since the temperature used in this work was of 450°C. The increase in chromium and carbon concentration is related to the decrease in volatile matter. The reduction in the sulfur concentration can be associated with the H_2S release during the pyrolysis. The high carbon concentration in char leads to an increase in HHV. The value obtained, 22.05 MJ kg^{-1}, indicates that it is possible to use the char as a fuel.

Oil Characterization

The bio-oil presented significant amounts of nitrogen compounds (nitriles, piperazines, etc.), non-oxygenated organic compounds (alkanes, alkenes, aromatics) and organic oxygenates (alcohols, phenols, ketones). Each component presents a retention time, which is the time elapsed between injection and elution of sample that helps to differentiate the compounds. The area is the size of the peak proportional to the quantity of the corresponding compound. The quality factor corresponds to the positive identification of the mass spectrum and retention time of unknown compound and the reference found in the MS library.

According to the results (Table IV), 18 compounds with quality factor higher than 30% were identified in the bio-oil submitted to the GC/MS analysis. Sharifzadeh *et al.*[22] indicated that the calorific value of the bio-oil is low due to the high content of organic oxygenates and water. In this case, to use bio-oil as a liquid fuel, it is usually necessary to pre-treat it to remove water and oxygen. Yilmaz *et al.*[19] carried out pyrolysis of leather shaving waste and indicated steam cracking, hydrogenation, and Fischer-Tropsch synthesis as possible pre-treatments for the bio-oil.

Characterization of bio-oil identified its major compounds as nitrogenates, nitrogenates and oxygenates, and phenols, as observed in Figure 2. The high amount of N and N/O compounds is due to the composition of the leather shaving waste, which is a proteinaceous material. Sulfur compounds were not detected in the bio-oil from leather shaving waste. According to Marcilla *et al.*,[3] the high amount of NH_2 groups in the bio-oil makes it attractive for fertilizers production. Bio-oil carbonyl and carboxyl groups, in turn, can react with alcohols to produce acetals (R'-$CH(OR)_2$) and esters (R-COO-R'). The bio-oil from lignocellulosic material is well characterized in the literature. Among its possible applications, the replacement of heavy and light fuels for industrial boilers, electricity production and synthesis gas production can be cited.[23]

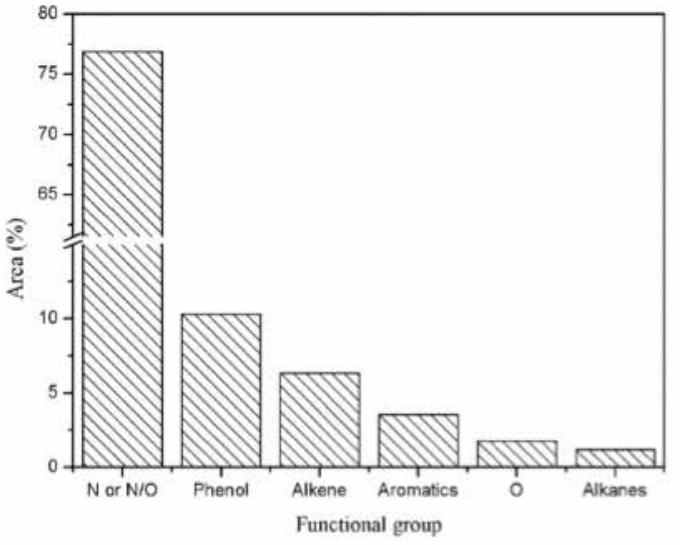

Figure 2. Classification and % area of compounds identified in bio-oil from leather shaving waste pyrolysis (N or N/O = compounds containing nitrogen or nitrogen and oxygen; O = compounds containing oxygen).

Table III

Char, oil, and gas yield obtained in the pyrolysis process (450°C, residence time of 30 min).

	Product yield (%)			
Product	**Present work***	**Gil et al.[18]**	**Yilmaz et al.[19]**	**Sethuraman et al.[20]**
Char	38.5 ± 5.3	35.4	44.5	32.0
Oil	26.8 ± 7.7	39.7	31.5	34.6
Gas	34.7 ± 7.1	24.9	24.0	33.3
*The values represent the mean of three tests.				

Gas Characterization

The pyrolytic gas is composed of water vapor and non-condensable gases obtained from the volatilization of organic compounds present in the pyrolyzed material.[24] It is know that the pyrolysis process may generate a different number of gases, even heavy gases such as CxHy.[25] However, in this work, it was only analyzed the presence of H_2, CO, CH_4 and CO_2.

The concentration of H_2 presented a slight increase from 0.2% to around 1.2% after 60 minutes of pyrolysis, as observed in Figure 3. The H_2 formation is probably due to water release from the leather shaving waste. The CO production (3%) and higher concentration of CO_2 (15%) may be attributed to the high degree of deoxygenation produced during the pyrolysis experiments, which, according to Gil *et al.*,[18] is related to decarbonylation and decarboxylation reactions. CH_4 was detected in low concentrations, around 0.3%. Because of the nitrogenated composition of leather shaving waste, nitrogen gas may be formed in high concentration and this could explain the low concentration of the gases measured in the gas stream.

Effect of Physical Activation

Surface area and porosity of activated carbons are developed during the activation process. According to Allen *et al.*,[26] the activating agent, in this case CO_2, burns away the pyrolysis tar trapped within the pores, initializing the porosity development. Micro and mesoporous structures are developed as the oxidizing agent burns away the more reactive areas of the carbon material.

Table IV

Characterization of bio-oil obtained during the leather shaving waste pyrolysis at 450°C.

Peak number	Retention time	Area (%)	Compound name	Quality factor (%)
1	3.193	1.78	1,5-Hexadien-3-yne,2-methyl	83
2	5.781	4.65	Phenol	91
3	7.004	4.10	Pyridine, 4-ethyl	59
4	7.227	2.59	2-(Dimethylamino)-3-methyl-1-buten	64
5	7.439	1.31	4-Ethyl-5-methylthiazole	47
6	7.919	10.07	1H-Pyrrole-2-carbonitrile	72
7	8.530	1.52	2-Heptyl methylphosphonofluoridate	35
8	8.547	5.51	3-Octen-1-yne, (E)	38
9	9.850	11.75	Pyrazine, methyl-, 1-oxide	43
10	9.884	2.921	Pyrrole-2-carboxamide	43
11	9.907	5.27	2-Aminopyridine N-oxide	47
12	10.776	3.79	dl-5-Ethyl-5-methyl-2,4-imidazolidinedione	72
13	12.810	6.20	Cyclopentanecarbonitrile	58
14	12.999	1.73	2-Cyclobutene-1-carboxamide	35
15	14.382	4.31	3-Pyrrolidin-2-yl-propionic acid	47
16	14.593	9.88	Pyrrolo[1,2-a] pyrazine-1,4-dione, hexahydro	87
17	15.467	1.03	1,4-Dioxaspiro[4.5]decane, 6-methylene	32
18	16.610	8.48	12-Dimethylamino-10-oxododecanoic acid	32

Table V presents the coded and real values of the factors (temperature, residence time, and particle size) of the factorial experimental design used to evaluate the carbon activation conditions. Lower burn-off and BET surface areas were obtained using the low temperature (700°C) and particle size of 0.45 mm (runs 1 and 5). In this temperature, the burn-off was not capable to develop the porosity in the same way as observed at 900°C, resulting in a lower surface area. According to the analysis of variance (Figure 4), the burn-off was significantly affected by the temperature and by the particle size ($p < 0.05$). In the case of surface area, the temperature had a significant effect on the final result. The BET surface area increased from 96.5 m^2g^{-1} at 700°C to 241.4 m^2g^{-1} at 900°C. This result is in accordance with results observed by Kong *et al.*,[27] in which the temperature affected the BET surface area of the activated carbon from leather shaving waste, increasing it from 420 m^2g^{-1} at 700°C to 493 m^2g^{-1} at 800°C.

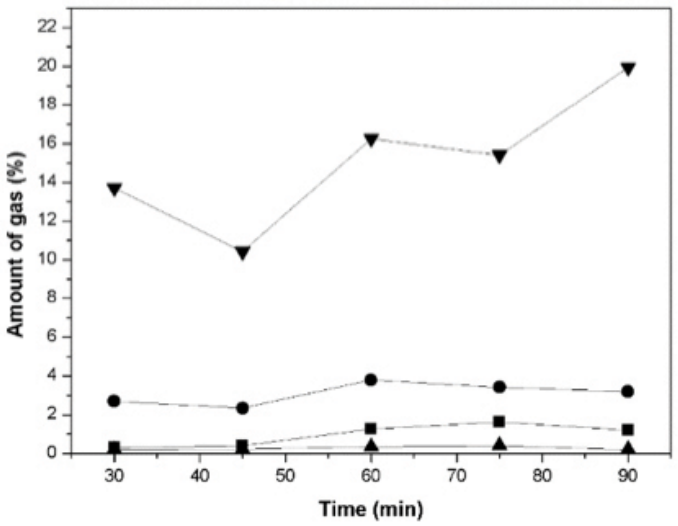

Figure 3. Amount of H_2 (▪), CO (●), CH4 (▲) and CO_2 (▼) produced during the pyrolysis of leather shaving waste in a semi-continuous pilot screw reactor.

Textural Properties

The adsorption/desorption isotherms of activated carbons obtained from the experiments 2, 3, 8 and 10 are shown in Figure 5. All tests were performed with nitrogen (N_2), at atmospheric pressure and temperature of 77 K. The behavior is typical of type

Table V
Experimental design matrix (coded and real values) and burn-off and BET surface area results.

Run	Codes			Values				
	X_1	X_2	X_3	X_1	X_2	X_3	Burn-off (%)	S_{BET} (m^2g^{-1})
1	-1	-1	-1	700	0.45	30	44.0	51.5
2	+1	-1	-1	900	0.45	30	53.5	191.2
3	-1	+1	-1	700	10.0	30	54.7	162.2
4	+1	+1	-1	900	10.0	30	55.4	177.4
5	-1	-1	+1	700	0.45	60	43.3	96.5
6	+1	-1	+1	900	0.45	60	51.0	241.4
7	-1	+1	+1	700	10.0	60	51.8	120.7
8	+1	+1	+1	900	10.0	60	59.8	219.5
9	0	0	0	800	5.0	45	53.8	129.3
10	0	0	0	800	5.0	45	54.0	153.1

X^1 – temperature (°C); X^2 – particle size (mm);
X^3 – residence time (min)

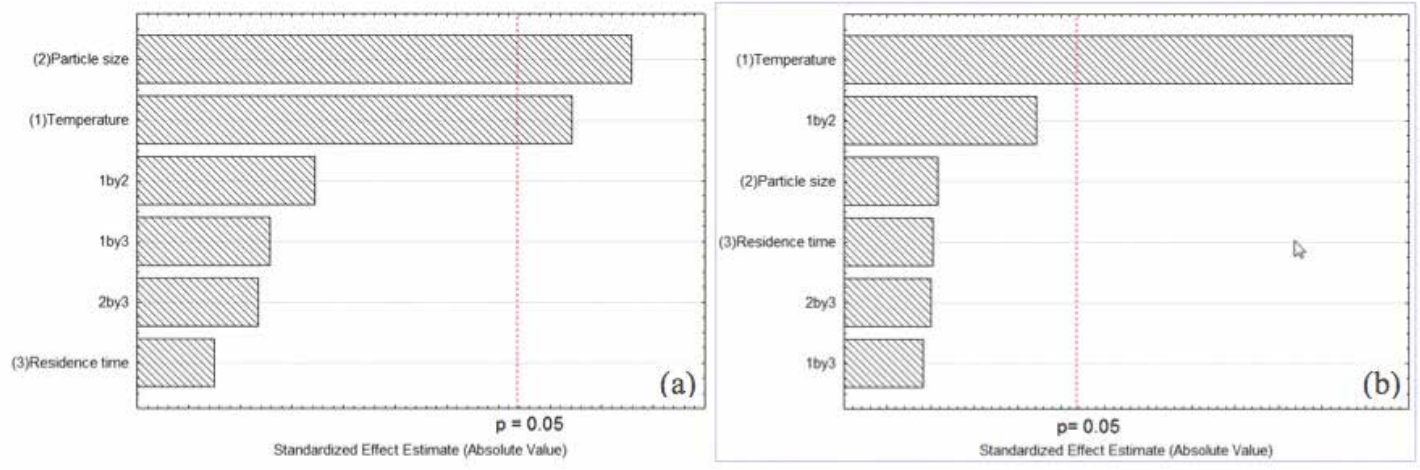

Figure 4. Pareto chart for the effects of temperature, particle size, and residence time on the burn-off (a) and surface area (b).

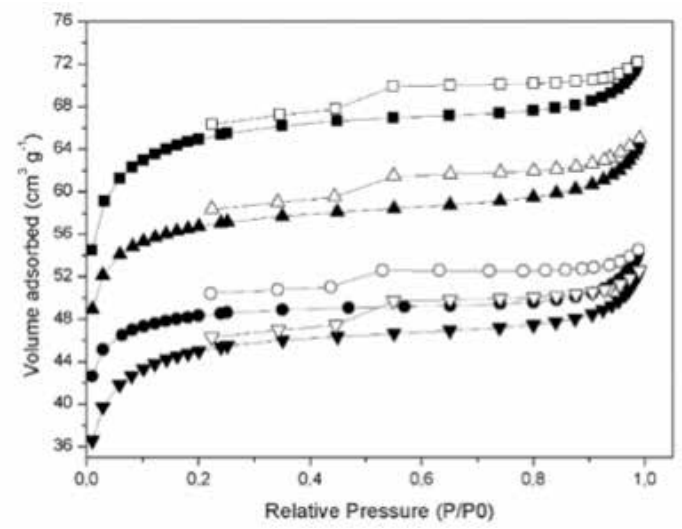

Figure 5. Adsorption (closed symbols) / desorption (open symbols) isotherms of runs 2 (▲) (900ºC x 0.45 mm x 30 min), 3 (●) (700ºC x 10 mm x 30 min), 8 (▪) (900 ºC x 10 mm x 60 min) e 10 (▼) (800 ºC x 5 mm x 45 min).

I isotherms,[28] which indicates that this is a solid material with small pores. According to IUPAC, the hysteresis may be classified as H4 type, which characterizes solids formed by micro and mesopores.

The isotherms were evaluated based on the parameters studied in the activation tests (particle size, temperature, and residence time). The adsorption capacity of the activated carbons was compared in the relative pressure (P/P0) of 0.98. The tests performed at 900ºC for 30 minutes and with different particle sizes (runs 2 and 4) were plotted in Figure 6-a. The activated carbon prepared with the low particle size (0.45 mm) presented the highest volume adsorbed, 65.0 cm^3.g^{-1}. In its turn, the one prepared with the high particle size adsorbed 60.0 cm^3.g^{-1}. Figure 6-b indicates that the high temperature, 900ºC, increased the volume adsorbed to 60.0 cm^3.g^{-1} (run 4) while the activated carbon produced at 700ºC adsorbed 54.5 cm^3.g^{-1} (run 3). The activation time was an important parameter that contributed to increase the volume adsorbed (runs 4 and 8). As observed

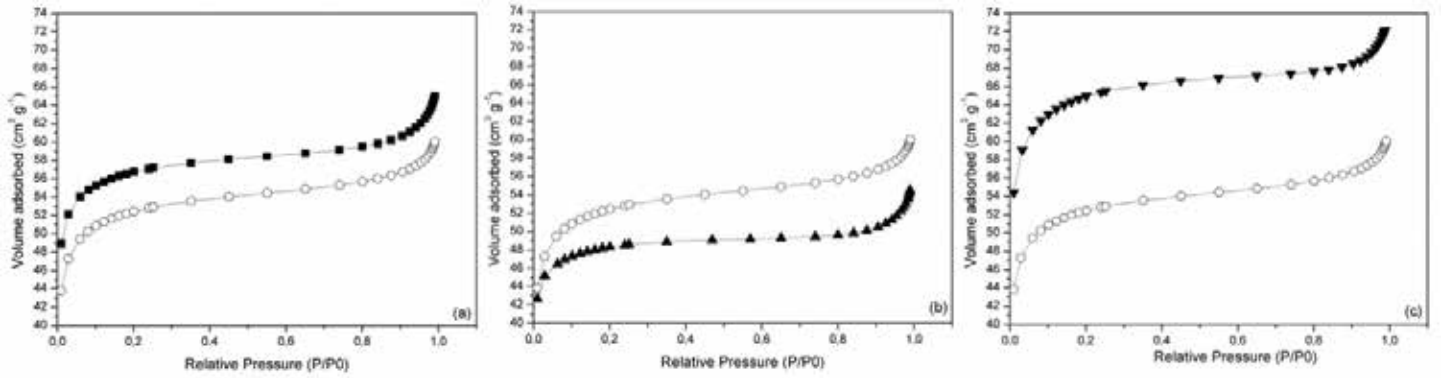

Figure 6. Comparison of isotherms of run 4 - 900ºC, 10 mm, 30 min (○) with: run 2 - 900ºC, 0.45 mm, 30 min (▪) (a); run 3 - 700ºC, 10 mm, 30 min (▲) (b); run 8 - 900ºC, 10 mm, 60 min (c) (▼).

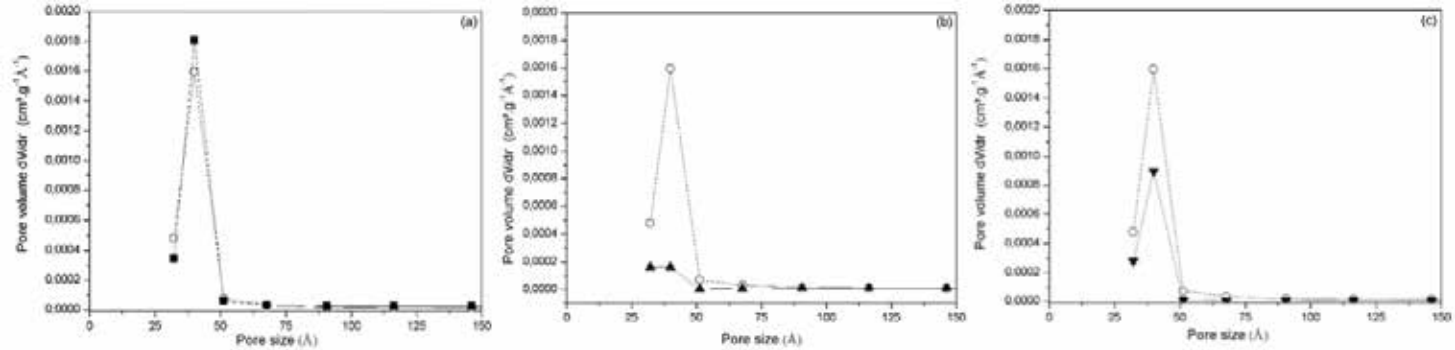

Figure 7. Comparison of pore size (radius) of run 4 - 900ºC, 10 mm, 30 min (○) with: run 2 - 900ºC, 0.45 mm, 30 min (▪) (a); run 3 - 700ºC, 10 mm, 30 min (▲) (b); run 8 - 900ºC, 10 mm, 60 min (c) (▼).

(Figure 6-c), the volume adsorbed was higher when the carbon was activated for 60 minutes (run 8). In other works, the temperature of 800°C presented higher BET surface area when compared to 850°C and 900°C. Kantarli & Yanik[9] evaluated different activation times. The authors observed that times of 3 and 4 hours resulted in higher BET surface areas. However, excessive activation times could collapse the pore structure, reducing the surface area and the pore size.[29]

The comparison made for isotherms was also made for the pore size distribution (Figure 7). Pore diameters of around 40 Å presented the highest adsorbed volume in all tests. This activated carbon can be classified as a mesoporous material according to its pore size. However, differences in volume adsorbed were identified when different temperatures and times were used. The results indicate that the volume adsorbed in pore size of 40 Å was higher when the temperature of 900°C and the time of 60 minutes were used. This data showed the influence of the activation parameters on the activated carbon characteristics.

Conclusions

This work proved that the conversion of leather shaving waste into activated carbon by thermo-chemical process is possible. The liquid and gas fractions characteristics suggest that it is possible to use them as fuels in different applications. The mesoporous activated carbon obtained from char presented surface area and pore size suitable for use in separation and adsorption processes. The results obtained in this work indicate that the activation parameters still need to be investigated. Therefore, in the second part of this work, activation time and char pre-treatment (demineralization) were performed to increase the surface area and to promote the microporous structure development.

Acknowledgments

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