

THE SPECIFIC PORE VOLUME OF MULTI-PLANAR WEBS: THE ROLE OF THE SHORT AND LONG FIBRE FRACTIONS

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ABSTRACT

Pore volume of paper sheets as measured by mercury intrusion porosimetry can provide an alternative structural description to solid phase-based measures such as density and may be used to examine sheet structure. We measured sheet densities and specific pore volume, i.e. the pore volume per unit sheet mass, for sheets made from whole pulp and the long fibre fraction of five different pulps. The coefficient of variation was 50% and 28% for specific pore volume and density of different pulps, respectively. Pore volume was more sensitive to structural differences than density. A theoretical measure of specific pore volume of the long fibre fraction (R48) was derived from the Interactive Multi-Planar Model (IMPM) of sheet structure. For the whole pulp we assumed that the shorter material (P48) filled voids and thus diminished the specific pore volume of the long fibre fraction (R48). Model predictions of specific pore volume agreed well with mercury porosimeter determinations for most of the samples. The effect of

P48 fraction on sheet porosity was greater for newsprint than for hardwood kraft pulps.

INTRODUCTION

Multi-planar models conceptualize sheet structure as superimposition of two-dimensional networks, which interact when wet pressure is applied [1–4]. Using network statistics, the structure of two-dimensional networks can be expressed in terms of fibrous properties, such as the average distance between fibre crossings and the number of crossings per unit mass of fibres [1]. But, structure may also be expressed in terms of the void properties of the networks, such as the total projected void area per unit fibre mass or the average area of individual voids [1].

The relationship between network void structure and fibre properties has been used to calculate fibre coarseness from a thin network [5], and to explain airflow through a sheet [6]. Void structure is not only related to the transport phenomena through a sheet but also to printability [7,8] and optical properties of paper [9]. In addition, pore structure may be used to investigate the validity of paper structure models from an alternative viewpoint.

Despite its importance, few workers have quantified the pore volume of paper and related it to fibre or network properties [7,12]. The objectives of this work were

- To test whether the Interactive Multi-Planar Model, IMPM [2,3] could predict total sheet porosity from fundamental fibre properties.
- To evaluate the effect of short material (P48) on the porous and fibrous structure of paper.

EXPERIMENTAL

Five pulps were chosen for this work: Two hardwood kraft pulps, one softwood kraft and two newsprint furnishes composed of a mixture of mechanical and recycled pulps. Table 1 lists fibre properties of the R48 fraction and the percentage of the P48 fraction in each pulp. Standard handsheets were made and sheet properties were measured using PAPTAC standards. Fibre coarseness and length were measured using the Fibre Quality Analyzer (FQA), fibre thickness was measured with a stylus method [18], fibre width and wet fibre flexibility were measured using the method described by

Table 1 Fibre properties of pulps used in this study.

Pulp	P48 (%)	Fibre		Thickness (μm)				Width (μm)	WFF ⁽¹⁾ 10 ¹¹ 1/N.m ²
		Length [mm]	Coarseness (mg/100m)	t _M	t _o	t _x	t _{2w}		
Hardwood Kraft 1	40.2	1.77	14.2	4.8	27	2.2	2.2	42	8.8
Hardwood Kraft 2	50.3	1.49	11.7	4.7	19	2.5	2.5	30	10.4
Softwood Kraft	12.3	2.56	15.3	4.2	20	3.1	3.1	32	8.9
Newsprint 1	39.1	1.55	14.1	5.8	16	4.8	3.6	25	12.8
Newsprint 2	50.4	2.14	20.8	4.9	24	7.3	3.5	38	5.1

(1) WFF – wet fibre flexibility [24]

Steadman and Luner [24]. We included four measures of fibre thickness in our report because of the sensitivity of the IMPM to this fibre property: the median of the measured thickness distribution, t_M, the double cell wall thickness, t_{2w} [25,26], the estimated uncollapsed thickness, t_o [18], and the thickness t_x for a computed degree of collapse for the newsprint pulps [18].

Mercury porosimetry

Mercury intrusion porosimetry measures the volume of mercury that can be forced into a porous solid under increasing pressures. The final volume of mercury pushed into the solid gives the pore volume of the solid. Mercury intrusion porosimetry has been used in paper research to characterize pore size distribution of sheets [7] and to relate pore size and porosity of sheets to fibre properties such as coarseness and fibre thickness [12]. In other fields of study it has been shown that mercury intrusion porosimetry does not affect pore structure of compressible solids even when high pressures are applied [15].

Mercury intrusion porosimetry quantifies the pore size distribution of a solid by the volume of mercury that intrudes into structure at a defined pressure. However, it does not measure the volume of unconnected pores in the sheet. The intrusion pressure is inversely related to the diameter of the pores through which intrusion occurs. The relationship is given by the Washburn equation [16]:

$$D = \frac{-4\gamma \cos(\alpha)}{P} \quad (1)$$

where γ is the surface tension of mercury and α is the contact angle of mercury on cellulose. Pore size distributions and pore volume were measured from 0.1 to 100 μm diameter using a Micromeritics 9400 Pore Sizer (Micromeritics, Norcross, Georgia, USA). For each pulp, 3 to 5 replicate measurements were made. Each sample weighed 0.1 g and was taken from the center of a handsheet. Samples were dried in a desiccator and degassed to a vacuum pressure of 50 $\mu\text{m Hg}$ prior to analysis.

THEORETICAL

The IMPM stipulates that the basis weight of a single two-dimensional layer is determined by the mass of fibres required to cover exactly one percent of the network area with fibre crossings. This stipulation makes it possible to equate layer thickness with fibre thickness [2]. Network statistics [1] predicts that the probability of finding one or more fibres at any point in such a network is $P(F) = 0.144$. This fraction is the same for any pulp. Conversely, the fraction of the area covered by voids is always $1 - P(F) = 0.856$, regardless of the pulp used. The porosity, ε , of a single sheet layer that is unaffected by any other layer is:

$$\varepsilon = 1 - P(F) \quad (2)$$

However, when a sheet is wet pressed, network layers interact and the probability of finding a fibre within a given plane is greater by a factor, $\Lambda(m)$, which gives the penetration of fibres from m surrounding layers into the target layer. $\Lambda(m)$ depends on fibre coarseness, thickness, width, length and wet flexibility, and on the position of the layer within the sheet. A layer at the surface will have a lower $\Lambda(m)$ than the central layer because fewer layers are available to interact. After wet pressing the porosity of a layer is:

$$\varepsilon = 1 - P(F)\Lambda(m) \quad (3)$$

In the whole pulp the shorter materials reduce the layer porosity by filling spaces. To a first approximation, the porosity is corrected by a factor proportional to the weight fraction of shorter materials (r_f), thus,

$$\varepsilon = 1 - P(F)\Lambda(m)(1 + r_f) \quad (4)$$

Mercury porosimetry measures the specific pore volume, V_s , that is, the volume of voids per unit mass of fibre. V_s can be expressed as a function of layer basis weight, g_l , layer thickness, t_f , and porosity,

$$V_s = \frac{\epsilon t_f}{\Lambda(m)(1 + r_f)g_l} \quad (5)$$

Equations 4 and 5 do not account for the effect of bridging and blocking [10] that the finer material may have on the long fibre matrix, and is a first approximation of sheet porosity in the presence of the P48 fraction.

To test whether the P48 fraction primarily bridged or blocked the long fibre matrix, we computed the fibrous density and compared it to the long fibre density. Fibrous density [10,14], ρ_F , can be calculated as:

$$\rho_F = \rho(1 - r_f) \quad (6)$$

where ρ is sheet apparent density including the fines, and r_f is the P48 fraction. If bridging by P48 fraction dominates, the fibrous density should be greater than that of the long fibre fraction alone. If blocking dominates, the fibrous density should be less.

Predictions of $\Lambda(m)$ and apparent density are most sensitive to fibre thickness, which cannot be determined accurately from mounted fibre samples [18]. The measurement techniques probably do not account for collapse of fibres at fibre crossings during wet pressing and could explain underestimates of mechanical pulp densities by the IMPM. Apparent density calculations with the IMPM using the assumption that fibre thickness was equal to the double cell wall thickness (100% collapse) have been successful for hardwood and softwood kraft fibres [12,17]. For mechanical pulps we assumed that fibres were collapsed 94% (recycled) and 83% (newsprint). We computed the percent collapse for newsprint pulps from a regression of collapse-coarseness data in Gorres et al. [18] to account for possible mechanical pulp components in these commercial pulps.

RESULTS AND DISCUSSION

Figure 1 shows the mercury intrusion curves for five whole pulps which are distinguished by the magnitude and the position of intrusion modes in the pore size distributions.

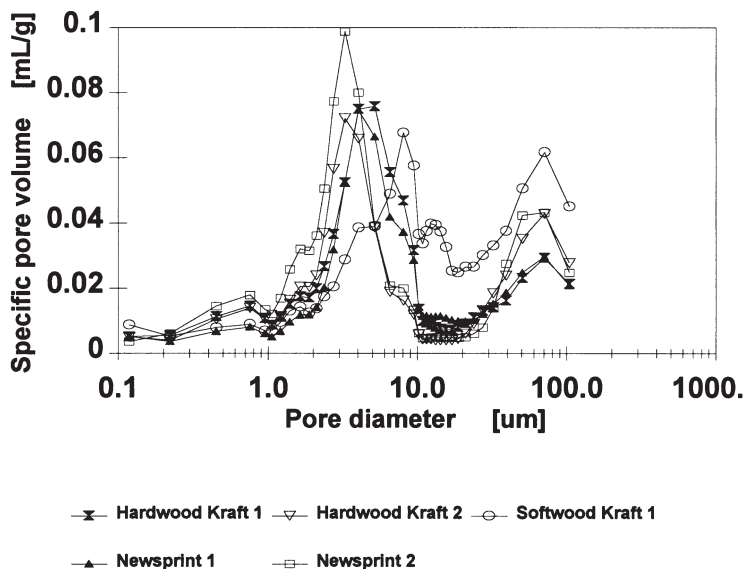


Figure 1 Pore size distributions for the five whole pulps.

The pore size distribution of sheets made from the whole pulp and the long fibre fraction are shown in Figure 2 for a newsprint furnish (A), a hardwood kraft pulp (B), and a softwood kraft pulp (C). Removing the fine material shifted the pore size distribution to the right and increased the average pore volume. The peaks between 10 and 100 μm are associated with surface pores whereas those smaller than 10 μm are primarily pores in the sheet interior [7].

The pore size distributions for the long fibre fractions have three peaks: *a* and *b* are for pores accessible through the surface and *c* for pores in the interior of the sheet [7,12]. There are only two intrusion peaks for the sheets made from the whole pulp. In these samples the *a* peak is shifted towards smaller volume and *b* is absent probably as a result of filling some of the voids by the fine material of the P48 fraction.

In addition peak *c* in the pore size distribution of the whole pulp is shifted to a smaller pore neck diameter. There is little intrusion into pores of less than 1 μm in diameter regardless of the sheet type investigated, which is consistent with the findings of Chiody and Silvy [7].

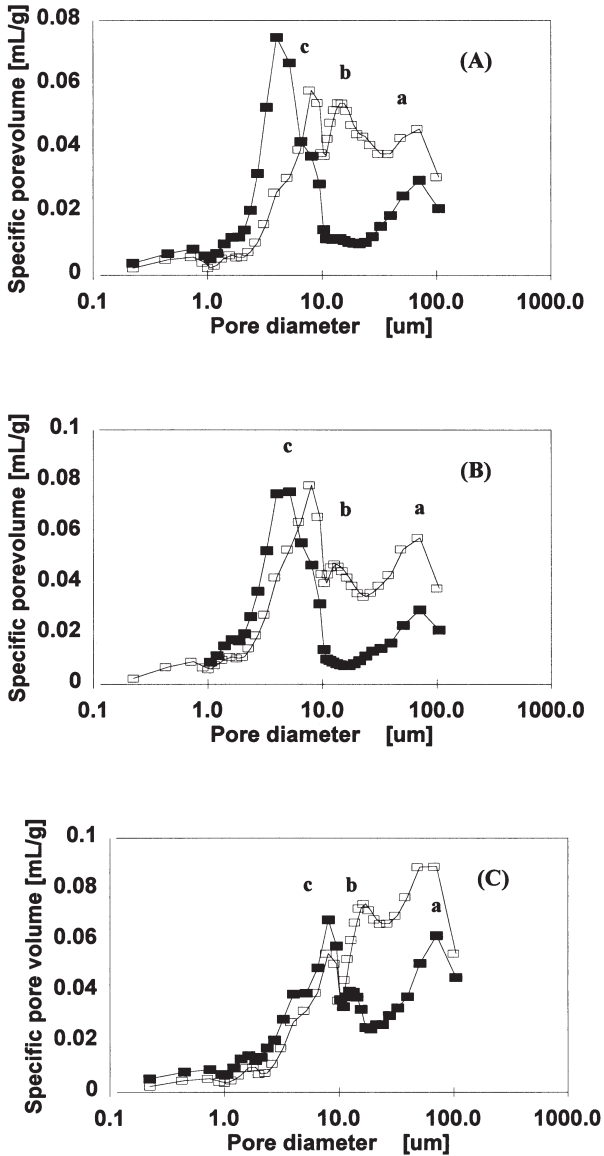


Figure 2 Pore size distribution for Newsprint 1 (A), hardwood kraft 1 (B) and softwood kraft (C). (■) represents pore size distribution for whole pulp and (□) for the long fibre (R48) sheet.

Table 2 Specific pore volume for pores greater than 1 μm .

Pulp	Whole Pulp (mL/g)		Long Fibre Fraction (R48) (mL/g)	
	Mean	Std. Deviation	Mean	Std. Deviation
Hardwood Kraft 1	0.70	0.02	1.14	0.05
Hardwood Kraft 2	0.71	0.14	1.21	0.25
Softwood Kraft	1.09	0.11	1.34	0.16
Newsprint 1	0.66	0.06	2.29	1.11
Newsprint 2	0.89	0.16	2.60	0.80

Table 2 lists the total pore volume intruded by mercury through pores larger than one μm . Specific pore volume of the long fibre fraction was always higher than that of the corresponding whole pulp sheets.

Most of the differences in specific pore volumes of whole pulp and long fibre fraction occur in the pore diameter interval of 10 to 100 μm . This is the range in which intrusion is believed to occur mainly through surface pores of the sheet. The P48 fraction appears to fill voids either at the surface or in pore volume that is directly accessible through the surface pores.

Using the fines model presented by Görres et al. [10], we also investigated whether the P48 fraction affected the density of the long fibre fraction. We computed the fibrous density (long fibre weight considered only) with equation 6 and compared it with the sheet density of the long fibre fraction. We found that in all pulps, except the softwood Kraft pulp for which the amount of P48 was much less than the other pulps, the long fibre fraction density was greater than the fibrous density of the whole pulp. The P48 fraction, thus, blocked the long fibre deflections by filling the voids through which fibre deflection occurs in the sheet structure. The difference between the long fibre fraction and the whole pulp pore volumes was 3–4 times greater for the newsprint than for the kraft pulps (Figure 3). This difference may be a function of the distribution of particles within the P48 fraction (Table 3) and the nature of the fines material in this fraction. It could also be related to the properties of the long fibres in kraft and newsprint pulps. Kraft fibres are generally more flexible and collapsed than mechanical or recycled fibres. Thus, sheets made with these fibres are denser and contain less internal voids. Consequently, the difference in pore volume of sheets made from the whole pulp and the long fibres is less for kraft than for mechanical or recycled pulps, such as present in the newsprint furnishes.

The newsprint furnishes contained some mechanical pulp components. The density of short fibres and fines in newsprint samples may be different

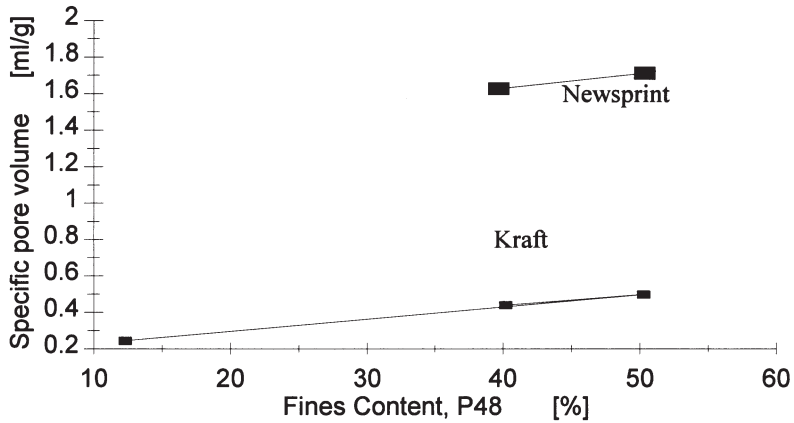


Figure 3 Porosity difference between whole pulp and R48 fraction as a function of P48 content. Differences for newsprint pulps are about 3 times higher than for kraft pulps.

Table 3 Bauer-McNett fractions for five pulps.

Pulp	R14	P14/R28	P28/R48	P48/R100	P100/R200	P200
Hardwood Kraft 1	18.7	15.5	25.6	22.9	6.2	11.1
Hardwood Kraft 2	6.1	15.8	27.9	22.1	6.7	21.5
Softwood Kraft	57.8	19.2	10.6	1.6	5.6	7.2
Newsprint 1	8.5	17.8	34.0	22.8	6.9	10.0
Newsprint 2	13.9	18.3	17.4	14.0	11.1	25.3

from that of similar material in kraft pulps. For example, Retulainen [19] found that the density, shape and surface area of TMP fines differed from Kraft fines. The efficiency with which finer material can block, bridge or fill the voids may depend on characteristics of the particles. It has been suggested that different types of fines may take different roles in the fibrous matrix [21,22,10], as determined by different characteristics [23].

We have no information about the nature and properties of the fine particles in these pulps and cannot evaluate at this stage their role in the filling and blocking in the whole pulp sheets.

It has been recognized that improvements in sheet properties can be achieved by adding fines material. However gains are limited to additions below a threshold called the limiting state [11]. Within the framework of the IMPM, the critical state was represented by the balance of two competing processes [10]. In the one process, fines provide bridges between sheet layers that are too far apart to bond in the absence of fines. In the other process, fines block the deflection, and, thus, prevent direct bonding between fibres in different layers. It was hypothesized that the limiting state is reached when the two processes are balanced. Fibrous density results (not shown) showed that the P48 fraction effectively blocked deflections of the long fibre fraction in all but the softwood kraft pulp. This occurs primarily because the P48 fraction contains not only fines but also material coarser than the fines fraction (P100) which block long fibre deflections in the sheet. For the softwood kraft pulp the total P48 fraction amounts to 14%, with 1.6% in the P48/R100 fraction. There was not enough finer material (P48) in the softwood kraft pulp to exceed the limiting state.

Specific pore volumes were computed with Equation 5, setting $r_f = 0$ for fines free sheets. We used the fibre properties listed in Table 1 and the following assumption: partial fibre collapse for the newsprint pulps was calculated from regressions using data from Gorres et al. [18] and 100% collapse for the kraft pulps [17]. The predicted and measured specific pore volumes were linearly related ($r^2 = 0.832$, $P(t) < 0.00022$), with the same regression line fitting both long fibre and whole pulp sheets (Figure 4). Equation 5 assumes implicitly that P48 material fills pore spaces. The strong linear relationship between predicted and measured pore volume confirmed that the P48 fraction primarily fills void space in most pulps studied in this work. The specific pore volumes were substantially overpredicted for both the whole pulp and the long fibre fraction (R48) of newsprint 2. Experimental error in determining fibre properties for this pulp may be one explanation for the discrepancy. This pulp has the most stiff, coarse and thick fibres among the samples we studied (Table 1). The variability in fibre property measurements, in particular in flexibility and thickness, is higher for very rigid fibres. This could cause the model to overestimate pore volumes for newsprint 2. The effect of the fines fraction on a network of stiff and thick fibres could also be different from other pulps. These issues will be further studied and clarified in future work.

Specific pore volume and sheet density reflect different aspects of paper structure. Specific pore volume determinations had a coefficient of variation across the pulps of 50% whereas for density the coefficient of variation was 28%. Specific pore volume may be a more sensitive measure of structure than density. Porosimetric analysis may provide information about sheet structure that is complementary to the density measurements.

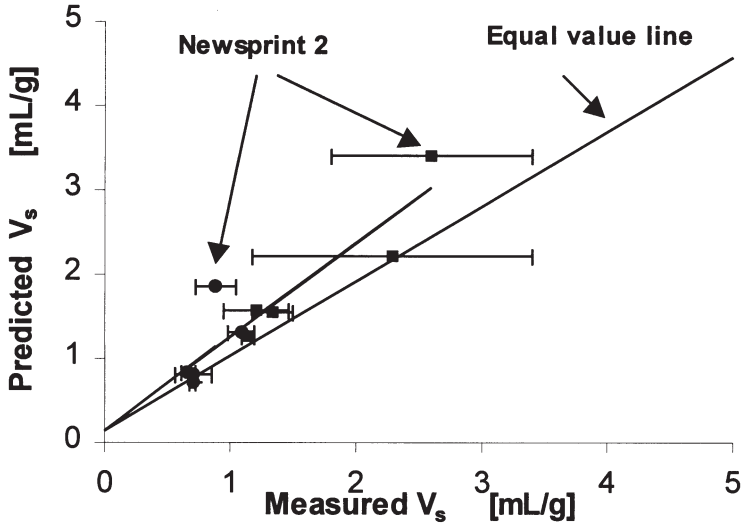


Figure 4 Relationship between predicted and measured specific pore volume. (■) represents fines free sheets and (●) represents whole pulp sheets. Error bars represent one standard deviation around the mean of the measured values. The regression line represents the relationship between predicted and measured specific pore volumes of whole and long fibre pulps.

CONCLUSION

The Interactive Multi-Planar paper structure model was used to predict the specific pore volume of sheets made with whole and long fibre fractions of various pulps. For most pulps studied in this work, a good agreement was obtained between the predicted pore volume and the corresponding volume measured with mercury porosimetry. We found that, for a given pore diameter, there were more voids in sheets made of long fibres than those made from the corresponding whole pulp. The P48 fraction filled the voids in the sheet and thus reduced the pore volume of the fibrous matrix. The effect of P48 fraction on sheet porosity was greater for newsprint than for softwood kraft sheets.

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Transcription of Discussion

THE SPECIFIC PORE VOLUME OF MULTI-PLANAR WEBS: THE ROLE OF THE SHORT AND LONG FIBRE FRACTIONS

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Lars Wågberg Mid-Sweden University

I have a question regarding your measurement techniques with mercury. Mercury intrusion is not a very suitable equipment for measurement of large pores and I am a bit worried when I see that you measured pores that are 100 micro-meters with a mercury intrusion. So I wondered how can you do that with high accuracy on an 0.1 g sample as you are stating in your text.

Josef Görres

Absolutely, that is a very good question and the trick is to get the right instrument. Most instruments that you can buy have a sample holder with a very long neck and you put the paper into the sample holder and put the neck on, and when you measure intrusion what you measure is how quickly mercury disappears in that neck. You can do that either by electrical methods or by optical methods by just looking at where that happens, so most instruments that I have worked with in the past had necks that were orientated vertically. When you were filling mercury into the sample holder after the sample was evacuated you fill the sample up and sometimes when you have a sample that is really porous, perhaps not with paper but with soils; you see that you can't put enough mercury in because it keeps disappearing into the sample. You have but 15 cms of mercury pressure right on top of the sample as you are filling it and that wipes out 50% of your pore space, so the trick is to get an instrument that has a horizontal sample holder that evacuates and

Discussion

fills the sample holder with mercury in a horizontal position so you only have maybe 2 or 3 mms of mercury on top of the sample.

Lars Wågberg

That is correct but you need a pressure regulation to measure a 100 micro-metre pore that is unbelievable. Maybe you have that and that is good.

Josef Görres

I believe that we can ascertain that by using standards, and we usually use standards for QCQA on our measurements. That is a very good question though, it is really important that you take care at that point. If you had that instrument and you were interested in porous solids then most porous solids people are not interested in anything larger than 20 microns. They just fill the low pressure port and put in a high pressure port and then increase pressure on until they reach pore dynamics that of interest. Of course with paper you can't do that as I am interested in two dimension network structures too.

Lars Wågberg

We are using the pore volume distribution equipment from TRI. In this equipment you can fill the paper with a non-swelling liquid and by applying a gently increase in air pressure and reading the amount of liquid leaving the sample you can, with high accuracy determine the amount of large pores in the 'dry' paper. Maybe you could cross correlate the measurements.

Josef Görres

That is a great technique to compare the two measurements also.

Bill Sampson Department of Paper Science, UMIST

It is very interesting that you say that the co-efficient variation across these pulps was about the same at 50%. What this means is that we have standard deviation proportional to the mean as given by theory and by the porosimetry method of measuring pore radius also. I think the persistence across all those pulps is another example of structural stability across a range of furnishes – so very nice to see.