Paper C11

Characterization of solid materials from the leather industry by mercury porosimetry

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1. Introduction.

Living skin cannot be penetrated by water since the only pores it contains are sweat glands. The rest of the skin surface is completely closed off by the epidermal system. When the skin has been removed from the animal and has gone through the necessary operations in the tanning process to obtain leather, pores of different forms and sizes appear in the end product. It is an arduous task for the tanner to obtain leather that offers an excellent porosity and, at the same, is impervious to water. Many of the properties of leather such as elasticity, plasticity and resistance to water are related with its porosity (pore volume and size and connectivity between pores). The study of the porous structure of skin is also very important for understanding the processes of diffusion and/or adsorption through skin in both biological and industrial applications [1-3].

Mercury injection porosimetry is a commonly used method for the characterization of porous materials [3-10] and it is widely used in industry. This technique allows the characterization of the porosity of different kinds of materials in order to obtain the distribution of porosity over the macropore (pore sizes higher than 50 nm) and mesopore (pores of 2–50 nm) range in addition to other important parameters such as total porosity, total volume of mercury intrusion, bulk density, skeletal density, etc. Mercury porosimetry is a very popular technique because it is relatively straightforward to use and also because it can be used to study a wide range of pore sizes between 360 µm to 6 nm. This technique is based on the basic physical principle that mercury requires an external pressure in order to force it into the pores of a porous system. Increasing pressure moreover is required to force mercury into pores of decreasing size. The present study is supported by another technique, scanning electron microscopy which is very useful for the examination and surface characterization of all kinds of materials.

2. Materials and methods.

The solid materials used in this research: dehydrated skin, pickled skin, wet blue skin and tanned leather with silicates were obtained from the Leather Industry. A sample of skin tanned with vegetable tannins was also examined. Dehydrated skin is a skin that has been treated with acetone in order to degrease and dehydrate it; pickled skin is a skin that has been treated with saline solutions and acids in the same bath; this operation prepares the skin for preservation. Finally, wet-blue skin is a skin that has been semi-tanned with chromium salts. Pickled skin, wet blue skin and skin tanned with vegetable tannins are examples of semi-processed leather and they are available on the market; dehydrated skin and tanned leather with silicates are experimental samples. All the samples were cow skin except for the material tanned with silicates which was from lamb.

The samples were characterized as follows:

Chemical characterization: A proximate and ultimate analysis of the samples was conducted following the procedures usually applied to coals. The ash content was determined according to norm UNE 32004 and the volatile matter (V.M.) content according to norm UNE 32019. The ultimate analysis was carried out on a LECO CHN-2000 and LECO Sulphur Determination S-144-DR instrument, and the oxygen content was calculated by difference.

Textural characterization. The mercury porosimetry was carried out on a Micromeritics AutoPore IV 9500 Series apparatus, which provided a maximum operating pressure of 227 MPa. The mercury porosimetry was conducted as follows: The sample was weighed in a penetrometer, degassed and then filled with distilled mercury at a low pressure. The mercury was then pressurized at different pressures and the corresponding volumes of intruded mercury were determined. The pore diameter was calculated from the pressure, the surface tension of the mercury and the wetting angle. The following parameters were calculated: bulk and skeletal densities (ρ_b and ρ_s respectively), the specific total pore volume corresponding to the intruded volume of mercury at maximum pressure (V_T), the porosity (ε) and the pore size distribution using the Washburn equation [11] with a mercury surface tension of 480 N m^{-1} [12] and a mercury contact angle of 140º.

From the skeletal, (ρ_s), and bulk, (ρ_b), densities the total pore volume, V_T, was calculated from:
$V_T = (1/\rho_b - 1/\rho_s)$

and the open porosity, ε, from:
$\varepsilon = (1 - \rho_b / \rho_s)\ 100$

SEM-EDX. The materials were examined using a Scanning Electron Microscope (ZEISS Model DMS-942) equipped with an Energy-Dispersive X-Ray analyzing system (Link-Isis II).

The samples that arrived in the form of strips or as one large piece were converted into the appropriate size for the different analyses. In order to obtain a representative sample of the precursor for chemical analysis they were ground to a very fine particle size. For the mercury porosimetry experiments small pieces of skin measuring approximately 1 x 1 x 0.1 cm were used. Prior to analysis the samples were dried slightly in an oven at 55 ° C for 1 hour. A low temperature was chosen so as not to denature the protein of the skin.

3. Results and discussion.

3.1.1 Chemical characterization

Table 1 shows the results of the proximate and ultimate analysis of the samples. The results of the chemical analysis of these materials reveal a low ash content; only the skin tanned with silicates presents a moderate value in mineral matter which is attributed to chemical reagents introduced in the process of tanning the skin; the dehydrated skin presents the lowest ash content, 1,23%. The samples present carbon contents higher than 40% and a very interesting nitrogen content with values up to 18%. Similar results for the chemical composition of tannery waste of vegetable-tanned leather have been reported by I. Cem Kantarli et al.[13].

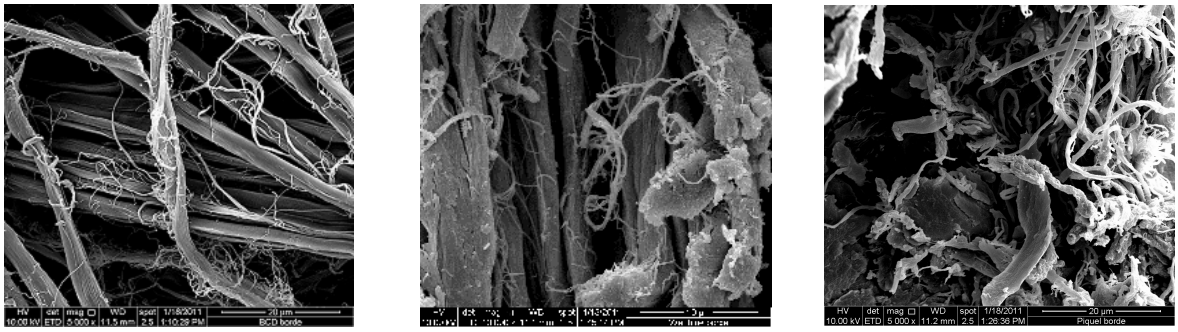
Table 1. Proximate and ultimate analysis of the samples

Sample	Proximate and ultimate analysis (wt%, dry basis)					
	Ash	C	H	N	S	O
Dehydrated Skin	1.23	46.40	6.38	17.89	0.49	27.61
Pickled Skin	5.66	44.72	6.30	15.81	0.27	27.24
Wet Blue Skin	9.15	44.50	5.83	15.20	0.91	24.41
Skin Tanned with Silicates	13.98	41.30	6.22	14.48	2.13	21.89
Skin Tanned with Vegetable Tannins	5.16	49.16	5.20	8.33	2.57	29.58

The chemical composition of these materials makes them highly suitable bioprecursors for obtaining activated carbons [13-18]. Several studies on the physical activation with CO_2 of tanned leather wastes [13-16], and on the chemical activation of leather shavings wastes [13,18] and leather buffing dust wastes [17] are reported in the literature.

3.1.2 SEM-EDX.

Figure 1 shows SEM micrographs of the samples at two magnifications, 5000x and 10000x. It can be seen that the collagen fibrous structure of the samples is maintained during the process of skin tanning. The aim of this process is to ensure the stability of the skin, which is the main characteristic of tanned skin.



BCD Wet Blue Skin Pickel Skin

Figure 1. SEM micrographs of BCD and Pickled Skin at 5000x and Wet Blue Skin at 10000x

Figure 2 shows the EDX spectra of the samples. Chrome is present only in the wet-blue skin because this skin has been semi-tanned with chromium salts. Silicon is present mainly in the lamb skin because it has been tanned with silicates. Sulphur and oxygen are present in all the samples, possibly in the form of sulphates. Iridium is present because the samples have been metalized for examination by SEM-EDX. They may also contain small amounts of sodium chloride, potassium chloride, etc.

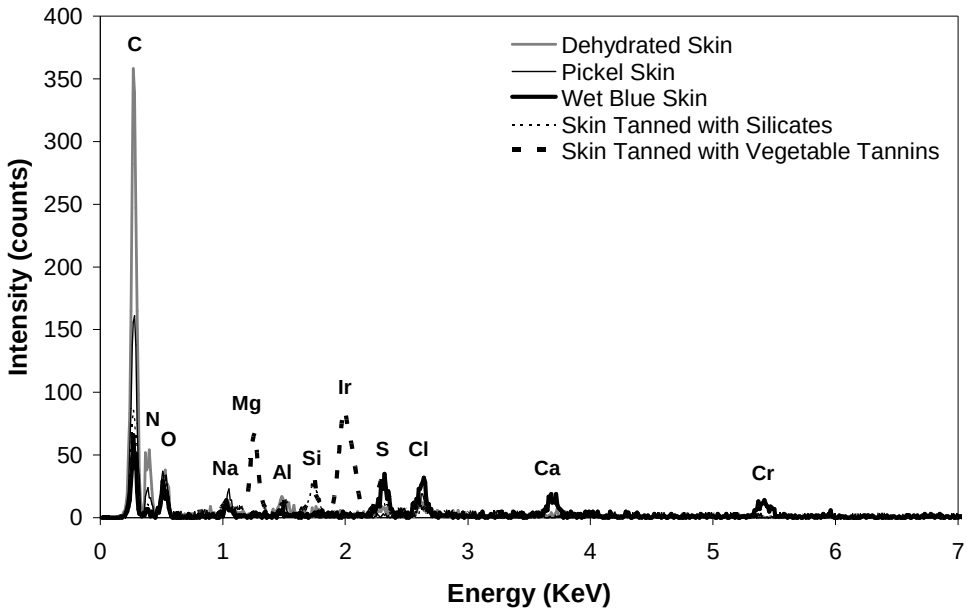


Figure 2. EDX spectra of the skin materials

3.1.3 Textural characterization

Table 2 shows the results of the textural characterization of the samples by mercury porosimetry. The total intrusion volume, total surface area, median pore diameter (volume), bulk density at 0.0045 MPa, skeletal density at 227 MPa and porosity were determined by mercury porosimetry.

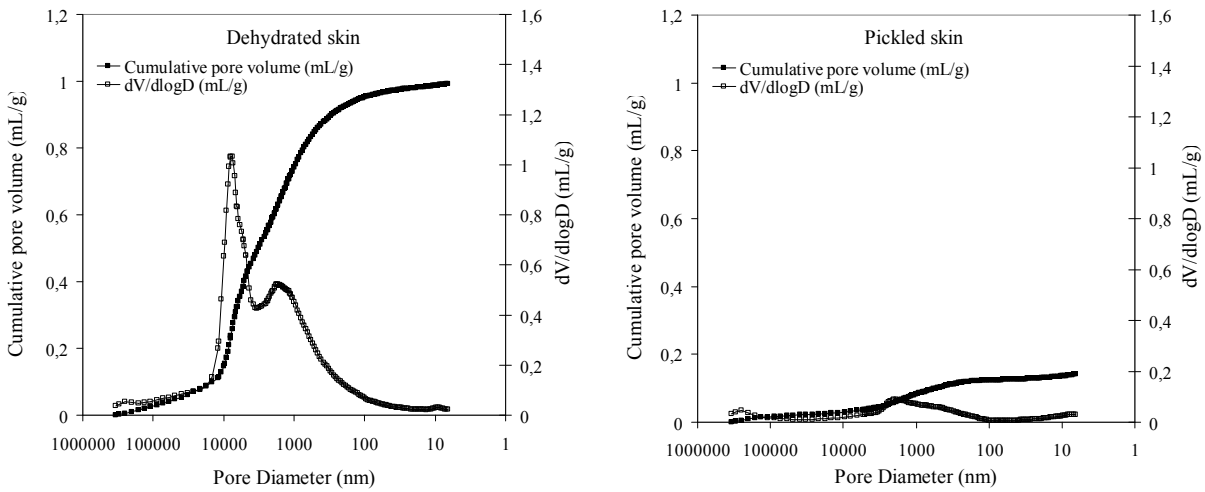
The results obtained vary widely for the different samples. The samples present a total pore volume of mercury intrusion of approximately between 0.7 and 1 mL g^{-1}, except for the pickled skin which has the lowest value, 0.14. This can be attributed to the reduction or blockage of porosity resulting from the chemical treatment to which the pickled skin was subjected. This preservation treatment protects the skin against external agents. The porosity value from 17% for pickled skin to 50-61% for the other samples confirms the above findings. The bulk density obtained at a pressure of 0.0045 MPa for pickled skin, 1.19 mL g^{-1}, was twice as high as the value obtained for the other samples, which showed values of around 0.6 mL g^{-1}. All the results suggest that the chemical treatment to which the pickled skin was subjected reduced its porosity.

There are numerous studies in the literature on the pore structure of different materials. Fatima et al. have studied the influence of crosslinking agents on the pore structure of skin [10]. They have also studied the effect of thermal shrinkage on the pore structure of native skin, and chromium and vegetable treated skin. The percentage reduction in porosity was greater for the vegetable skin than for the chromium treated sample.

Table 2. The intrusion data from the mercury porosimetry technique

	Dehydrated Skin	Pickled Skin	Wet Blue Skin	Skin Tanned with Silicates	Skin Tanned with Vegetable Tannins
Total Intrusion Volume, V_T, (mL/g)	0.992	0.141	0.671	1.015	0.682
Total Surface Area (m²/g)	10.1	5.6	3.7	2.8	20.9
Median Pore Diameter (Volume) (nm)	3251.5	1431.9	8585.4	15230.0	691.1
Bulk Density at 0.0045 MPa, ρ_b, (g/mL)	0.597	1.189	0.738	0.598	0.754
Skeletal Density at 227 MPa, ρ_s, (g/mL)	1.462	1.429	1.461	1.520	1.552
Porosity, ε, (%)	59.2	16.8	49.5	60.7	43.0

The cumulative pore volume and the pore volume size distribution obtained by mercury porosimetry for the samples are shown in Figure 3. The mercury porosimetry measurements show an important macroporosity development in the dehydrated skin and the skin tanned with silicates. The macropore volume development in these samples is more than seven times greater than that of the pickled skin. The latter was subjected to chemical treatment to reduce its porosity for purposes of preservation. Finally, wet-blue skin (skin semi-tanned with chromium salts) and skin tanned with vegetable tannins show a moderate development of macroporosity but less than that observed for the skin tanned with silicates. In general, it is apparent from these results that the development of macroporosity also depends on the tanning agent. There are numerous studies on the macropore volume development of different materials. In their work B. Ruiz et al. oxidised a coal and they studied the effect of oxidation on macropore volume development in carbonized coals [9]. Fatima et al. studied the cumulative intrusion volume of mercury in the porosity of native and shrunken samples of skin. It can be seen from the results that the cumulative intrusion of mercury is greater in the case of native skin than in the shrunken samples [10].



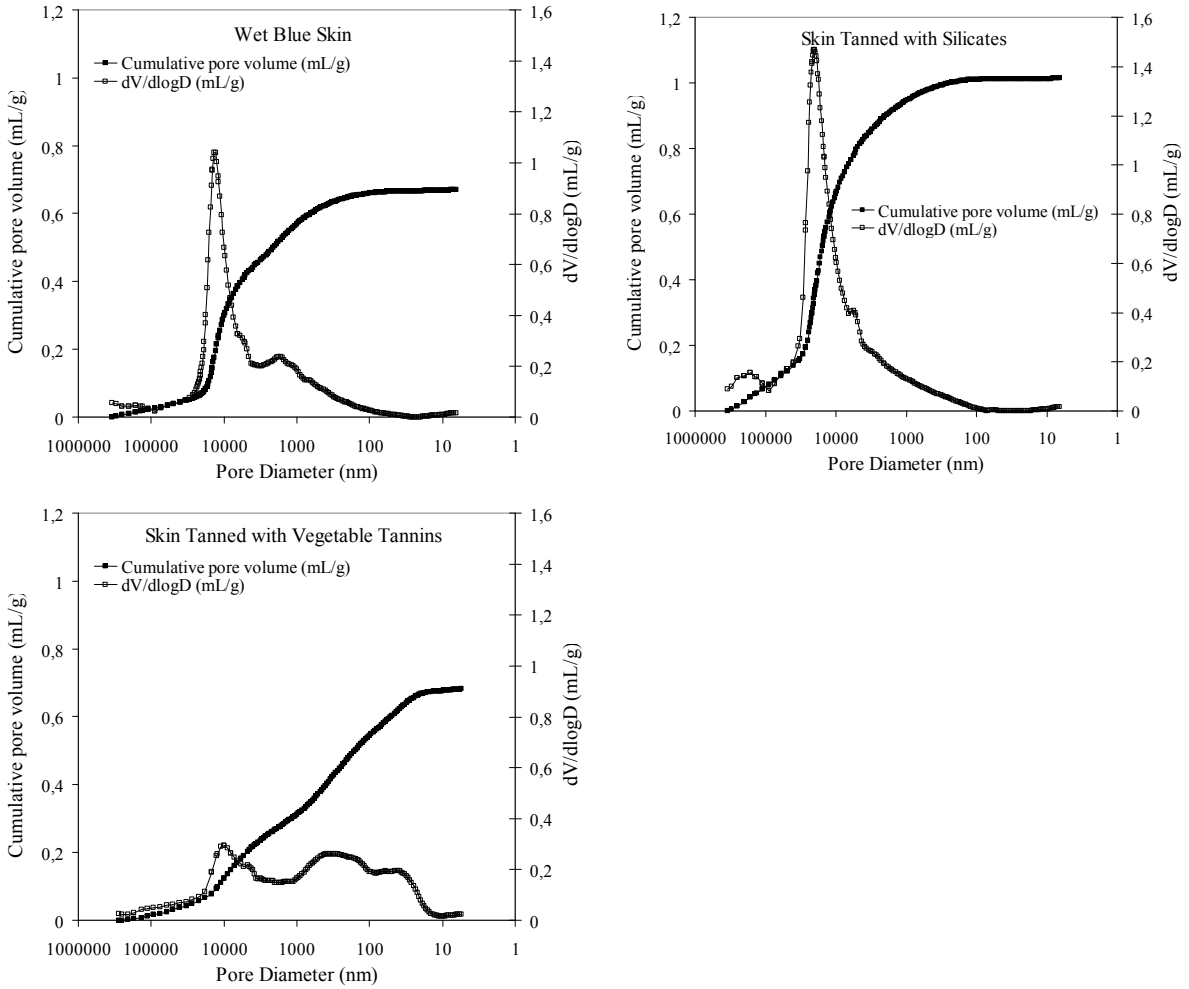


Figure 3. Cumulative Pore Volume and Pore Volume Size Distribution by mercury porosimetry for the samples of this research: Dehydrated Skin, Pickled Skin, Wet Blue Skin, Skin Tanned with Silicates and Skin Tanned with Vegetable Tannins.

The pore volume size distribution highlights the differences in the pore sizes of the samples (Fig. 3). Dehydrated skin, wet blue skin and skin tanned with silicates show bimodal volume pore size distributions with two maximum peaks at 7.5 - 1.5 µm, 13 - 1.7 µm and 19.5 – 5.2 µm respectively. The skin tanned with silicates presents a narrower distribution and higher pore sizes. The skin tanned with vegetable tannins shows a wide distribution pore size with three maxima at approximately 10 µm and 300 and 40 nm. Finally, pickled skin presents the lowest volume mercury intrusion with a maximum at 2 µm on the pore size distribution curve. The chemical treatment to which this sample was subjected seems to eliminate macropores larger than 5 microns.

4. Conclusions.

The mercury porosimetry studies carried out for this study have shown that the different skin treatments cause some changes in porous structure. The skin tanned with silicates presents a narrow distribution pore size. The skin tanned with vegetable tannins shows a wide distribution pore size. Pickled skin presents the lowest volume mercury. The chemical treatment to which this sample was

subjected seems to eliminate macropores larger than 5 µm. Therefore, mercury porosimetry is proposed as a suitable technique for the characterization of these kinds of materials.

5. References.

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