Drying kinetics as a new tool for the estimation of pore size of materials

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ABSTRACT
The rate of drying of porous materials is constant up to a critical degree of drying (x_c), where it starts decreasing as the process occurs. This critical extent of the process correlates with mean pore size. Determination of x_c is useful for the assessment of porosity between materials of a particular chemical composition. This new approach is much simpler than the usual determination of surface features.

Key words: Drying curves, diffusibility of liquids in porous materials, porous materials, pore size.

RESUMEN
La rapidez de secado de materiales porosos es constante hasta llegar a un valor crítico de secado (x_c), en donde la rapidez del proceso disminuye conforme avanza el proceso. Este grado de avance crítico correlaciona con el tamaño medio de los poros. La determinación de x_c es de utilidad para comparar la porosidad de materiales de una cierta composición química. Este nuevo enfoque de análisis de curvas de secado es mucho más simple que las determinaciones usuales de caracterización de superficies.

Palabras claves: Curvas de secado, difusibilidad de líquidos en sólidos porosos, materiales porosos, tamaño de poros.

Drying is an essential process in many technological areas. This unit operation reflects primarily the diffusivity of liquids (*e.g.* H_2O) within porous matrices of materials. Liquid diffusivity is also an important factor in heterogeneous catalysis; either classical (mobile reagents and fixed catalyst) or in the saccharification of lignocellulosic materials (fixed substrate and mobile catalyst).

Lignocellulosic residues have great potential as renewable energy sources, thus offering a partial solution of the shortage problems of conventional fossil fuels. Whatever technology is developed based on this kind of feedstock, small and dry particles are required. Drying kinetics is therefore a useful way to achieve better design and improvement of drying equipment.

In this paper, I describe a new simple method for the estimation of the relative diffusivity of H_2O in filter paper as model, based on the drying kinetic parameter x_c (*vide infra*).

The qualitative model. The mathematical description of drying curves is useful for the understanding of the supramolecular features of materials in the drying process:

$$\text{fluid}_{\ (\textit{in solid matrix})} \longrightarrow \text{fluid}_{\ (g)} + \text{dry solid}$$

It is useful to express the experimental data as drying rates, *dx/dt*, where *x* is the extent of the process that has occurred at time *t*, plotted as a function of the fraction of residual moisture (1 – *x*) associated with the solid material (Mujumdar & Devahastin, 2000), under specific environmental conditions of temperature, relative humidity and barometric pressure. This type of representation is known as Krischer curve (Kemp et al., 2001). It must be noted that *x* is conceptually different to the commonly used "*X*" in the literature: the dry-basis moisture content, kg of moisture content per kg of dry bone material (Geankoplis, 2006).

Curves given as mass (or *x*) vs. *time* show an initial linear relationship. This means that *-dm/dt* (or *dx/dt*) is constant (see Figure 1 as example). Once a certain critical value is reached (t_c, x_c), the rate of drying decreases as the process takes place. During the first period, the surface of solid particles is entirely covered by liquid molecules. This film of free liquid behaves as if no solid substrate were present beneath, thus its evaporation rate is independent of the chemical nature of the solid material (Geankoplis, 2006). This constant rate process is defined by the liquid vapour pressure above the particle surface. The linear kinetics continues for as long as the rate of liquid arrival at the surface equals the rate of evaporation.

Once the system achieves the condition t_c - x_c, the surface is no longer covered uninterruptedly by the liquid molecules, and the fraction of surface covered by the liquid decreases during the period beyond t_c due to internal transport limitations.

The ease of flow of liquids through solid porous matrices is given by the diffusivity of the moving particles and takes place by either Fickian diffusion or by capillarity. Diffusivity is given by the porosity of the matrix (void fraction), by the corresponding constrictivity (ratio of the radii of moving particles to radii of pores) and the tortuosity of pores themselves (Fogler, 1992).

Regardless of the mechanism involved, one can state the hypothesis that liquids diffuse more easily in porous solids which show higher x_c values.

Thus, x_c can be used as a relative measure of diffusivity of liquids amongst a group of porous materials, such as the drying of foods, construction materials, textiles or biomasses in general. This work presents results on the drying of filter paper saturated with H_2O as model for the proposed methodology.

METHODOLOGY

Materials. Filter papers of different pore size were obtained from the stockroom. Their commercial identity and pore size are indicated in table 1, as given by the supplier. *O-Cel-O*® home scrub sponges (3M US) were obtained from a local store.

TABLE 1

x_c values for cellulose-based materials at 22°C and 87kPa.

Filtering material	Pore diameter / µm	x_c
Phenomenex nylon®	0,20	0,77
Sartolon polyamid®	0,45	0,81
Advantec® 5A	2,5	0,86
Whatman 3	6,0	0,91
Whatman 2	8,0	0,92
Whatman 1	11	0,91
Whatman 4	20 – 25	0,94
Advantec® 5C	20 – 25	0,95
O-Cel-O® scrube sponge	Millimetre sized	0,96

Drying kinetics. The runs were carried out in duplicate or triplicate, according to the reproducibility

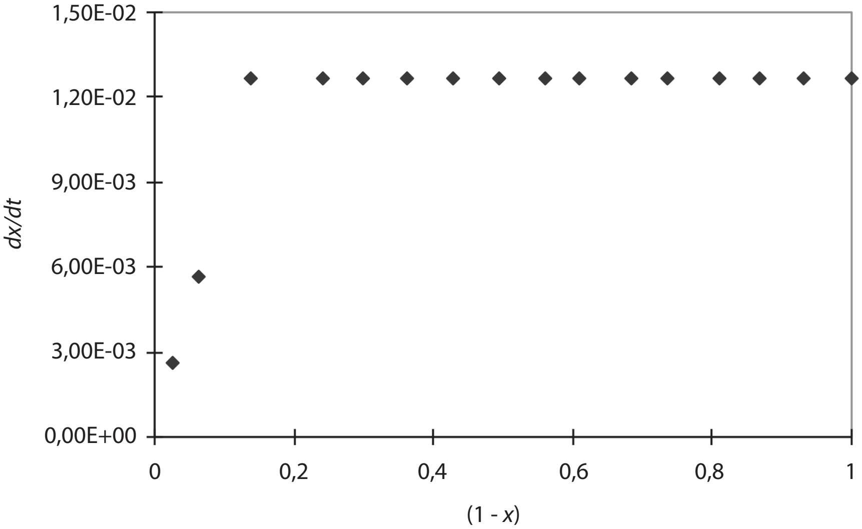

Fig. 1 Krischer curve for the drying of *Advantec 5A* filter paper, 22°C and 87kPa.

obtained. The relative humidity in the laboratory was kept at 60±5%, by means of a common commercial dehumidifier (*Air-Pro* dehumidifier, condensation capacity 0,7dm^{3}h^{-1}). All measurements were done at 22°C (laboratory acclimatized by a *Hi-Wall* air conditioner, Carrier Interamerica Corporation, maximal cooling capacity 19MJh^{-1}) and under the usual 87kPa barometric pressure in this part of the Country. The filter paper disks were wetted with distilled water and the excess liquid was allowed to rinse off by gentle flapping.

Mass loss was followed by monitoring the samples put on Petri dishes placed on a Shimadzu four-decimal place analytical balance. Care was taken to avoid air-currents flow near the balance. Data collection was done manually.

Data analysis. The raw *mass – time* data were recalculated as *x - time*, obtained from the simple mass relation $x = [m(0) - m(t)] / [m(0) - m(\infty)]$. The extent of the initial kinetic phase was calculated by determining the group of *x - time* data pairs for which a linear correlation is valid with a Pearson's correlation coefficient $r_p = 0{,}9990$. This allows the calculation of the data pair $x_c - t_c$.

RESULTS

Figure 1 shows the Krischer curve of *Advantec 5A* filter paper, and Figure 2 and Table 1 give the observed x_c results for the different cellulose-derived materials as a function of pore size *r*. The data points to an asymptotic value of $x_c \rightarrow 1$.

A reference experiment was carried out on *O-Cel-O*® home scrube sponge, an article made of cellulose with millimetre-size pores (10^3 μm) as a test for "very wide pores". The x_c value for this material was 0,96±0,02 and is not included in Fig. 2.

DISCUSSION

The basic approach of this work is the proposal that liquids diffuse more easily in porous solids which show high x_c values.

The total restriction to diffusion in pores arises from the combined effect of the steric hindrance of diffusing molecules relative to pore size and the frictional resistance to flow inside. For the case of molecules that interact weekly with pore walls, Renkin (1954) obtained the following equation for the diffusion coefficient of molecules of radius *a* diffusing in pores of radius *r* :

$$\frac{D_p}{D_b} = (1 - a/r)^2 \left[1 - 2{,}104(a/r) + 2{,}09(a/r)^3 - 0{,}956(a/r)^5\right]$$

where D_p and D_b are the diffusion coefficients of molecules in the pore and in bulk, respectively. The first term defines the steric hindrance of molecules caged in the pores. The second term gives the increase in hydrodynamic drag as the solute diffuses through the pore.

A reviewer pointed out the need to consider the small size of H_2O molecules (~ $3\text{x}10^{-10}$m), relative to micrometre-sized pores ($10^{-10}\text{m}/10^{-6}\text{m} = 10^{-4}$). The steric hindrance

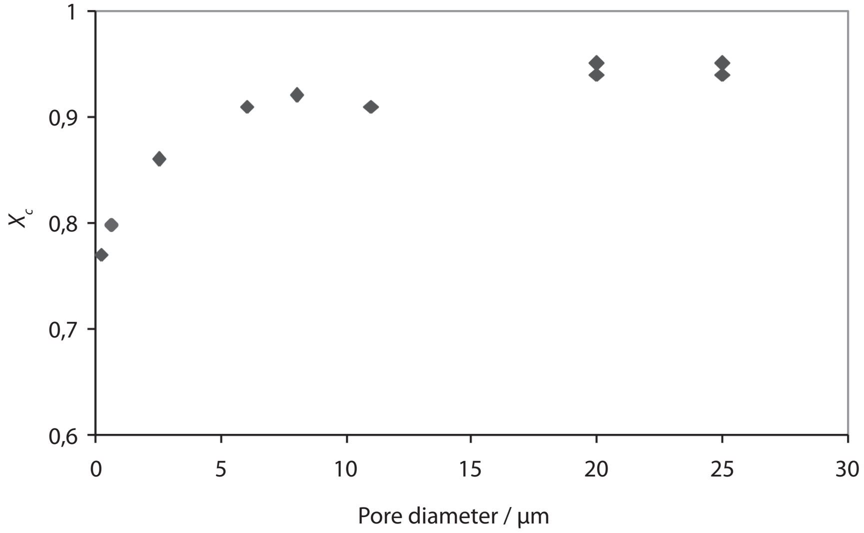

Fig. 2 Correlation between x_c and pore size of filter paper, 22°C and 87kPa.

is of low significance. The case of H_2O as the diffusing species is complicated by the observation that there is an increase in the liquid viscosity due to the attractive interactions of H_2O with the hydrophilic walls of cellulose (Tovbina, Kutz & Strelko, 1969; Kutay, 2009; Chaudhary, Cardenas, Dengo & Bennett, 2013). The Renkin polynomial can be corrected by the different viscosities of the diffusing liquid in bulk and in the pores, but it is not handy for practical uses. Thus, Renkin approach is merely a first approach that conceptually lends partial intuitive support to the hypothesis stated in this work: wider pores imply higher x_c.

A simple empirical way to use the obtained results is by fitting the $x_c - r$ data in the form of a double logarithmic linear equation. It should be borne in mind that it is an empirical correlation equation, not the mathematical description of a formal theoretical model. For the case of the six regular micrometer-pore filter papers, least-square linear fitting yields:

$$\log x_c = 0{,}039 \log (r / \mu\text{m}) - 0{,}077$$

The existence of correlation between log x_c and log r is quite significant, as given by the statistical parameters $r_p = 0{,}95$, $p<0{,}005$ (Student t = 6,0, tabulated value 4,6 for 4 degrees of freedom).

The predicted x_c values for *Phenomenex nylon*® and *Sartolon polyamid*® are 0,79 and 0,81, respectively. These calculated results are quite agreeable with observation (see table 1).

Thus, the empirical relation allows the estimation of pore size in cellulose derived materials for which x_c is determined. The good agreement between observed and calculated x_c values is due to the similar chemical nature of the filtering materials.

The same type of calibration can be carried out for other materials of particular chemical compositions.

This new method is much easier to perform than usual measurements such as N_2 BET curves (ASTM D4641-12) or Hg intrusion porosimetry (ASTM D4404-10).

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