

Moisture equilibrium isotherms for pinnus long-fiber cellulose

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ABSTRACT. Moisture equilibrium isotherms are very important in the analysis of solids drying and storage processes. This work intends to experiment the moisture equilibrium isotherms for long-fiber cellulose and the temperature effects on them, using the traditional methodology of exposing the solid material to different ambient conditions of temperature and relative humidity, controlled by means of saline solutions. Oven temperature ranged from room to the limit condition for handling the saline solutions. The long-fiber cellulose moisture equilibrium isotherms were calculated from the experimental results obtained and temperature effects on their behavior were analyzed. Finally, results were adjusted and analyzed according to different equations and models available in the literature.

Key words: cellulose, equilibrium isotherms, moisture equilibrium content.

RESUMO. Isotermas de equilíbrio para celulose do tipo fibra longa. O conhecimento das isotermas de umidade de equilíbrio se faz importante na análise de processos envolvendo a secagem e a estocagem de diversos materiais sólidos. Dentro deste contexto, este trabalho teve como objetivo a determinação experimental das isotermas de umidade de equilíbrio para celulose do tipo fibra longa, bem como a influência da temperatura sobre estas isotermas, através da utilização da metodologia tradicional de exposição do material sólido a diferentes ambientes de temperatura e umidade relativa, controlada pelo uso de soluções salinas saturadas. A faixa de trabalho para a temperatura da estufa foi da ambiente até a de condição limite para o manuseio das soluções salinas. Com os resultados obtidos foram construídas as isotermas de umidade de equilíbrio para este tipo de celulose e analisado o efeito da temperatura no seu comportamento. Finalmente, estes resultados foram ajustados e analisados a partir de diferentes equações e modelos disponíveis na literatura.

Palavras-chave: celulose, isotermas de equilíbrio, umidade de equilíbrio.

Introduction

The knowledge of moisture isotherms equilibrium is very important for the analysis of drying and storage processes. The separation processes research group of the Chemical Engineering Department (DEQ/UEM), State of Paraná, is developing studies in both experimental determination and literature research to organize a small, but certainly useful, data bank for cellulose, paper and textile isotherms and their adjustment with available literature equations/models (Motta Lima *et al.*, 2001; Souza *et al.*, 2001).

In the specific case of paper manufacturing, and because of the hygroscopic characteristic of cellulose fibers (Seborg *et al.*, 1936; Seborg and Stamm, 1931) and its importance for this kind of industry, this work intended to experiment the moisture equilibrium isotherms for Brazilian “pinnus” wood long-fiber cellulose, as well as the temperature influence on their behavior.

The experimental equilibrium data were obtained by using the traditional methodology of exposing the solid material to different ambient temperature and relative humidity conditions, controlled by saline solutions (static method), inside an oven with air recirculation.

Long-fiber cellulose moisture equilibrium isotherms were built from the experimental results obtained and the temperature effects on their behavior were analyzed. Finally, these results were adjusted by some of the equations and models available on literature about isotherm and drying which had, or could be adapted to have, the temperature influence incorporated in their structure.

Material and methods

Material

Experiments were accomplished with long-fiber cellulose used as intermediary in the production of

different types of paper by *KLABIN-PR*, being the samples cut in the right size and amount for their adequate weight at the end of each experiment.

Equilibrium Isotherms

The experimental equilibrium data were obtained by the traditional/classical methodology of exposing the solid material to different conditions of temperature and relative humidity, controlled by saline solutions (Young, 1967; Perry and Chilton, 1980). An air recirculating oven was used to adjust and maintain the different working temperatures.

The dimensions of the long-fiber cellulose samples were 4.0 x 5.0 cm (about 1.5 to 3.0 g), with round borders, due to the opening size of the glass flasks used. The samples were placed over a steel support inside the flasks so that they were not in contact with the salt solutions, which were homogenized through a magnetic agitator to provide a uniform atmosphere and a constant relative humidity inside the flasks.

The flasks were tightly shut and left inside the oven for about 21 days and cellulose samples were periodically weighed, until reaching constant weight. Then, samples dry basis (d.b.) moisture equilibrium content were determined from their water content, together with the stove method (105°C, 24 hours). To verify the temperature influence upon the moisture equilibrium isotherms, oven temperatures ranged from near ambient (~25°C) to the limit condition for handling the saline solutions due to boiling up/evaporation, salt dragging, etc. (about 80°C).

After this procedure, cellulose samples were changed, as well as salt solutions, if necessary, and the flasks were returned to the oven in a different temperature. The experiments were done with samples in triplicate for better comparison and validation of the three results obtained for each saline solution. More details about the experimental procedure applied in this work can be found elsewhere in the works of Canha *et al.* (2000) and Souza *et al.* (2001).

The saline solutions were prepared by solubilization of the salts showed on Table 1 in distilled water, and the temperature dependence on air relative humidity inside the flasks is observed on Table 2 (Perry and Chilton, 1980).

Table 1. Temperature effect on salt solubility in water (g/L). (Perry and Chilton, 1980)

T (°C)	LiCl	MgCl ₂ ·6H ₂ O	K ₂ CO ₃	NaNO ₃	NaCl	KCl	CH ₃ O ₂ K	Mg(NO ₃) ₂ ·6H ₂ O
20	78.5	57.5	110.5	88	36	34		
30	84.5		113.7	96	36.3	37		
40	90.5	57.5	116.9	104	36.6	40		88.74
50	97		121.2	114	37	42.6	337.3	
60	103	61	126.8	124	37.3	45.5	350	108.04
70			133.1		37.8	48.3	364.8	
80	115	66	139.8	148	38.4	51.1	380.1	
90			147.5		39	54	396.3	137
100	127.5	73	155.7	180	39.8	56.7		

Table 2. Temperature effect on air relative humidity (RH).

T (°C)	LiCl	MgCl ₂ ·6H ₂ O	K ₂ CO ₃	NaNO ₃	NaCl	KCl	CH ₃ O ₂ K	Mg(NO ₃) ₂ ·6H ₂ O
20	0.118	0.334	0.447	0.675	0.772	0.873	0.249	0.547
25	0.114	0.329	0.443	0.659	0.762	0.855	0.237	0.536
30	0.111	0.323	0.440	0.643	0.752	0.837	0.226	0.525
35	0.108	0.318	0.436	0.628	0.743	0.821	0.216	0.515
40	0.105	0.313	0.433	0.614	0.734	0.806	0.206	0.506
45	0.103	0.308	0.430	0.601	0.726	0.791	0.197	0.497
50	0.100	0.304	0.427	0.588	0.718	0.777	0.189	0.488
55	0.098	0.300	0.424	0.576	0.710	0.764	0.182	0.480
65	0.094	0.291	0.418	0.554	0.696	0.739	0.168	0.465
80	0.088	0.281	0.411	0.524	0.676	0.705	0.151	0.445

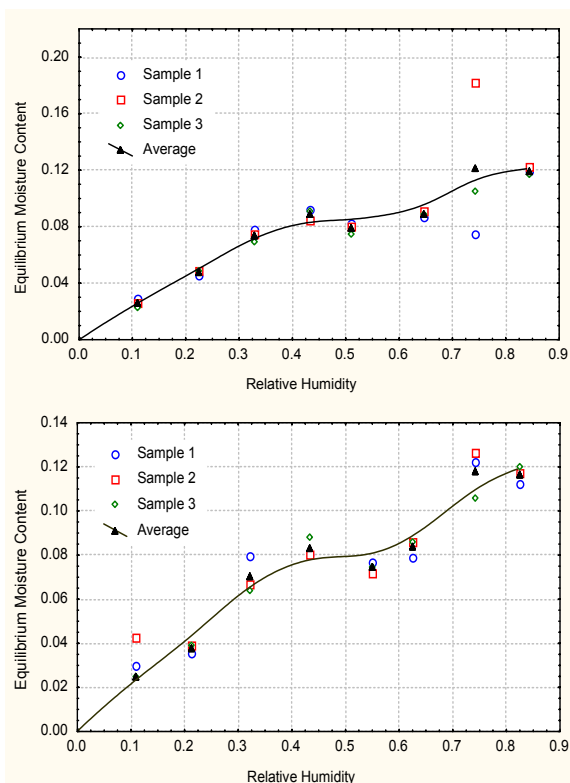
(Note: Relative humidities for the solutions at 55, 65 and 80 °C are an extrapolation of their behavior from 20 to 50°C).

Table 2 shows that temperature variations might affect the relative humidity promoted by the saline solutions. As in the work of Souza *et al.* (2001), this effect was considered when correcting the values of saline solutions relative humidity, used in the long-fiber cellulose isotherms calculating (Figures 1 to 6, below).

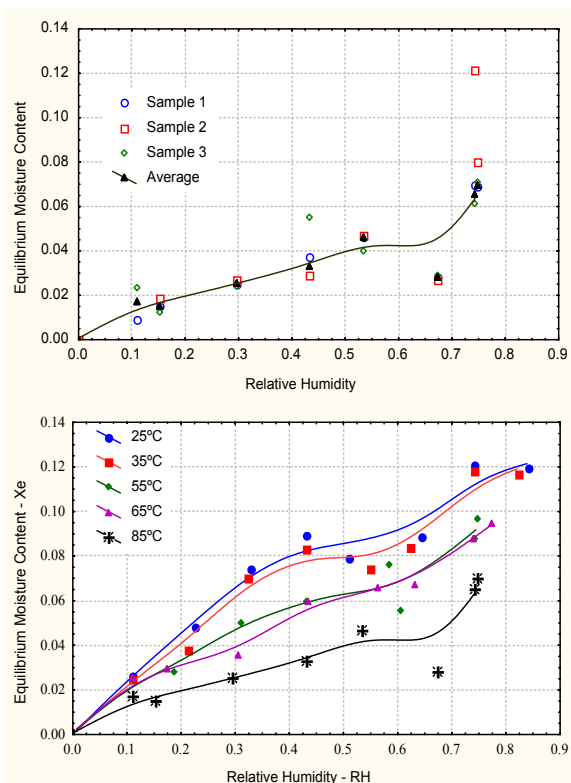
Results and discussion

Equilibrium Isotherms

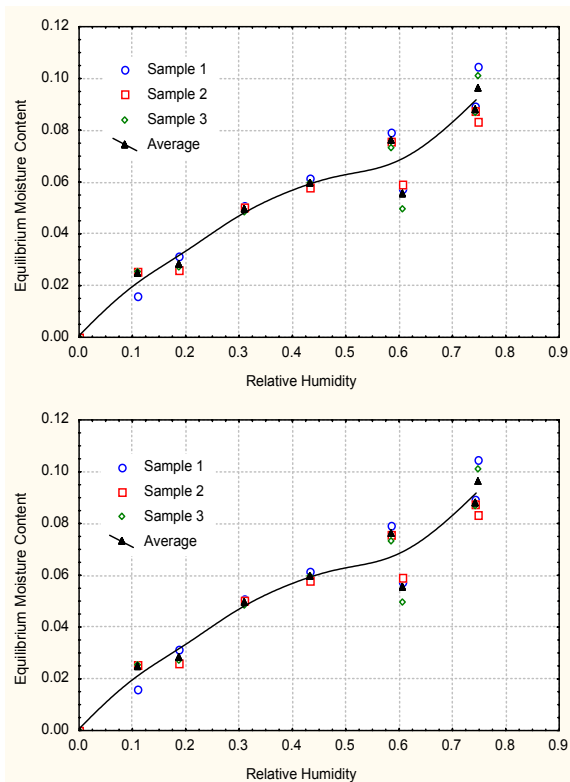
The experiments were done for temperatures of 25, 35, 55, 65 e 80°C. Some of the experimental values were not considered and the arithmetic mean of the valid ones were used to build the equilibrium isotherms shown in Figures 1 to 5, for each temperature, and Figure 6, for all together. Representative equilibrium isotherms calculated through least square fit are also presented to give an idea of the curves behavior.



Figures 1 and 2. Equilibrium isotherms and least square fit: 25 and 35°C.



Figures 5 and 6. Equilibrium isotherm and least square fit: 80 °C and general.



Figures 3 and 4. Equilibrium isotherms and least square fit: 55 and 65°C.

The analysis of Figures 1 to 6 shows that long-fiber cellulose equilibrium isotherms are in agreement with those found in paper and cellulose isotherms literature (Motta Lima, 1999; Motta Lima *et al.*, 2001). The inverse temperature influence on isotherms behavior can be also verified.

Equilibrium Isotherms - Modeling

A group of equations/models from isotherm literature (Motta Lima, 1999; Motta Lima *et al.*, 2001) and two modified equations proposed in this work were tested in the adjustments of the long-fiber cellulose isotherms obtained (Figure 6). The equations with the best adjusting performance are listed below:

- Henderson (Henderson, 1952 in Motta Lima, 1999):

$$X_e = c_1 \left(\frac{-\ln[1 - RH]}{T} \right)^{c_2} \quad (1)$$

- Henderson/Thompson (Thompson *et al.*, 1968):

$$X_e = \left(\frac{\ln[1 - RH]}{-(c_1 T + c_2)} \right)^{c_3} \quad (2)$$

- modified Henderson (Neuman *et al.*, 1986):

$$X_e = \left(\frac{-\ln[1 - RH]}{c_1 \cdot T \cdot \exp(-c_2/T)} \right)^{c_3} \quad (3)$$

- equation proposed in this work from Henderson (Henderson, 1952):

$$X_e = \left(\frac{-\ln[1 - RH]}{c_1 \cdot \exp(-c_2/T)} \right)^{c_3} \quad (4)$$

- modified Jaafar/Michalowski (Motta Lima (2001), from Massarani and Silva Telles, 1992):

$$\frac{X_e}{c_1} = \frac{(c_2/T)(RH)}{[1 - (c_3/T)(RH)][1 - [(c_2 - c_3)/T](RH)]} \quad (5)$$

- Motta Lima (1999), from Smith (1947) (Crapiste and Rotstein, 1982):

$$X_e = \frac{\ln[1 - (RH)^c]}{c_1 T} \quad (6)$$

- equation proposed in this work from Smith (1947) (Crapiste and Rotstein, 1982):

$$X_e = \frac{\ln[1 - (RH)^c]}{c_1 \cdot \exp(-c_2/T)} \quad (7)$$

- GAB (Labuza *et al.*, 1986):

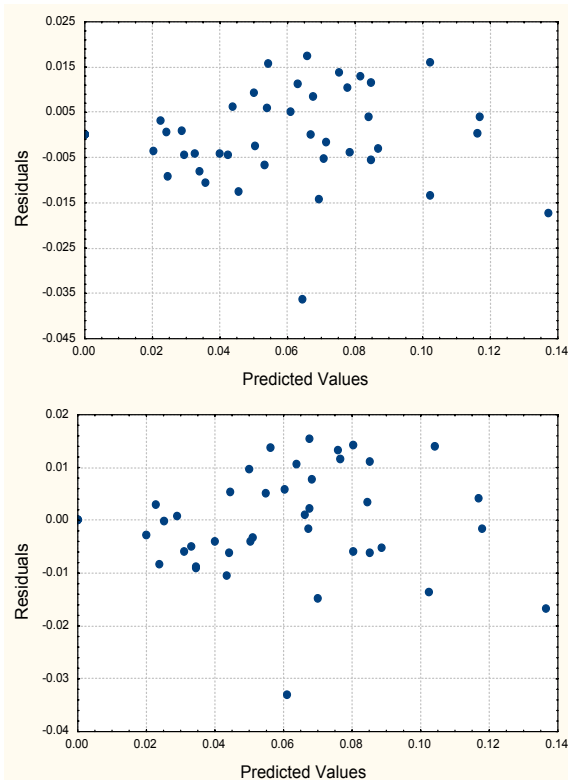
$$\frac{X_e}{c_1} = \frac{(c_2 c_3 / T^2)(RH)}{[1 - (c_3/T)(RH)][1 - (c_3/T)(RH) + (c_2 c_3 / T^2)(RH)]} \quad (8)$$

Table 3, Figures 7 to 10 and 11 to 14 show, respectively, parameters estimation results, the residual values and the fitted isotherms (response surfaces) for the equations which obtained the best performance (R^2 , F test and residual distribution): Equations 2, 3, 4 and 7.

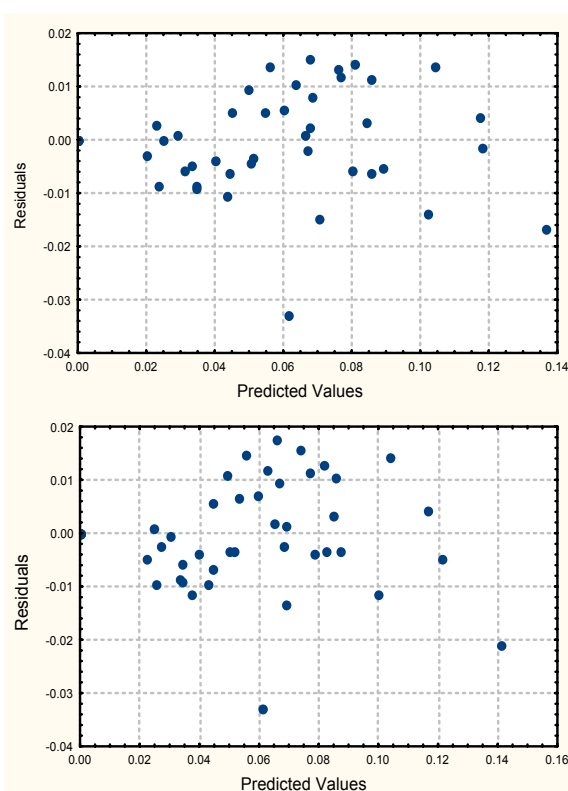
Table 3. Parameters estimation: X_e [d.b.], RH [%/100], T [K].

Equation	R^2	F	Parameter
2	0.958	42.2	$c_1 = 2.887$; $c_2 = -767.0$; $c_3 = 0.5060$
3	0.962	47.0	$c_1 = 152.9$; $c_2/R = 1818$; $c_3 = 0.4962$
4	0.962	46.8	$c_1 = 1.35 \times 10^5$; $c_2 = 2141$; $c_3 = 0.4959$
7	0.959	42.9	$c_1 = -724.3$; $c_2 = 1037$; $c_3 = 0.2563$

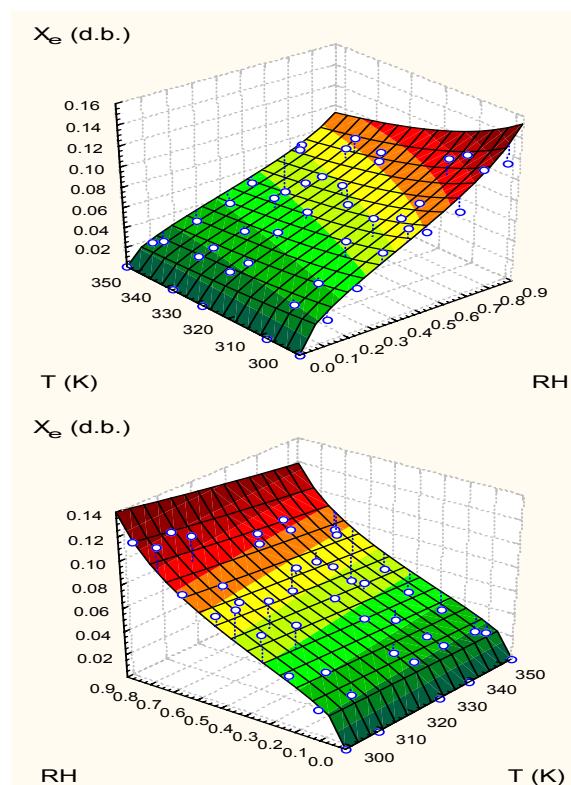
Finally, Figures 15 and 16 show the simulated equilibrium isotherms calculated from Equations 3 (modified Henderson, Neuman *et al.* (1986)) and 4 (Henderson/this work), respectively.



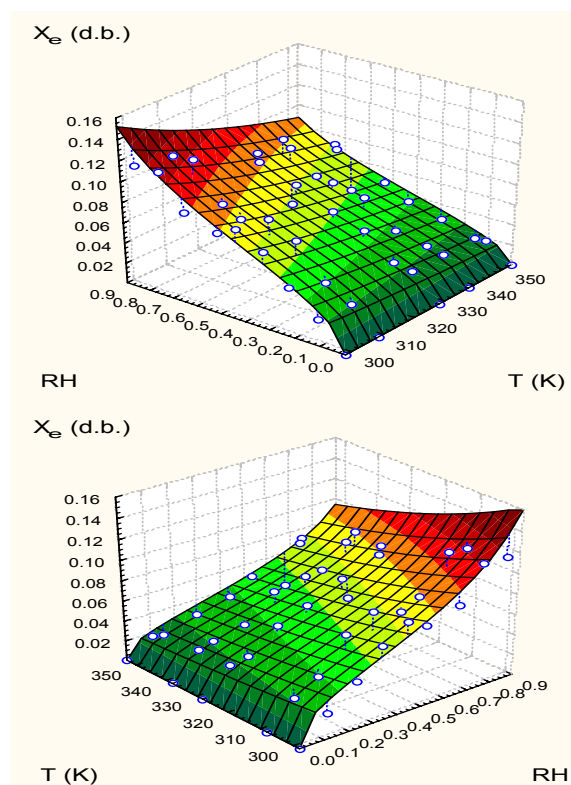
Figures 7 and 8. Equilibrium isotherms: Fitting residual - Equations 2 and 3.



Figures 9 and 10. Equilibrium isotherms: Fitting residual - Equations 4 and 7.



Figures 11 and 12. Equilibrium isotherms: Response Surface - Equations 2 and 3.



Figures 13 and 14. Equilibrium isotherms: Response Surface - Equations 4 and 7.

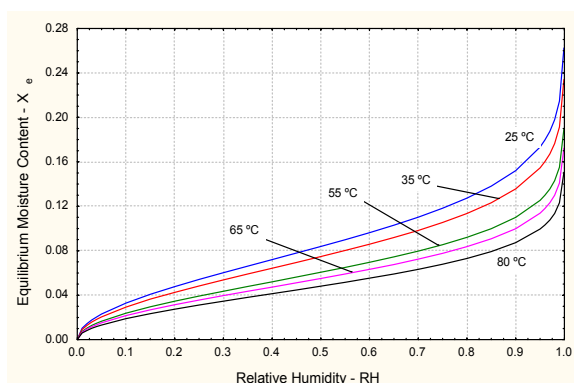


Figure 15. Long-fiber cellulose equilibrium isotherms: Simulation: Equation 3.

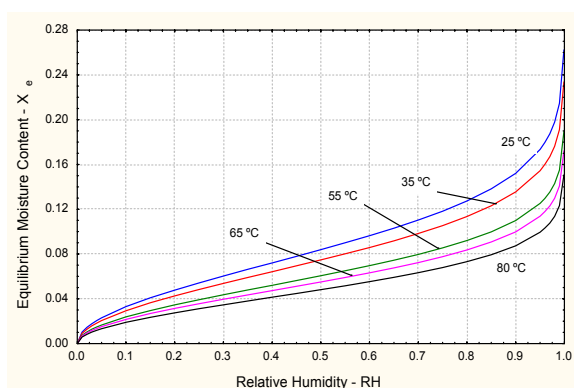


Figure 16. Long-fiber cellulose equilibrium isotherms: Simulation: Equation 4.

The analysis of Table 3 results (R^2 , F test), Figures 7 to 10 (estimation residuals) and 11 to 14 (response surfaces) show a better performance of Equations 3 and 4. The observation of the simulated isotherms, Figures 15 and 16, however, shows that these two equations might be considered equivalents in the region of relative humidity and temperature studied in this work.

It is very important to make clear that, in the region of relative humidity upon 80 %, fitting results are an extrapolation of the real isotherms behavior. They are shown because the knowledge of isotherms behavior in the entire range of relative humidity (0 – 100%) is important and desirable.

Conclusion

The long-fiber cellulose equilibrium isotherms obtained agree with those found in paper and cellulose isotherms literature (Motta Lima, 1999; Motta Lima *et al.*, 2001), the retained water decreasing with temperature rising. Temperature effects can be observed from Figures 6 (experimental) and Figures 15 and 16 (fitted isotherms).

Equations 3 (modified Henderson - Neuman *et al.*, 1986) and 4 (modified Henderson - this work) had the

best adjusting performance among those equations/models analyzed and might be considered equivalent to represent the moisture equilibrium isotherms for the long-fiber cellulose and the range of relative humidity and temperature studied here.

Nomenclature

c_1, c_2, c_3	- parameters of Equations 1 to 6	[see equations]
d.b.	- dry basis	
F	- F statistics, \equiv values and the ratio between mean of the the mean of the square of the predicted estimation residual	[-]
R^2	- fitting correlation coefficient	[-]
RH	- relative humidity	[-]
T	- absolute temperature	[K]
X_e	- long-fiber cellulose moisture equilibrium (d.b.)	[-]

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