THE USE OF MERCURY INTRUSION POROSIMETRY TO THE CHARACTERIZATION OF EUCALYPTUS WOOD, PULP AND PAPER

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Abstract

Mercury intrusion is frequently used for the characterization of porous materials, giving access to parameters such as porosity and pore size distribution as well as density (skeletal and bulk). In the pulp and paper technology field, measurements of wood porosity are important, for instance to anticipate the liquor impregnation ability in the pulping stage. With regard to pulp and paper, porosity data also contribute to study the fibre network structure, enabling a better understanding of the influence of the process conditions on this structure. The present work aims at studying the suitability of the mercury intrusion technique to evaluate the pore structure of wood (Eucalyptus globulus) and also of pulp handsheets and commercial paper sheets. From the intrusion curves of the wood samples, it was possible to identify the pores corresponding to the vessels and to the fibre lumens. In the beaten pulp sheets as well as in the commercial papers, a consistent bimodal distribution of pores was obtained corresponding to two ranges of porosity: the internal porosity, with pores from 0.1 to 10 μm, and the surface porosity, that includes pores in the range 10⁻¹⁰⁰ μm. Changes in fibrous raw materials and in process conditions could be easily detected by differences in these porosities. Additional measurements by gas pycnometry, used to determine the true density of the samples, revealed the existence of a small quantity of pores inferior to 0.007 μm that are not accounted for by the porosimeter utilized.

Keywords: Eucalyptus globulus, mercury porosimetry, porosity, pore size distribution, density.

Introduction

Mercury porosimetry continues to be the technique of choice in many applications in which knowledge of porosity is critical. In addition it can provide measurement-derived values such as pore size distribution, density and surface area. Nevertheless, the number of studies devoted to the application of this technique to determine the pore structure of wood, pulp and paper is limited, the exception being the characterization of some coated papers (1,2) and specially pigment coatings (3,4).

This work focuses on the applicability of the mercury intrusion technique to the study of the porosity and pore size distribution of samples of wood, of pulp sheets produced in laboratory and of commercial paper sheets. The study of the wood is part of a more extensive work concerning the variability of the density and porosity of E. globulus wood with the radial position and along the stem in one tree (5,6). In the case of the sheets, the objective is twofold: firstly, to evaluate the suitability of the mercury intrusion technique to follow the influence of the papermaking operations, namely refining, on the fibre network porous structure; secondly, to provide a comparison between the structure of papers produced with different species or of distinct grades, in order to better interpret final paper performances like, for instance, printability.
Additional experiments were performed by gas pycnometry, basically to compare the absolute density with the density derived from mercury intrusion data at maximum pressure (30000 psia).

**Equipment Fundamentals**

**Mercury Intrusion Porosimetry**

The principle of this technique (7) is based on the fact that mercury does not wet most substances and, therefore, will not penetrate pores by capillary action, unless it is forced to do so. Liquid mercury has a high surface tension ($\gamma$) and also exhibits a high contact angle ($\theta$) against most solids. Entry into pore spaces requires applying pressure ($P$) in inverse proportion to the pore diameter ($D$), according to:

$$ D = \frac{-4 \cos \theta}{P} $$

(1)

For the present study, a contact angle of 130º and surface tension of 520 dyne/cm were used (8), and thus Equation 1 reduces to:

$$ D = \frac{220}{P} $$

(2)

where $D$ is expressed in $\mu$m and $P$ in psia. In mercury porosimetry, the sample is first evacuated, then surrounded with mercury and, finally, pressure is applied to force mercury into the void spaces whilst monitoring the amount of mercury intruded. Data of intruded volume of mercury versus applied pressure are obtained and the pressures are converted to pore sizes using Equation 2. The fact that these equations assume pores with cylindrical geometry is one of the major drawbacks of the technique.

In addition to porosity, mercury porosimeter is often used to perform measurements of density: bulk density and skeletal density (7). Bulk density is defined as the unit weight per unit volume of a material after the volume of the largest open pores has been subtracted. In the present study, the typical value for the largest pore included in the bulk density is approximately 200 $\mu$m (which corresponds to an intrusion pressure of about 1 psia). Skeletal density is usually computed after the volume of all pores larger than those measured at maximum intrusion pressure have been excluded from the volume presumed occupied by material. In this work, the highest intrusion pressure was 30000 psia, corresponding to pores of about 0.007 $\mu$m in diameter.

**Gas Pycnometry**

Gas pycnometry is based on Boyle’s Law, which states that pressure decreases when a confined volume of gas is allowed to expand into a larger confining space. If the volumes of the confined and the expanded spaces are known, then the volume of a sample previously weighted and placed in the confined space can be determined by measuring gas pressure changes (7). Helium is the most frequently used gas because of its inertness and small size of atoms. The difference between the absolute density and skeletal density indicates the quantity of pores that is not accounted for by porosimetry.

**Materials**

In this study mercury intrusion measurements were performed in the Poresizer 9320 from Micromeritics. The porosity of *E. globulus* wood was assessed by using 1.2 cm$^3$ cubic blocks collected at different radial and axial positions along the stem of a 7 year old tree. For the pulp laboratory sheets as well as for the commercial paper sheets, small square samples, corresponding to a total weight of approximately 0.5 g, were used. The laboratory sheets were produced with both *E. globulus* and Birch bleached kraft pulps, obtained by cooking wood chips
at 160°C in a 6 L batch digester using a pulping liquor with an alkali charge of 16 % Na₂O and a sulphidity of 30 %. These pulps were bleached by a conventional ECF sequence (DEDED) and finally beaten in a PFI mill so that 30ºSR was reached. Additional tests were conducted with the unbeaten *E. globulus* bleached kraft pulp (19º SR) in order to investigate the influence of the beating operation in the pore structure of the pulp handsheets. Measurements were also carried out with sheets of printing and writing commercial paper and of decorative print base paper, both mainly of *E. globulus*, in order to test the sensitivity of the technique to changes in the amount of fillers.

With regard to the determination of the absolute density, a helium pycnometer was used – Accupyc 1330 from Micromeritics –, being the sample chamber filled with wood (previously reduced to sawdust), pulp or paper up to 2/3 of its volume.

For each sample and technique, measurements were repeated, on average, three times, and in the following discussion typical results will be presented.

**Results and discussion**

Figure 1 shows a typical plot of the relative and cumulative pore size distributions obtained for eucalypt wood. The first peak on the left, corresponding to the intrusion in the range 10-150 µm, certainly represents the penetration of the mercury into the vessels. However, the other two peaks, that should reflect the volume intruded in the fibres, are apparently displaced to rather small diameters (fibre diameter is about 10 µm (5)). This is a consequence of the presence of pores of non-cylindrical shape, in particular with restricted necks opening to large void volumes (ink–bottle shape). Indeed, the intrusion of mercury into the fibres takes place through small openings in their walls, called pits, whose diameter is below 1 µm (9). In this case, all the volume intruded in the fibres will be assigned to the pit diameter and not to the lumen diameter. The second larger peak can be related to the existence of smaller pit apertures or to wood pits that include a membrane (9). In both situations a higher pressure is required to force the mercury inside the fibres and consequently a lower diameter is calculated. The mean value for the total porosity, weighted for the whole stem according to the radial distance of the sample, was 54% (5).

As mentioned before, mercury porosimetry data was also obtained for handsheets of *E. globulus* pulps, before and after beating. Considerable differences were found for both pulp sheets not
only in terms of total porosity (79.1 % and 47.6 %, respectively for the unbeaten and the beaten pulp) but also in pore size distribution, as shown in Figure 2.

Figure 2. Relative pore size distributions of handsheets of *E.globulus* bleached kraft pulps, before and after beating.

Figure 3 compares the pore size distributions of handsheets produced with beaten pulps of different fibres. As can be seen, the distribution curve of the birch pulp sheet is similar to that of the eucalypt pulp. However, although being both predominantly bimodal, the peaks corresponding to the birch pulp are more separated. These two ranges of porosity have been defined by Silvy *et al.* (10) as: i) surface porosity, that includes pores in the range 10-100 µm, and ii) internal porosity, with pores from 0.1 to 10 µm. Table 1 quantifies the differences between both types of handsheets in terms of total, surface and internal porosity, showing that *E. globulus* handsheets possess slightly higher internal porosity.

Figure 3. Intrusion data obtained for handsheets of Birch and *E.globulus* bleached kraft pulps beaten at 30°SR.

The examples of Figures 2 and 3 (and Table 1) illustrate the suitability of mercury porosimetry to easily detect differences in the pore structure of pulp handsheets, being therefore a valuable
tool to anticipate (or confirm) properties like drainability, air permeance, roughness and printability.

Table 1. Total porosity, surface porosity and internal porosity of Birch and *E. globulus* pulps, obtained by mercury intrusion.

<table>
<thead>
<tr>
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<th>Total Porosity, %</th>
<th>Surface Porosity, %</th>
<th>Internal Porosity, %</th>
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<tbody>
<tr>
<td>Birch pulp</td>
<td>41.2</td>
<td>19.6</td>
<td>19.0</td>
</tr>
<tr>
<td><em>E. globulus</em> pulp</td>
<td>47.6</td>
<td>19.2</td>
<td>23.6</td>
</tr>
</tbody>
</table>

The similarity between the pore size distribution curves of pulp handsheets and of sheets of a commercial printing and writing paper (both *E. globulus* based), evident in Figure 4, is remarkable and somehow unexpected, since the industrial papermaking process is quite different from that of the laboratory.

![Figure 4. Comparison of pore size distributions of a commercial printing and writing (P&W) paper and of a bleached kraft pulp handsheet (both *E. globulus* based).](image)

Nevertheless, even though both distributions are bimodal and have very close modes, the values of Table 2 reveal that the total porosity of the paper sheet is slightly higher than that of the pulp handsheet, reflecting the increase in the internal porosity of the paper presumably due to the effect of fillers.

Table 2. Total, surface and internal porosity of a commercial printing and writing (P&W) paper and a bleached kraft pulp handsheet (both *E. globulus* based).

<table>
<thead>
<tr>
<th></th>
<th>Total Porosity, %</th>
<th>Surface Porosity, %</th>
<th>Internal Porosity, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial P&amp;W paper</td>
<td>54.2</td>
<td>15.8</td>
<td>35.3</td>
</tr>
<tr>
<td>Pulp handsheet</td>
<td>47.6</td>
<td>19.2</td>
<td>23.6</td>
</tr>
</tbody>
</table>

The effect of fillers in the internal paper network is more visible in Figure 5, where a commercial printing paper and a decorative print base paper (the latter with a quantity of fillers approximately double of the former) are compared in terms of intrusion data. Clearly seen on the right side of the distribution is one small peak that most certainly corresponds to the filler porosity of the decorative paper.
Figure 5. Relative pore size distributions of a commercial printing and writing (P&W) paper and of a decorative print base paper.

One of the limitations of the porosimeter used is that no measurements above 30000 psia are allowed, which, accordingly to Equation 2, means that pores with diameters below about 0.007 µm are not detected. Thus, if the sample possesses pores smaller than this limit the density determined at maximum pressure (skeletal density) will differ from the sample absolute density. In order to check how close the skeletal density provided by porosimetry is of the sample absolute density, the latter was measured in a gas pycnometer. The results of the comparison are listed in Table 3. As can be seen, almost coincident values are obtained for the density of the wood sample measured by the pycnometer and by the porosimeter at maximum pressure whereas some higher deviation was detected for the corresponding values of the pulp and the paper sheets. This result indicates that a small quantity of pores (< 0.007 µm) is really not accounted for in the intrusion measurements. The fact that the values of the absolute density of the sheets are larger than that of cellulose (1.54 g/cm³) is probably related to the presence of other components, namely non-cellulosic compounds like fillers in the case of the commercial P&W paper.

Table 3. Wood, pulp handsheet and commercial P&W paper densities (absolute, skeletal and bulk), evaluated by distinct methods.

<table>
<thead>
<tr>
<th></th>
<th>Absolute Density* g/cm³</th>
<th>Skeletal Density** g/cm³ (P=30000 psia)</th>
<th>Bulk Density** g/cm³ (P≈1 psia)</th>
<th>Bulk g/cm³ (ISO standard)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood</td>
<td>1.46</td>
<td>1.44</td>
<td>0.57</td>
<td>----─</td>
</tr>
<tr>
<td>Pulp handsheet</td>
<td>1.65</td>
<td>1.50</td>
<td>0.78</td>
<td>0.78</td>
</tr>
<tr>
<td>Commercial P&amp;W paper</td>
<td>1.70</td>
<td>1.60</td>
<td>0.73</td>
<td>0.76</td>
</tr>
</tbody>
</table>

* Measured by Helium pycnometry
** Measured by Mercury porosimetry

The results of the bulk density given by mercury intrusion at the lowest intrusion pressure (1 psia) and those calculated from the standard sheet grammage and thickness measurements (ISO 534) are also displayed in Table 3. The similarity between these values indicates that mercury intrusion is a good alternate method to evaluate this very important structural property.
Conclusions

The present work has demonstrated the ability of mercury porosimetry to characterize the porous structure of materials like wood, and pulp and paper sheets. This technique not only provides information about the sample total pore volume, which enables the evaluation of porosity, but also about pore size distribution and density. This information can be very useful to anticipate paper performance, namely in terms of surface roughness, printability and coating distribution.

Some caution is however required in data interpretation since the theory behind the conversion of applied pressures into the diameter of pores assumes these as perfect cylinders, which is obviously an approximation in the present case.

Nevertheless, for the pulp and paper sheets, and based on the pore size ranges, it was possible to detect differences in the surface and internal porosities due to changes in the characteristics of the raw material and in process conditions. Work is under development in order to distinguish the pore size distribution on each side of the paper sheet, enabling a more detailed study of the surface porosity and consequently of the properties which depend on this parameter.

References