MATHEMATICAL MODELING OF HANDMADE RECYCLED PAPER DRYING KINETICS AND SORPTION ISOTHERMS

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Abstract - The objective of this work is to analyze and compare the natural and forced convective drying of handmade recycled paper. Drying of recycled cellulose pulp was carried out under laboratory environment conditions and in a convective dryer with forced air circulation and controlled conditions of air temperature and velocity. The tests were conducted following a two-factor central composed factorial design of experiments, with six runs at the central point. The drying results were analyzed and fitted to mathematical models of Fick, Henderson and Pabis (Fick's modified equation), Page and He (considering the nonlinear Fick effect). The model of Page represented best the experimental data and the one of Henderson and Pabis resulted in an adequate fit for the paper drying kinetics. Sorption isotherms were determined for the dried paper and the models of GAB (Guggenheim-Anderson-de Boer) and GDW (Generalised D'Arcy and Watt) resulted in excellent fits of the experimental data. The water sorption mechanism was suggested by the analysis of the calculated parameters of the GDW model.
Keywords: Drying modeling; Convective drying; Paper drying.

INTRODUCTION

In the paper industry, drying is an important stage of the pulp processing, since it is characterized by high energy consumption and has direct influence on the paper quality. Studies on paper drying refer to the influence of the initial moisture content of the pulp, type of fiber, dryer configuration, operating conditions, among other parameters, on the quality of the final product (Rueff and Faloui (1994), Nazhad and Pazner (1994), Poirier and Pikulik (1996) and Coumans and Kruf (1995)).

Several drying technologies have been proposed for paper drying on a large scale. A new technique for the drying of paper, denominated "high intensity drying", was proposed by Pikulik and Poirier (1994), in which a wet screen is pressed by cylinders heated at 120ºC. Compared to the conventional method with a cylinder dryer, this new technique resulted in higher drying rates and produced a paper of better quality. However, none of them was capable of substituting the multi-cylinder dryer. The dilemma for the introduction of innovative technologies in the paper industry is the high capital investment and level of risk involved (Mujumdar, 1996).

Paper recycling is increasing nowadays, as it contributes to the preservation and conservation of natural resources, to the reduction of urban residues and decreases the energy consumption in the paper industry. Paper recycling plays a significant role in Brazil, as about 44% of the paper and 60% of the carton boards are recycled. Equally important are the activities developed in small cooperatives that produce recycled paper crafts, mainly of card type. This kind of activity contributes to families' subsistence in underdeveloped countries.

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In Brazilian small productions of recycled paper, the drying of paper sheets is conducted outdoors. The natural environment drying, although without a direct cost to the producer, depends on the environmental conditions that may result in differences in the quality of the final product. Also, the long time needed for total drying represents an indirect cost, which is not always considered.

An analysis of paper drying on a laboratory scale is found in the works of Mota Lima *et al.* (2000a, b, 2004, 2005). The paper sheets were dried over a heated surface under natural and forced convection conditions. The proposal of the dryer design and operation was to simulate the cylinder movement during drying of paper pulp, in the same manner as in the paper industry. A reduction of the drying time and higher drying rates were found with increasing air temperature. Moreover, it was verified that drying rates for paper made from long fibers were smaller than the respective ones for short fibers, which are encountered in recycled paper.

The drying process involves simultaneous heat and mass transfer phenomena, making its mathematical description difficult. Mathematical modeling of any drying process is important for optimum management of operating parameters and predicting the performance of the drying system.

In addition to the drying kinetics, the knowledge of sorption isotherms is very important for design, modeling and optimization of many processes. The literature points out the importance of those data in drying, aeration and predicting of stability and quality during packaging and storage of products.

Based on the above, the objective of this work is to determine and compare the drying kinetics of recycled paper dried under natural convection and in a laboratory scale forced convective drier. The drier design is a versatile proposal, of easy construction, which allows the increase of recycled paper production by the addition of other drying modules. The drying curves are analyzed using mathematical models described in the literature and selecting the most suitable ones by statistically comparing the implemented models. Sorption isotherms were also determined and analyzed using GAB (Guggenheim-Anderson-de Boer) and the recently proposed GDW (Generalised D'Arcy and Watt) models.

MATHEMATICAL MODELING OF DRYING KINETICS AND SORPTION ISOTHERMS

Several mathematical models that intend to represent drying kinetics are found in the literature. The model developments have been based on three fundamental approaches, namely, theoretical, semi-theoretical and empirical.

The theoretical models are based on the theory of moisture diffusion as liquid or vapor, represented by Fick's second law. The one-dimensional form of Fick's law of diffusion can be expressed as (Crank, 1975):

$$\frac{\partial X}{\partial t} = D_{ef} \left(\frac{\partial^2 X}{\partial r^2} + \frac{q}{r} \frac{\partial X}{\partial r} \right) \qquad (1)$$

where:

X: moisture content (dry basis, d. b.);
r: distance of a point to the center of the material;
t: drying time;
D_{ef}: effective diffusivity;
$q=0$ (plane plate); $q=1$ (cylinder) and $q=2$ (sphere).

Analytic solutions of Equation (1), in the form of series, for several initial and contour conditions, considering the diffusivity constant or as a function of water concentration are found in Crank (1975). Those solutions are applied for simple and constant geometries of the solid during the drying process and consider uniform initial moisture content and constant moisture at the center of the material and at the solid surface. Equation 2 shows the analytic solution for plane plate geometry.

$$\frac{X - X_{eq}}{X_0 - X_{eq}} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2}$$
$$\exp\left(-(2n+1)^2 \pi^2 \frac{D_{ef} t}{4l^2} \right) \qquad (2)$$

where:

X_0: initial moisture content (d. b.);
X: average moisture content (d. b.);
X_{eq}: equilibrium moisture content (d. b.);
D_{ef}: effective diffusivity;
t: time;
l: plate thickness.

Moisture migration in solids can be represented by Fick's second law for several materials that have none or small volume reduction during drying. For porous materials with high initial moisture content, the volume variation due to drying is significant and for this reason the analytical solutions of Equation 1 may not be applied. Fick's model is also not appropriate for materials that present a long period of constant drying rate.

Some semi-theoretical models based on diffusion theory assume that the resistance for heat and mass transfer is restricted to a fine layer on the particles surface (Parry, 1985). One of these models establishes that the drying rate is proportional to the content of free water and is expressed as follows:

$$\frac{dX}{dt} = -K\left(X - X_{eq}\right) \qquad (3)$$

where:

K: drying constant

Equation 4 is also often used to model drying kinetics. It represents the expression of Newton's law of cooling, in the integral form.

$$\frac{X - X_{eq}}{X_0 - X_{eq}} = \exp(-Kt) \qquad (4)$$

Modifications of this model (Equations 5 and 6), preserving the exponential form and including two and three parameters, have resulting in good fittings.

$$\frac{X - X_{eq}}{X_0 - X_{eq}} = a \cdot \exp(-Kt) \qquad (5)$$

$$\frac{X - X_{eq}}{X_0 - X_{eq}} = a \exp(-Kt^n) \qquad (6)$$

where:

a, K and n: models parameters.

Equation (5) is similar to the solution of Fick's model for long drying times, when only the first term of the series is significant. It is usually referred to as Henderson and Pabis' equation (Mc Cormick, 1983). The difference from the analytical solution given by Equation (2) is mainly the empirical fit of the model parameters a and K, which become then independent of the material geometry and lose their physical meaning.

Empirical equations for drying simulation are easy to apply and have been widely used. The main justification for the empirical approach is the satisfactory fit to the experimental data. Equation (6) is known as Page's model and is quite used in modeling agricultural products drying.

Equation (7) represents the recent mathematical model of He (He, 2006). This model may be applied when Equation (5) (Henderson and Pabis model) leads to large error compared to the experimental data. It is the solution of a nonlinear equation considering the nonlinear Fick effect.

$$\frac{X - X_{eq}}{X_0 - X_{eq}} = a \exp(-Kt).\left(1 + \exp\left(-bt\right)\right) \qquad (7)$$

where:

a, K and b: model parameters

One of the most applied models to analyze vapor sorption isotherms is the one of GAB (Guggenheim-Anderson-de Boer).

GAB is considered a versatile model, as it is satisfactory applied in an ample range of relative humidity (10<RH<90%) for the adjustment of sorption data of many materials (Marinos-Kouris and Maroulis, 1995), being widely applied to foodstuffs.

Recently proposed, the GDW (Generalised D'Arcy and Watt) model assumes the existence of multilayer adsorption sites on the solid surface and the possibility that one water molecule attached to a primary site can create more than one secondary adsorption site (Furmaniak et al., 2007b).

The models referred to above are given by Equations (8) and (9).

$$X_{eq} = \left(\frac{m.K.C.RH}{(1 - K.RH)(1 - K.RH + K.C.RH)}\right) \qquad (8)$$

$$X_{eq} = \left(\frac{m.K.RH}{(1 + K.RH)} \cdot \frac{1 - k\left(1 - w\right)RH}{1 - kRH}\right) \qquad (9)$$

where:

C: kinetic constant related to the sorption in the first layer;
k: kinetic constant related to sorption on secondary sorption sites (GDW model);
K: kinetic constant related to multilayer sorption (GAB model); kinetic constant related to the sorption on primary sorption sites (GDW model);
m: monolayer capacity (GAB model); concentration of primary active surface sites (GDW model);
RH: relativity humidity;
w: parameter determining what part of water molecules adsorbed on primary sites convert into secondary adsorption sites;
X_{eq}: equilibrium moisture content, % (d. b.);

MATERIAL AND METHODS

Material

The material used in the experiments consisted of cellulose pulp made from white extra (75g/m^2) used paper. Cassava starch, carboxymethyl cellulose (CMC - adhesive agent) and titanium dioxide (white pigment) were added to the pulp in order to provide the necessary characteristics for the production of a card type paper.

Drying Kinetics

a) Natural Convective Drying

For the kinetics determination of natural convective drying of the recycled paper, a similar procedure used in Brazilian small productions was adopted. The paper pulps were pressed and hung on a horizontal support, submitted to the environmental conditions of the laboratory. Figure 1 shows the experimental apparatus used for the natural drying tests.

The support consists of a horizontal stem, with claws, that sustain five screens with the pulp. This system allows the movement of the screens, which were rotated 90º every hour during the drying test to enhance uniformity of the sheet moisture content. Also, this procedure has the purpose of avoiding that the pulp flow down, resulting in the variation of the paper sheet density. Moreover, the sheets shrink and suffer deformations when dried naturally, without the screens. The shrinkage is due to irregular contractions of the fibers during drying, as a consequence of heat and mass transfers in preferential areas (Vieira *et al.*, 2006).

The screens were weighed after each 20 minutes for the first two hours and every hour during the following twelve hours. After that, some other measurements of the screen weight were done to determine the total time needed for complete drying of the sheets under each environmental condition.

The sheets' moisture contents were obtained by the oven gravimetric method at 105ºC, for 24 hours. Temperature and relative humidity of the environmental air were measured by a digital thermo-hygrometer. The solids concentration of each pulp used in the tests was also determined.

The experiments were conducted on different days, thus at different conditions of air temperature and relative humidity, making it possible to verify the influence of these parameters on the paper drying time, as well as on the final quality of the dry paper. The natural convective drying kinetics was analyzed and fitted using Page's model.
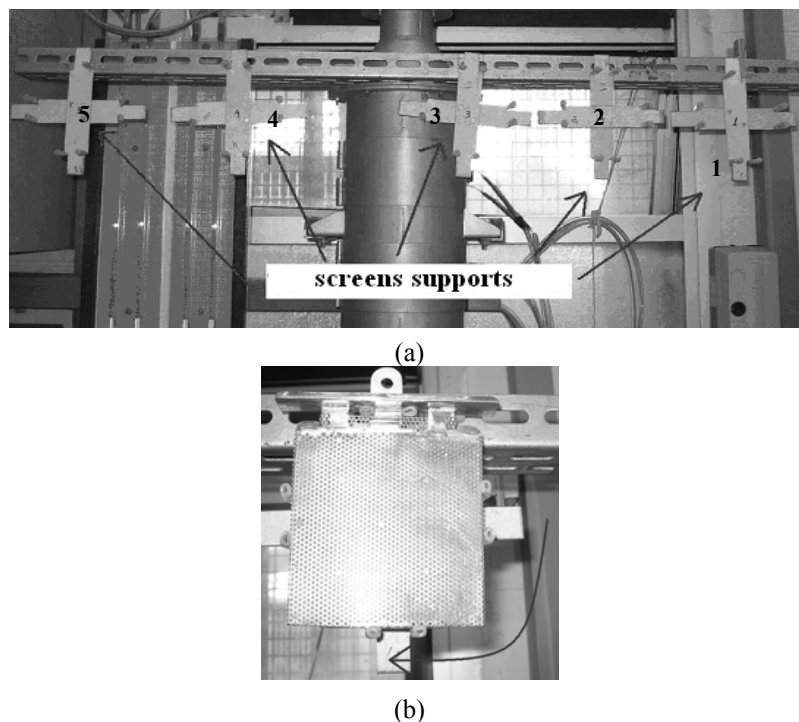

(a)

(b)

Figure 1: Experimental set

b) Forced Convective Drying

Figure 2 illustrates the experimental system used in this work. The paper surface temperature was obtained by contact thermocouples. Two thermo-hygrometers were inserted at the entrance and exit of the dryer, for the air temperature and relative humidity measurements.

For forced convective drying, the pulp is inserted in a sample holder screened on both sides with 10 cm x 10 cm of sides and a 1 mm thickness. The sample holder is constituted externally of a rigid screen and internally of a finer screen. The dryer is provided with appropriate connections to support five screened sample holders, which give support to the cellulose pulp, therefore producing 5 cards in each drying run. The screen holders can be designed and constructed to produce different sizes of cards and other drying modules can be inserted in series to increase the number of cards produced per batch. More details about the dryer construction and operation can be found in Vieira *et al*. (2005, 2006).

The moisture content of the sample holders was measured every five minutes during the drying experiments to obtain the drying kinetics. For the initial drying rate determination, a tangent line to the first point of the drying curve (at $X/X_0 = 1$) was drawn. To obtain the constant drying rate, the linear part of the drying curve was fitted to a linear function.

The experiments were conducted according to a composed factorial design, with the air temperature and velocity as the independent variables analyzed. Six replicates at the central point ($x_i = 0$) were done, corresponding to intermediate values between inferior and superior levels of the independent variables. In addition, experiments were conducted at the points of coordinates $x_i = \pm 1$, for both variables (corresponding to the factorial part) and at the points of coordinates $x_i = \pm 1.4$ (corresponding to the axial part), totalizing fourteen experiments. The results were analyzed using the software STATISTICA®, version 5.5.

The levels of the two factors, air temperature and velocity, defined in preliminary tests and applied for the experimental design are presented in Table 1.
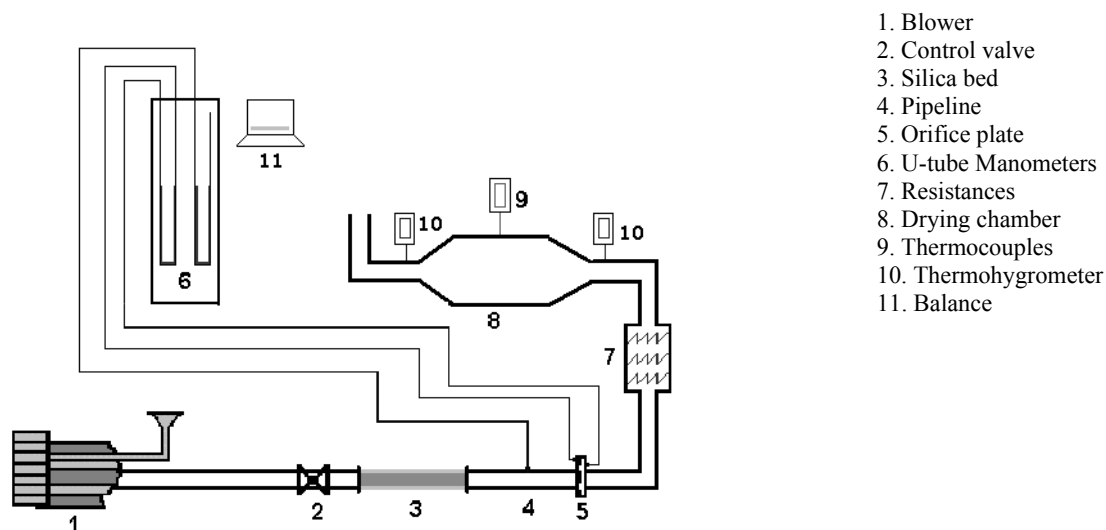

1. Blower
2. Control valve
3. Silica bed
4. Pipeline
5. Orifice plate
6. U-tube Manometers
7. Resistances
8. Drying chamber
9. Thermocouples
10. Thermohygrometer
11. Balance

Figure 2: Experimental set-up for the forced convective drying tests.

Table 1: Factorial design for the forced convective drying analysis.

Code	-1.4	-1	0	+1	+1.4
T_{air} (ºC)	66	70	80	90	94
v_{air} (m/s)	0.22	0.30	0.50	0.70	0.78

Based on the drying curves obtained, the forced convective drying results were analyzed and fitted to the mathematical models of Fick, Henderson and Pabis (Fick's modified), Page and He, represented, respectively, by Equations 2, 5, 6 and 7.

In this work, the dimensionless moisture content ratio, $(\dfrac{X - X_{eq}}{X_0 - X_{eq}})$, was reduced to the ratio $(\dfrac{X}{X_0})$, because the equilibrium moisture content obtained for the material is very close to zero, as verified in previous works (Mota Lima *et al.*, 2004) and in laboratory tests, where desorption isotherms for the dried recycled paper at different operating conditions were determined.

c) Vapor Sorption Determination and Modeling

Sorption isotherms of the paper dried under forced convection, at 70ºC and 0.30m/s, were obtained by the dynamic method, using the DVS-Dynamic Vapour Sorption 2 equipment. Two isotherms were determined, at ambient temperature of 25ºC and at 50ºC, the highest temperature available for the equipment utilized.

The isotherms were adjusted using the GAB model (Equation 8) and the recently proposed GDW model (Furmaniak *et al.*, 2007a) (Equation 9).

RESULTS AND DISCUSSIONS

Drying kinetics results

Drying of the pulp by natural convection under different conditions of environmental relative humidity and temperature was carried out, as described in the previous item. Table 2 shows these operating conditions, the pulps solid concentrations and the results of the drying processes.

The environmental conditions, mainly the relative humidity, had a great influence on the results of the natural drying of the pulps. Different environment conditions are then responsible for long and different drying times, resulting in the production of papers with different characteristics, as happens in Brazilian small cooperatives of recycled paper. The very long time needed for complete drying of the sheets by the traditional outdoors method, even when conducted under good environmental conditions (high temperature and low relative humidity of the ambient air) justifies the use of the forced convective dryer. Figure 3 shows the comparison of the drying curves obtained under three different conditions of forced convection and under good environmental conditions (run1, Table 2).

Table 2: Operating conditions and results for natural convective drying.

Run	T_{amb} (ºC)	$R.H_{amb}$ (%)	C_s (%)	$X_{0 (b.s)}$ (kg/kg)	$X_{cr (b.s)}$ (kg/kg)	t_{cr} (h)	t_{dry} (h)	N_i (h^1)	N_C (h^{-1})
1	26.87 ±0.69	47.50 ±3.04	7.21	8.009	4.772	5	31	0.1098	0.0727
2	21.67 ±0.79	55.02 ±4.87	6.73	8.478	5.391	6	25.75	0.1050	0.0539
3	24.97 ±0.34	78.25 ± 0.30	6.21	9.592	5.137	11.95	33.08	0.0680	0.0364
4	23.12 ±1.47	69.20 ±1.20	5.36	11.938	5.975	10	25	0.0920	0.0446
5	25.83 ±0.35	69.41 ±2.66	5.00	13.399	5.646	10	24.67	0.0902	0.0531
6	23.85 ±1.01	67.78 ±1.93	5.02	10.500	4.631	10	27	0.0924	0.0492
7	24.19 ±0.29	88.38 ±2.23	5.28	11.697	4.092	25.5	45	0.0545	0.0248
8	24.75 ±0.46	63.19 ±1.78	6.26	10.218	4.536	9	31	0.0750	0.0576
9	25.28 ±0.23	80.58 ±1.07	5.56	11.432	4.115	20	35	0.0650	0.0328

The experimental design defined in the previous item was applied to analyze the forced convective drying kinetics. A summary of the experimental conditions, as well as the pulps solid concentrations and the drying rates is presented in Table 3.

It can be verified, as expected from theory, that the increase in air temperature and velocity influences positively the process, increasing the initial and constant drying rates, consequently reducing the total drying time.

The constant drying rate ranges obtained by Mota Lima *et al.* (2000b) for the natural (0.0342 to 0.0811 min^{-1}) and forced (0.0560 to 0.1437 min^{-1}) conductive/convective drying of paper were much higher than the ones obtained in this work. The experimental apparatus used by those authors consisted of a metallic box heated by a thermostatic bath containing an upper surface over which the paper samples were placed. The system was submitted to ambient air under natural and forced convection. Therefore, the differences in the drying rates are due to the heating surface effect (conductive drying) and higher air drying velocities (2 to 6 m/s) (convective drying), which enhanced the mass transfer.

Based on the results of Table 3, it can be expected that Fick's diffusion model do not adjust well the experimental kinetic data for the recycled paper drying, due to the long constant drying rate period obtained, where the external conditions control the drying. However, as a significant falling-rate period was also observed, the model was still tested.
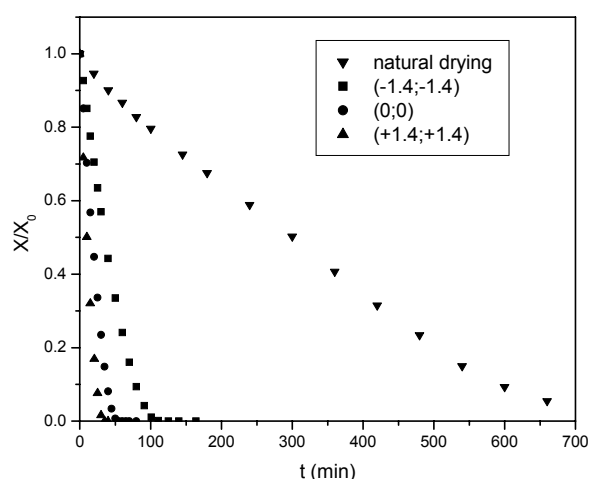

Figure 3: Drying curves for experiments carried out at 66ºC and 0.22m/s, 80ºC and 0.50m/s, 94ºC and 0.78m/s and under natural environment conditions.

Table 3: Operating conditions and results for forced convective drying.

Run	T_{air} (ºC)	v_{air} (m/s)	C_s (%)	$X_{0 (b.s)}$ (kg/kg)	$X_{cr (b.s)}$ (kg/kg)	t_{cr} (min)	t_{dry} (min)	N_i (min^{-1})	N_C (min^{-1})
1	70	0.30	5.58	12.745	7.868	20.00	105.00	0.0198	0.0189
2	70	0.70	6.19	10.636	4.708	20.00	60.00	0.0330	0.0260
3	90	0.30	6.31	9.937	4.880	20.00	60.00	0.0334	0.0228
4	90	0.70	6.15	10.958	4.406	15.00	45.00	0.0450	0.0370
5	66	0.50	5.43	11.720	5.741	20.25	70.00	0.0290	0.0239
6	94	0.50	6.57	7.941	2.695	20.00	45.00	0.0380	0.0314
7	80	0.22	5.57	12.106	5.273	35.00	45.50	0.0164	0.0161
8	80	0.78	6.35	10.263	4.403	15.00	45.00	0.0420	0.0360
9	80	0.50	5.48	12.302	4.702	20.00	55.00	0.0362	0.0291
10	80	0.50	5.41	11.139	4.472	20.00	55.00	0.0330	0.0289
11	80	0.50	5.42	9.610	4.293	20.00	55.00	0.0298	0.0269
12	80	0.50	5.53	10.693	4.400	20.00	55.00	0.0312	0.0289
13	80	0.50	5.46	10.072	5.477	15.00	60.00	0.0322	0.0295
14	80	0.50	5.54	10.152	4.739	20.00	60.00	0.0296	0.0257

Drying Kinetics Mathematical Modeling

The drying curves fit using the model represented by Equation 2 (simplified Fick's diffusion model) resulted in lack of adjustment. Some hypotheses are included in this analytical model, as follows: uniform product moisture content, homogeneous product and constant dimensions of the material during drying (non-shrinkage), which were not practically verified in the process, thus explaining the lack of adjustment obtained. Analyzing the drying methodology and the material applied in this work, it can be verified that, since the sheets are dried in the vertical position, the moisture is not uniformly distributed in the paper. Still, being the paper a capillary-porous material, its dimensions shrink during drying (Vieira *et al*, 2006). The use of screens maintained the width and the length of sheets fixed, but the thickness reduces during drying. Thus, the physical situation of non-accordance with the model assumptions led to the poor fit of the simplified Fick's model (Equation 2) to the experimental data and the determination of the recycled paper effective diffusivities was not done in this work.

The values obtained for the constants *a* and *K* and the regression coefficients (R^2) for the fit of Henderson and Pabis' model (Equation 5) are shown in Table 4. The regression coefficients higher than 0.97 for all experiments confirm the good fit of the drying curves using this kinetic model.

Figure 4 presents the kinetic curve for run 8, where an excellent adjustment of Henderson and Pabis' model to the constant drying rate period and an adequate adjustment to the drying falling-rate period can be verified. Similar results were obtained for the other runs.

Table 4: Fit of (X/X_0) as a function of time by Henderson and Pabis' equation (similar to Fick's model).

| Run	T_{air} (°C); v_{air} (m/s)	$\frac{X}{X_0} = a \cdot \exp(-K \cdot t)$			
		a	K	R^2	Deviation (%)
1	(70;0.30)	1.0869	0.0335	0.9861	5.31
2	(70;0.70)	1.0683	0.0530	0.9898	4.46
3	(90;0.30)	1.0657	0.0460	0.9874	4.89
4	(90;0.70)	1.0547	0.0732	0.9908	4.34
5	(66;0.50)	1.0706	0.0451	0.9900	4.27
6	(94;0.50)	1.0701	0.0638	0.9873	5.07
7	(80;0.22)	1.0612	0.0696	0.9897	5.50
8	(80;0.78)	1.0638	0.0573	0.9903	4.53
9	(80;0.50)	1.0683	0.0547	0.9908	4.30
10	(80;0.50)	1.0781	0.0513	0.9872	4.15
11	(80;0.50)	1.0715	0.0536	0.9907	5.12
12	(80;0.50)	1.0715	0.0536	0.9907	4.17
13	(80;0.50)	1.0750	0.0487	0.9877	4.43
14	(80;0.50)	1.1155	0.0268	0.9764	4.94
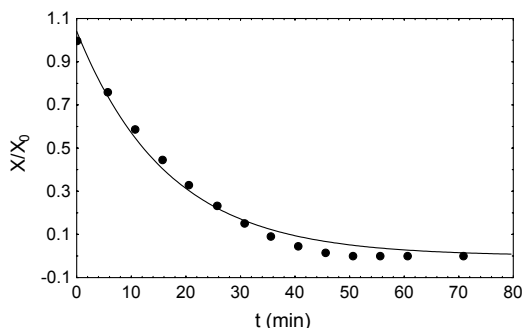
Figure 4: Fit of Henderson and Pabis' model (similar to Fick's diffusion model) for the paper drying curve (run 8) (T_{air} = 80°C; v_{air} = 0.78 m/s) (R^2 = 0.9903).

Similarly to the solution of Fick's model, parameter K can be thought to include the effective diffusivity. The statistical analysis of this parameter as a function of the operating conditions indicated that it is significantly influenced (95% confidence level) by the air temperature and velocity, individually, and by their interaction, the linear term of the air velocity having the most pronounced effect (Figure 5). The preponderant air velocity effect, over the temperature effect, is an indication that diffusive effects are not the only ones involved in the model parameter K, making the evaluation of an effective diffusivity inconsistent.

Tables 5 and 6 present the results for the non-linear fit of Page's model to the natural and forced convective drying data, respectively. Regression coefficients higher than 0.99 obtained for all experiments indicate the excellent fit of this model to the experimental drying curves for natural and forced convective drying.
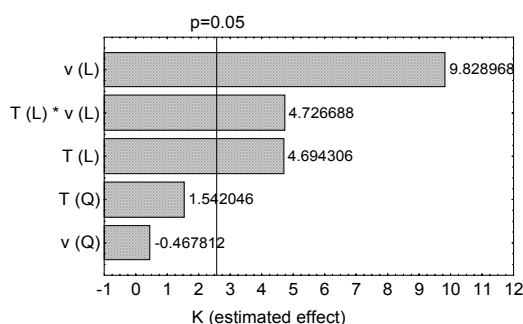

Figure 5: Pareto diagram for K parameter of Henderson and Pabis' model.

Table 5: Fit of (X/X_0) as a function of time by Page's model (natural drying).

		$\dfrac{X}{X_0} = a\exp\left(-kt^n\right)$				
Run	**T_{amb} (ºC); R.H$_{amb}$ (%)**	**a**	**k**	**n**	**R^2**	**Deviation (%)**
1	(26.87; 47.50)	0.9517	0.0505	1.4277	0.9984	1.96
2	(21.67; 55.02)	0.9349	0.0283	1.4818	0.9974	2.12
3	(24.97; 78.25)	0.9748	0.0394	1.1368	0.9982	1.71
4	(23.12; 69.20)	0.9611	0.0396	1.2177	0.9971	1.51
5	(25.83; 69.41)	0.9450	0.0311	1.4257	0.9974	2.05
6	(23.85; 67.78)	0.9293	0.0285	1.4323	0.9958	2.68
7	(24.19; 88.38)	0.9508	0.0174	1.2687	0.9979	1.83
8	(24.75; 63.19)	0.9523	0.0334	1.4313	0.9985	1.87
9	(25.28; 80.58)	0.9643	0.0143	1.5622	0.9984	1.96

Table 6: Fit of (X/X_0) as a function of time by Page's model (forced convective drying).

		$\dfrac{X}{X_0} = a\exp\left(-kt^n\right)$				
Run	**T_{air} (ºC); v_{air} (m/s)**	**a**	**k**	**n**	**R^2**	**Deviation (%)**
1	(70;0.30)	0.9612	0.0045	1.5181	0.9978	2.15
2	(70;0.70)	0.9735	0.0116	1.4445	0.9984	1.83
3	(90;0.30)	0.9541	0.0079	1.4901	0.9969	2.51
4	(90;0.70)	0.9843	0.0211	1.4093	0.9986	1.72
5	(66;0.50)	0.9681	0.0094	1.4349	0.9983	1.83
6	(94;0.50)	0.9740	0.0121	1.5187	0.9981	2.05
7	(80;0.22)	0.9589	0.0031	1.5700	0.9978	2.15
8	(80;0.78)	0.9814	0.0175	1.4452	0.9986	1.74
9	(80;0.50)	0.9769	0.0144	1.4144	0.9984	1.80
10	(80;0.50)	0.9797	0.0135	1.4148	0.9989	1.48
11	(80;0.50)	0.9712	0.0090	1.5070	0.9982	1.97
12	(80;0.50)	0.9802	0.0126	1.4257	0.9989	1.49
13	(80;0.50)	0.9767	0.0124	1.4223	0.9985	1.73
14	(80;0.50)	0.9638	0.0127	1.4290	0.9979	2.11

According to the literature, the two parameters of Page's model, *n* and *k* account for the effects of external drying conditions and the internal resistance to drying, respectively. The statistical analysis applied to these parameters showed that *k* is positively influenced by the air temperature and velocity, and *n* is significantly affected only by the air velocity, at a confidence level of 95% (Figures 6 and 7). These results are in agreement with the previous model analysis. Statistical models for *n* and *k* as a function of the codified variables (T and v) were obtained and are expressed by Equations 10 and 11, where only the statistically significant terms were considered.

$$k = 0,0115 + 0,0021 \cdot T + 0,0051 \cdot v \qquad (10)$$

$$n = 1,4603 - 0,0414 \cdot v \qquad (11)$$

Figures 8 and 9 show the drying kinetic curves for run 8 (forced convective drying) and for run 1 (natural convective drying), respectively. An excellent adjustment of the non-linear Page's model to the experimental data is verified.

The model recently proposed by He (Equation 7) was also used to fit the recycled paper drying curves. As stated before, it is indicated in the cases that Equation (5) leads to large deviations from experimental data. Table 7 shows the model parameters and the adjustment quality (correlation coefficient and percentage deviation) evaluated for the forced convective drying data. The high correlation coefficients (all values above 0.989) indicate the model adequacy to represent the drying curves; however, the comparison of the model predictions and the experimental data resulted in deviations, which are quite higher than the ones obtained with the other models applied.

Summarizing the results of the drying kinetics modeling, an excellent fit of the experimental data was obtained using Page's model (natural and forced convective drying) and an adequate adjustment was verified for the equations of Henderson and Pabis and of He. The analytical solution of Fick's law considering a flat plate did not fit as well the experimental data, since the necessary hypotheses for its applicability were not satisfied in the cases studied here.
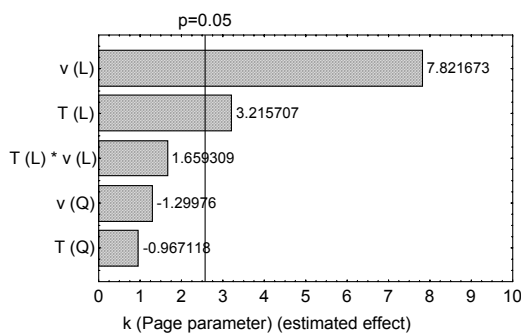

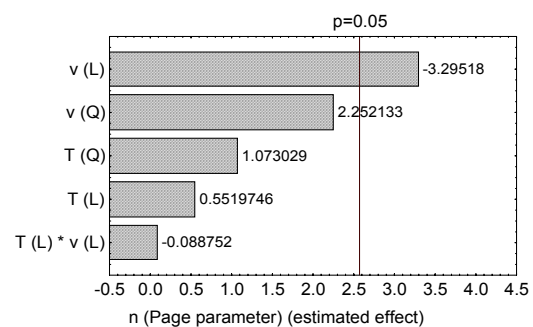**Figure 6:** Pareto diagram for parameter *k* of Page's model.
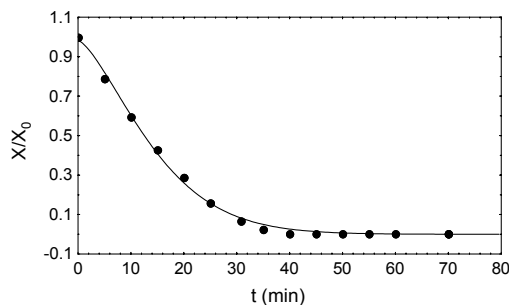

Figure 7: Pareto diagram for parameter *n* of Page's model.

Figure 8: Non-linear fit of Page's model for the forced convective drying curve (run 8) (T_{air} = 80ºC; v_{air} = 0.78 m/s) (R^2 = 0.9986).
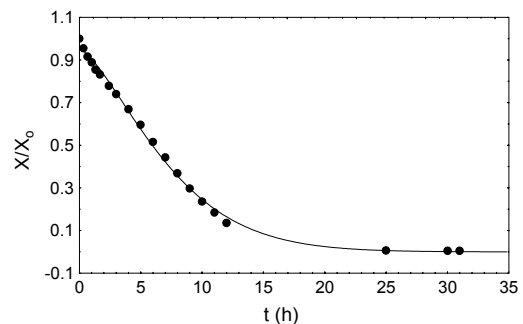

Figure 9: Non-linear fit of Page's model for the natural convective drying curve (run 1) (T_{amb} = 26.87ºC; R. H.$_{amb}$ = 47.50%) (R^2 = 0.9984).

Table 7: Fit of (X/X_0) as a function of time by He's equation.

		$\dfrac{X - X_{eq}}{X_0 - X_{eq}} = a\exp(-Kt).\left(1 + \exp(-bt)\right)$				
Run	**T_{air} (ºC); v_{air} (m/s)**	**a**	**K**	**b.(10^{-7})**	**R^2**	**Deviation (%)**
1	(70;0.30)	0.5439	0.0336	-1.9	0.9871	7.85
2	(70:0.70)	0.5342	0.0530	-1.5	0.9898	7.78
3	(90;0.30)	0.5329	0.0460	-2.9	0.9874	8.30
4	(90;0.70)	0.05274	0.0731	-1.5	0.9908	7.72
5	(66;0.50)	0.5370	0.0449	-2.2	0.9890	8.10
6	(94;0.50)	0.5350	0.0638	-9.1	0.9873	8.55
7	(80;0.22)	0.5501	0.0306	-2.5	0.9849	8.32
8	(80;0.78)	0.5306	0.0670	-1.9	0.9901	9.83
9	(80;0.50)	0.5318	0.0573	-2.7	0.9903	7.77
10	(80;0.50)	0.5342	0.0547	-2.8	0.9909	7.12
11	(80;0.50)	0.5391	0.0513	-2.5	0.9871	8.06
12	(80;0.50)	0.5358	0.0535	-2.6	0.9907	6.98
13	(80;0.50)	0.5342	0.0527	-2.8	0.9891	6.97
14	(80;0.50)	0.5376	0.0487	-3.3	0.9877	8.21

Vapor Sorption Mathematical Modeling

Figure 10 shows the sorption isotherms at 25ºC and 50ºC obtained for a sample of paper dried under forced convective operating conditions of 70ºC and 0.30m/s.

A significant increase of the equilibrium moisture content of the paper in the region of capillary condensation (R.H. > 60%) is verified. It is also observed that the increase of the isotherm temperature reduces the material equilibrium moisture content for the entire range of relative humidity analyzed. This is the usual tendency,

according to the theory of the physical adsorption (Dullien, 1992). The same behavior was verified by Mota Lima *et al*. (2004) for isotherms of handmade paper, of the Kraft type.

Analyzing the results in Figure 10, a safe limit for storage of the recycled paper can be recommended at relative humidity of 60%, from which an abrupt increase of the material equilibrium moisture content is verified at 25ºC and 50ºC.

The models of GAB and GDW (Equations 8 and 9) were used to fit the sorption isotherm data. Table 8 shows the model parameters and the correlation coefficients obtained.
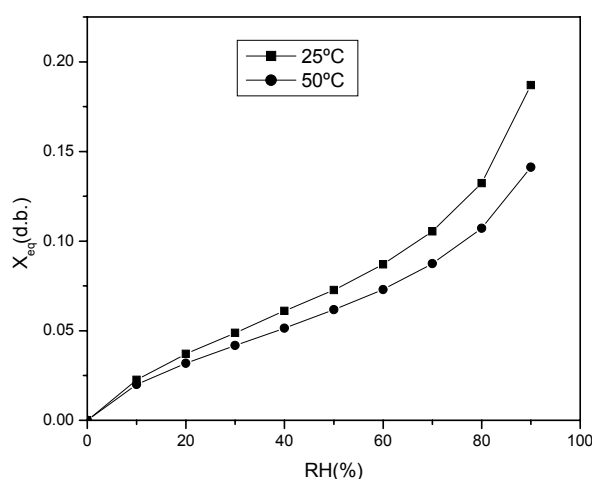

Figure 10: Water sorption isotherms of recycled paper.

Table 8: Parameters and correlation coefficients for the models of GAB and GDW applied to the vapor sorption data of recycled paper.

T (ºC)	GAB (Eq. (8)				GDW (Eq.(9))				
	m [%(db)]	K [% $^{-1}$]	C	R^2	m [%(db)]	K [% $^{-1}$]	k [% $^{-1}$]	w	R^2
25	4.7058	0.8381	9.8576	0.9995	9.0681	3.0222	0.9110	0.3995	0.9999
50	4.3224	0.7839	9.0998	0.9998	6.6666	3.8142	0.8406	0.5572	0.9999

The results show that the GAB and GDW models lead to very good fits. The GDW model describes the data with a slightly higher accuracy than the GAB model; however, the difference is not significant.

Both the GAB and GDW models assume the existence of primary (Langmuir-type) adsorption sites on the paper surface. Each site adsorbs one water molecule, which can be the secondary adsorption site for the next molecule. The GAB and GDW models differ by the assumption of the number of secondary sites created from primary ones. The assumption of the GDW model is that not all water molecules adsorbed on primary sites will be secondary centers. Moreover, the model takes into account the possibility that one water molecule attached to a primary site can give rise to more than one secondary adsorption site.

Analyzing the physical meaning of parameter w in the GDW model, one can assume that, since this parameter determines the ratio of water molecules adsorbed on primary sites that are converted into secondary sites, when $w = 1$, each primary adsorption site converts exactly into one secondary site. In this special case, the GDW equation becomes equal to the GAB equation.

The results in Table 8 show values of w less than 1; hence the analysis was made using the GDW model. In Table 8 the values of m, around 9% and 6.7%, correspond to the maximum sorption on primary sites, for maximum equilibrium moisture contents of 19% and 14% (dry basis), at 25ºC and 50ºC, respectively (Figure 10). According to the values obtained for w, around 40% and 56% (at 25ºC and 50ºC, respectively) of those strongly bound molecules become secondary adsorption sites for the next water molecules.

In addition, according to the GDW model, the decrease observed in the material equilibrium moisture content with the rise in temperature is due to the strong temperature dependence of K. The sorption on primary sites is strongly exothermic; therefore, their saturation occurs at larger values of the relative humidity.

CONCLUSIONS

On the basis of the results of this paper:
- The drying rates of paper sheets dried under natural conditions were influenced by the ambient relative humidity. The natural convective drying data were very well fitted by Page's model.
- The independent variables analyzed (air temperature and velocity) influence in a positive way the forced convective drying process, increasing the drying rates and reducing the paper drying time. Drying kinetics showed the occurrence of constant and falling-rate periods for the recycled cellulose pulp. Experimental drying curves were fitted by empirical models, as follows: Page's, Henderson and Pabis' and He's. The equation of Page resulted in better representation of the experimental data, being thus indicated to represent drying kinetics of the recycled paper. Parameter k of Page's model is influenced positively by the operating variables, air temperature and velocity, while for the parameter n only the air velocity had a significant influence. These parameters were statistically correlated with the significant independent variables.
- The analytical solution of the diffusion equation for a flat plate (Fick's simplified model) could not be used for the determination of the effective diffusivity coefficients, since the hypotheses of the model were not valid in the present study.
- The experimental water sorption data were well adjusted by the GAB and GDW models (a slightly better accuracy was obtained using the GDW model). The equilibrium moisture content decreases with the rise in temperature. The analysis of the GDW model parameters gives insights into the mechanism of water adsorption in the material tested.
- A significant increase of equilibrium moisture content of the paper was verified in the region of capillary condensation.

ACKNOWLEDGEMENTS

NOMENCLATURE

C	Kinetic constant related to the sorption in the first layer (GAB model)	(-)
a, b, n, *k*, *K*	Drying kinetics mathematical model parameters	(-)
C	Concentration	%
D_{ef}	Effective diffusivity	m^2/s
k	Kinetic constant related to sorption on secondary sorption sites (GDW model)	$\%^{-1}$
K	Kinetic constant related to multilayer sorption (GAB model); kinetic constant related to the sorption on primary sorption sites (GDW model)	$\%^{-1}$
L	Thickness of the plate	M
L	Linear term of codified independent variable (Pareto diagram)	(-)
m	Monolayer capacity (GAB model); concentration of primary active surface sites (GDW model)	% d.b.
N	Drying rate	s^{-1}
Q	Quadratic term of codified independent variable (Pareto diagram)	(-)
R.H.	Relative humidity	%
R^2	Regression coefficient	
t	Time	s
T	Codified variable for air temperature	(-)
T_{air}	Air temperature	ºC
v	Codified variable for air velocity	(-)
v_{air}	Air velocity	m/s
w	Parameter determining what part of water molecules adsorbed on primary sites convert into the secondary adsorption sites (GDW model)	(-)
X	Moisture content	d.b.

Subscript

0	Initial point	(-)
f	Final point	(-)
eq	Equilibrium	(-)
cr	Critical point	(-)
s	Solids	(-)
dry	Drying	(-)
amb	Ambient	(-)
C	Constant	(-)
i	Initial	(-)

REFERENCES

Dullien, F. A. L. Porous Media: Fluid Transport and Pore Structure. USA: Academic Press, 2. ed., 574 (1992).

Coumans, W. J. and Kruf, W. M. A., Mechanistic and lump approaches of internal transport phenomena during drying of paper sheet. Drying Technology, 13, No. 4, 985-998 (1995).

Crank, J., The mathematics of diffusion. Pergamon Press, Oxford (1975).

Furmaniak, S.; Terzyk, A. P.; Gauden, P. A.; Rychlicki, G. Applicability of the generalised D'Arcy and Watt model to description of water sorption on pineapple and other foodstuffs. Journal of Food Engineering, 79, 718-723 (2007a).

Furmaniak, S.; Terzyk, A. P.; Gauden, P. A. The general mechanism of water sorption on foodstuffs – Importance of the multitemperature fitting of data and the hierarchy of models. Journal of Food Engineering, 82, 528-535 (2007b).

He, J. H., Some asymptotic methods for strongly nonlinear equations. International Journal of Modern Physics, 20, No. 10, 1141-1199 (2006).

Marinos-Kouris, D.; Maroulis, Z. B., Transport Properties in the Drying of Solids. Handbook of Industrial Drying, ed. A. S. Mujumdar, 1, 113-159 (1995).

Mc Cormick, P. Y., Solids drying fundamentals. In: Perry, R. H. and Chilton, C. H. Chemical engineer´s handbook. Mc Graw-Hill Co. 5ed. Sec. 20-4 (1983).

Mota Lima, O. C., Pereira, N. C. and Machado, M. A. L. S., Generalized drying rate curves in paper drying. Drying 2000. Proceedings of the 12th International Drying Symposium (IDS`2000), Noordwijkerhout, Holanda (2000a).

Mota Lima, O. C., Pereira, N. C. and Machado, M. A. L. S., Generalized drying curves in

conductive/convective paper drying. Braz. J. Chem. Eng., 17, No 4-7, 539-548 (2000b).

Mota Lima, O. C., Machado, G. D., Lucheis, R. M. and Pereira, N. C., Moisture equilibrium isotherms for a handmade Kraft paper. Drying 2004. Proceedings of the 14th International Drying Symposium (IDS 2004), ed. M. A. Silva and S. C. S. Rocha, São Paulo, Brazil, B, 1241-1248 (2004).

Mota Lima, O. C., Rocha, S. A., Tofoli, C. M, Souza, L. H. C. D. and Pereira, N. C., Heat transfer of short- and long-fiber cellulose. Proceedings of the 3rd Inter-American Drying Conference, Montreal, Canada, August 21-23, 2005 (ISSN 0771706340) CD-ROM (2005).

Mujumdar, A. S., Innovation in drying. Drying Technology, 14, No. 6, 1459-1475 (1996).

Nazhad, M. and Paszner, L., Temperature effect on paper recycling. Drying´94. Proceedings of the 9th International Drying Symposium (IDS`94), ed. V. Rudolph and R. B. Keey, Hemisphere Publ., 1239-1246 (1994).

Parry, J. L., Mathematical modeling and computer simulation of heat and mass transfer in agricultural grain drying: A review, Journal of Agricultural Engineering Researches, 32: 1-29 (1985).

Pikulik, I. I. and Poirier, N. A., Combined convective and conductive drying of paper. Drying´94. Proceedings of the 9th International Drying Symposium (IDS`94), ed. V. Rudolph e R. B. Keey, Hemisphere Publ., 1163-1170 (1994).

Poirier, N. A and Pikulik, I. I., The effect of drying temperature on the quality of paper. Drying´96. Proceedings of the 10th International Drying Symposium (IDS`94), ed. C. Strumilo and Z. Pakouwski, Hemisphere Publ., 1189-1196 (1996).

Rueff, M. and Faloui, F., Influence of sheet structure and process conditions on paper drying. Drying´94. Proceedings of the 9th International Drying Symposium (IDS`94), ed. V. Rudolph and R. B. Keey, Hemisphere Publ., 1221-1228 (1994).

Vieira, M. G. A., Estrella, L. and Rocha, S. C. S., Energy Efficiency and Drying Kinetics of Recycled Paper in convective Drying. Proceedings of the 3rd Inter-American Drying Conference, Montreal, Canada, August 21-23, 2005, CD-ROM (2005).

Vieira, M. G. A., Estrella, L., Silva., M. A. and Rocha, S. C. S., Shrinkage of recycled paper sheet during drying. Drying Technology, 24, No. 4 (2006).