# EFFECT OF DRYING TEMPERATURE ON THE NUTRITIONAL QUALITY OF THE *PINHÃO* (*ARAUCÁRIA ANGUSTIFOLIA*) FLOUR

***Angela Gava Barreto*[1], *Regina Isabel Nogueira*[2], *Luzimar da Silva de Mattos*[2], *Rossana Catie Bueno De Godoy*[3] *and Suely Pereira Freitas*[4]**

[1]Centro Federal de Educação Tecnológica Celso Suckow da Fonseca – CEFET/RJ, Rua Voluntários da Pátria 30, Bairro Belo Horizonte, Valença, RJ, CEP: 27600-000, Brazil
[2]Embrapa Food Tecnology, Av. das Américas 29501, Guaratiba, Rio de Janeiro, RJ, CEP: 23020-470, Brazil
[3]Embrapa Forestry, Estrada de Ribeira Km 111 Guaraituba, CEP: 83411000 COLOMBO, Paraná, Brazil.
[4]Universidade Federal do Rio de Janeiro – UFRJ, Escola de Química, Av. Horácio Macedo 2030, Centro de Tecnologia, Bloco E, Cidade Universitária, Rio de Janeiro, RJ, CEP: 21941-909, Brazil

Tel.: 55 21 3622-9611 email: regina.nogueira@embrapa.br

*Abstract:* At present, there is quite limited market for *pinhão* products due to their low level of industrialization. This study aimed to evaluate the drying process of *pinhão* at 40 $^oC$, 50 $^oC$ and 60 °C for essential amino acids preservation in the final product. Effective diffusivity ($D_{eff}$) was $15.6x10^{-10} m^2.s^{-1}$ at 60 $^oC$ and the correspondent activation energy was 31.13 kJ. $mol^{-1}$. Compared to raw *pinhão*, it was observed greater retention of the amino acid content for the *pinhão* flour obtained at 50 $^oC$.

*Keywords:* diffusivity, drying kinetics, essential amino acids, activation energy

## Introduction

*Araucária angustifolia* is a traditional tree of the cultural and economic importance in Brazil and it has an important ecological role in Araucaria moist forests. These seeds have an endosperm that is used in a regional cuisine in the breads and cakes preparation which taste is much appreciate for sensory characteristics. The availability of this raw material is quite limited by the low level of industrialization (BALBINOT et al., 2008) and the lack of products with *pinhão* is one of the main challenges of the productive chain of this material. The development and the provision of value-added products (CORSO et al., 2002 and VIEIRA SILVA et al., 2009) may contribute to the conservation of the remaining forest species and additionally offer appropriate technologies for implementation in rural areas.

This study aimed to establish the drying kinetics of the of *pinhão* endosperm for the preservation of nutritional quality of their flour with respect to essential amino acids content to human health.

## Material and method

*Raw material*: *pinhão* seeds collected in the producing regions of the Paraná State, by Embrapa Forestry, according to the authorization number 30147-1 / 2014 of the Environment Ministry.

*Processing*: The seeds were peeled according to the procedure recommended by Cornejo et al. (2014) and presenting irregular cuts of 8 mm average thickness.

*Drying*: *Pinhão* endosperm was dehydrated in a forced convective dryer, in triplicate, at 40 °C, 50 °C and 60 $^{o}$C and the physical properties of air were monitored by a Traceable®Hygrometer Thermometer Dew Point, mark Cole-Parmer until the equilibrium moisture content.

*Drying rate*: The samples were weighed at 30-minute intervals until no mass of the sample remains unchanged over three successive weighing.

*Effective diffusivity*: it was estimated from fitting the dimensionless moisture and time data by the mathematical model proposed by Fick (Eq. 1) (CRANK, 1975).The parameters were estimated using non-linear regression by Gauss Newton method with STATISTICA 12.0. The effect of temperature on drying rate was estimated by the Arrhenius equation (Eq. 2).

*Eq. 1* $$M_R = \frac{M-M_S}{M_0-M_S} = \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{n^2\pi^2 D_{eff}t}{r^2}\right)$$

*Eq.2* $$D = D_o \exp\left(\frac{-E_a}{R.T_v}\right)$$

**Nomenclature**

| | | | |
|---|---|---|---|
| $D_{eff}$ | diffusion coeficiente, $m^2. s^{-1}$ | n | number of terms |
| $D_0$ | pre-exponential fator, $m^2. s^{-1}$ | R | universal gas constant, kJ/kg mol K |
| $E_a$ | activation energy, kJ. kg $mol^{-1}$ | $R^2$ | correlation coefficient |
| M | moisture content at time t, kg moisture/kg dry matter | r | radius of sphere, m |
| $M_0$ | initial moisture contente, kg moisture/kg dry matter | $T_v$ | air temperature, K |
| $M_S$ | equilibrium moisture content, kg moisture/kg dry matter | t | drying time, min |
| MR | moisture ratio | | |

*Essential amino acids analysis*: are carried out in a chromatographic Alliance$^{TM}$ 2695 (Waters$^{TM}$) system. Fluorescence detector (W475 Waters$^{TM}$) is used set at the excitation wavelength of 250 nm and emission of 395 nm. Thermo® chromatographic column (BDS Hypersil C18, 4.6 x 100 mm; 2.4 µm) is used at 37 °C with an injection volume of 5µL. The elution mode is a gradient of three mobile phases: A-Acetate Buffer Kit (AQC), B and C-Acetonitrile-Water, according to AOAC method 994.12/2000 and Liu et al. (1995).The results were evaluated by variance analysis (ANOVA) and Fisher's test (LSD) ($p < 0.05$).

## Results

Figure 1, 2 e 3 shows the dimensionless moisture as function of drying time of *pinhão* endosperm at 40, 50 and 60 $^{o}$C whose regression coefficient was 0.9643, 0.9716 and 0.9666, respectively.

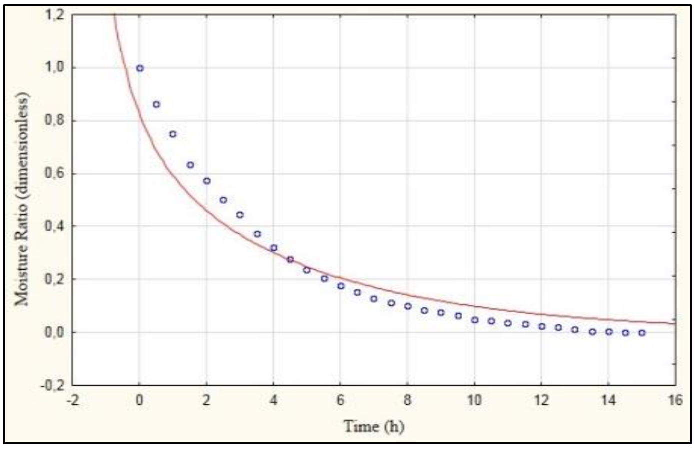

**Fig.1.** Experimental and predicted data for the *pinhão* endosperm drying at 40$^{o}$C.

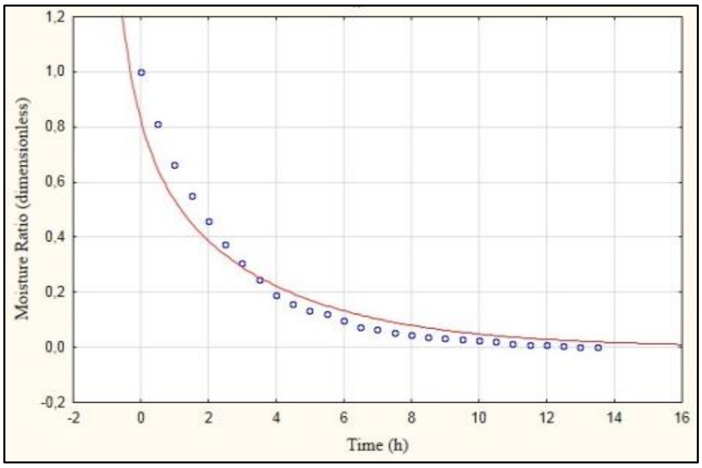

**Fig.2.** Experimental and predicted data for the *pinhão* endosperm drying at 50$^{o}$C.

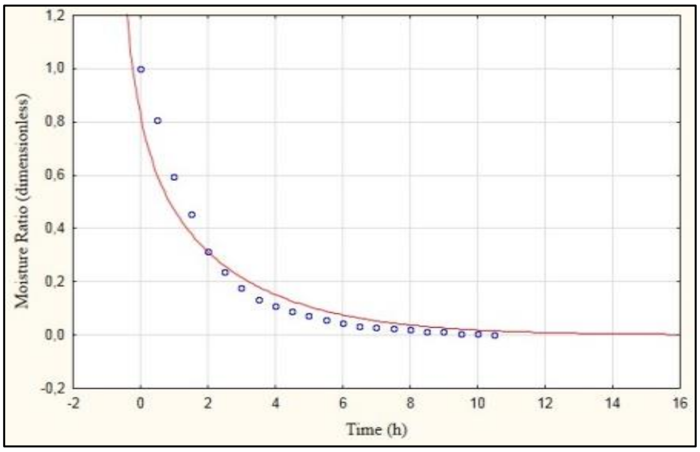

**Fig.3.** Experimental and predicted data for the *pinhão* endosperm drying at 60$^o$C.

Regarding the curves in figures 1, 2 and 3 was possible to see the relationship between the drying time and air temperature. The *pinhão* drying at 65 °C, closer to the present working condition, Capella (2008) found that it takes 8 hours to get the *pinhão* with constant ratio moisture, indeed similar to that found in the processing at 60 °C (fig. 3).

The effective diffusivity ($D_{eff}$) was $8.19x10^{-10}$, $11.4x10^{-10}$ and $15.6x10^{-10} m^2.s^{-1}$at the temperatures 40 °C, 50 °C and 60 °C respectively. Oliveira et al. (2008) reported the drying raw *pinhão* after peeled and cut into 5 mm thick slices, found magnitudes of effective diffusion coefficients between $1.64x10^{-10}$ to $4.52x10^{-10}$ $m^2.s^{-1}$ in the range of air temperature from55 to 85 °C. Comparing these results, it was revealed that water is removed of *pinhão* at slightly higher facility in the present study, probably due to variation in sample size as the peel removal process was carried out mechanically. Other factors may contribute like the maturation or the porosity of seeds.

The effect of temperature on moisture in *pinhão* is showed in Figure 4.

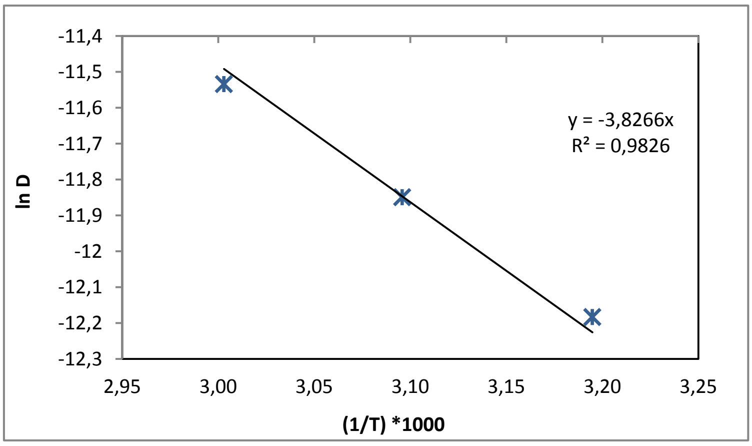

**Fig.4.** Arrhenius plot for the average diffusion coefficient in function of the drying air temperature

Figure 4 shows the dependence of the effective diffusivity with drying air temperature. Under these conditions, the activation energy (Ea) was 31.13 kJ.mol$^{-1}$. Oliveira et al. (2008) reported the value of 20.93 kJ.mol$^{-1}$, indicating a higher dependence of temperature in the raw material (*pinhão*) used in present study. Behavior similar to the present study was found for the other vegetables where the activation energy values for corn and carrots drying were 29.56 and 28.36 kJ.mol$^{-1}$, respectively (DOYMAZ, 2003; DOYMAZ & PALA, 2003).

The amino acid content in the *pinhão* endosperm and in their flours at the three temperatures is shown in the Table 1.

**Table1.**Amino acids content in the flour and raw *pinhão* endosperm$^{*}$

| Aminoacids | Raw *pinhão* | 40$^{o}$C | 50$^{o}$C | 60$^{o}$C |
|---|---|---|---|---|
| Asparticacid (Asp) | 47,17$^{a}$ | 35,12$^{b}$ | 37,63$^{b}$ | 35,95$^{b}$ |
| Glutamicacid (Glu) | 67,92$^{a}$ | 56,02$^{a}$ | 57,69$^{a}$ | 56,02$^{a}$ |
| Alanine (Ala) | 22,64$^{a}$ | 15,89$^{b}$ | 18,39$^{b}$ | 15,89$^{b}$ |
| Arginine (Arg) | 45,28$^{a}$ | 33,44$^{b}$ | 37,63$^{ab}$ | 34,28$^{b}$ |
| Phenylalanine (Phe) | 28,30$^{a}$ | 25,08$^{a}$ | 25,92$^{a}$ | 25,08$^{a}$ |
| Glycine (Gly) | 26,42$^{a}$ | 20,90$^{b}$ | 23,41$^{ab}$ | 21,74$^{b}$ |
| Histidine (His) | 11,32$^{a}$ | 6,69$^{c}$ | 8,36$^{b}$ | 8,36$^{b}$ |
| Isoleucine (Ile) | 15,09$^{a}$ | 13,38$^{b}$ | 12,54$^{b}$ | 13,38$^{b}$ |
| Leucine (Leu) | 35,85$^{a}$ | 30,10$^{b}$ | 30,10$^{b}$ | 30,94$^{ab}$ |
| Lysine (Lys) | 32,08$^{a}$ | 13,38$^{b}$ | 20,07$^{b}$ | 13,38$^{b}$ |
| Tyrosine and Phenylalanine (Tyr + Phe) | 49,06$^{a}$ | 39,30$^{b}$ | 40,13$^{ab}$ | 38,46$^{b}$ |
| Proline (Pro) | 11,32$^{a}$ | 11,71$^{a}$ | 10,87$^{a}$ | 10,87$^{a}$ |
| Serine (Ser) | 26,42$^{a}$ | 20,07$^{b}$ | 21,74$^{b}$ | 20,90$^{b}$ |
| Tyrosine (Tyr) | 20,75$^{a}$ | 14,21$^{b}$ | 14,21$^{b}$ | 13,38$^{b}$ |
| Threonine (Thr) | 22,64$^{a}$ | 15,89$^{b}$ | 20,07$^{a}$ | 15,89$^{b}$ |
| Valine (Val) | 30,19$^{a}$ | 24,25$^{b}$ | 25,08$^{b}$ | 25,92$^{b}$ |

$^{*}$values in mg amino acids.g$^{-1}$ protein; means in the same column with different superscript letters are significantly different at $p < 0.05$.

It was observed in Table 1 a behavior similar in amino acid composition to the end of the drying process under 40, 50 and 60 °C, it was reported by Leite et al (2008) performed when the *pinhão* was drying at 50 and 80 °C to flour production. As the observed at 50 $^{o}$C, in this study, only histidine and threonine composition was considered statistically different drying at 40 and 60 $^{o}$C, respectively. On the other hand, it was found greater retention at 50 $^{o}$C compared to raw *pinhão* ($p < 0.05$) of the following amino acids: arginine, glycine, threonine, and phenylalanine plus tyrosine. Prolonging the time or increasing the temperature of thermal processing may cause negative impacts in the content of different amino acids, as noted by Slupski (2010) that reported the effect of cooking and sterilization in seeds of bean. The loss of some amino acids during the heat treatment may be associated with reactions in food as denaturation or interaction with other substances (KORHONEN et al., 1998).

The Figure 5 show an essential amino acid score for raw *pinhão*, *pinhão* flour obtained from the drying at 50 °C and adapted values of Pires et al. (2006) for wheat and corn flour. This score was evaluated according to the recommendations of the FAO (1985) for needs of preschool children (2-5 years old), usually recommended values as a safe level for all groups age.

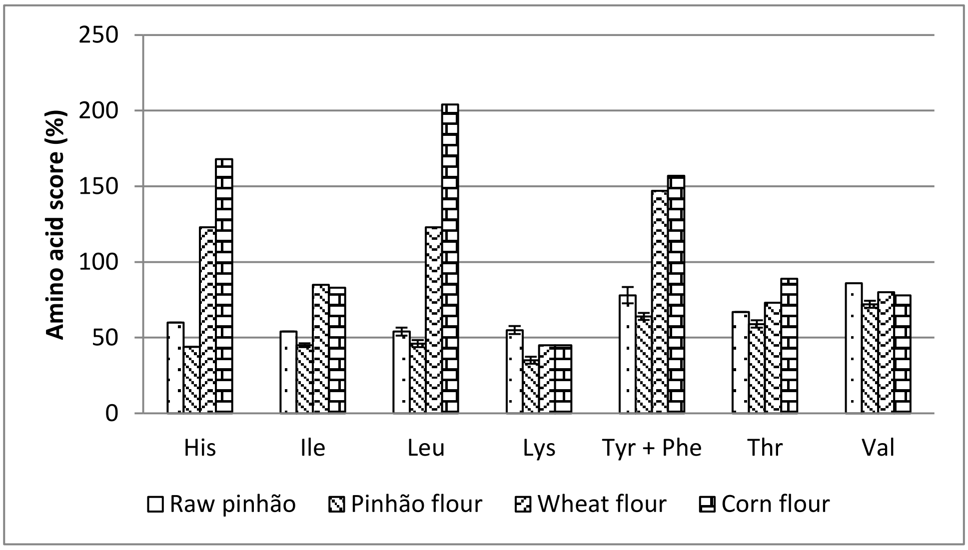

**Fig.5.** Essential amino acids score (%) of *pinhão* and others foods.

The limiting essential amino acid score of the *pinhão*, Figure 5, was similar to that found by Leite et al. (2008) whose name is lysine. The profile of at least half of the essential amino acid score is similar to that observed for cereals such as wheat and corn (PIRES, 2006). Despite of the limitations, the nutritional quality of a protein deficient in one or more essential amino acids can be improved by mixing it with another substrate is rich in this protein (s) amino acid (s) (DOMADARAN et al., 2010). The heat treatment may also be a means of increasing the bioavailability of proteins, where *pinhão* submitted to high temperatures prior to obtaining flour increases the bioavailability, possibly due to the anti-nutritional factor (trypsin inhibitor) was not detected (Leite el al., 2008).

## Conclusion

It can be concluded that the higher the temperature used in the process (60 ° C) greater the value found for the diffusion coefficient and thus there was a reduction of exposure time of the product.

The effective diffusivity was sensitive to variations in drying temperature, a fact confirmed by the activation energy value.

A better retention of amino acids in the flour, in comparison with the raw *pinhão* was observed at 50 ° C, since there is retention arginine, glycine and essential amino acids threonine, and phenylalanine plus tyrosine.

## References

AOAC. Association of Official Analytical Chemists. Official Methods of Analysis. Washington, methods 994.12, 2000.

BALBINOT, R.; GARZEL, J. C. L.; WEBER, K. S.; RIBEIRO, A. B. Tendências do consumo e preço de comercialização do pinhão (semente de *Araucaria angustifólia* (Bert.) O.kzte.) no Estado do Paraná. Ambiência. v. 4, n. 3, p. 463-472, set./dez. 2008.

CAPELLA, A.C.V. Farinha de pinhão (*Araucária angustifolia*): composição e estabilidade do gel. Dissertação (Mestrado em Tecnologia de Alimentos). Universidade Federal do Paraná, Curitiba, 2008.

CORNEJO, F. E. P., NOGUEIRA, R. I., DE CARVALHO, C. W. P, DE GODOY, R.C.B, OLIVEIRA, A. H., SANTOS, L. F. C., BARRETO, A. G., FREITAS, S. P. Descascamento e secagem de pinhão (*Araucaria angustifólia*) para a obtenção de farinha. Comunicado Técnico, n 206, dez, 2014.

CORSO, N. M.; MARTINS, G.; SANTOS, A. J.; BITTENCOURT, E. A cadeia produtiva do pinhão no Estado do Paraná: aspectos produtivos e comerciais. In: CONGRESSO ÍBERO-AMERICANO DE PESQUISA E DESENVOLVIMENTO DE PRODUTOS FLORESTAIS, II, Anais. Curitiba, Paraná: UFPR, 2002. p.138.

CRANK, J. The mathematics of diffusion, Oxford: Claredon Press. 2.ed. 1975. 414p.

DAMODARAN, S.; PARKIN, K. L.; FENNEMA, O. R. Química de alimentos de Fennema. 4 ed. Porto Alegre: Artmed, 2010. 900p.

DOYMAZ, I. Convective air drying characteristics of thin layer carrots. Journal of Food Engineering, v. 61, p. 259-364, 2003.

DOYMAZ, I; PALA, M.The thin-layer drying characteristics of corn. Journal of Food Engineering, v. 60, p. 125-130, 2003.

FAO/WHO/UNU. Energy and protein requirements: report of a joint expert consultation. Geneva: WHO, 1985 (WHO Technical Report Series, 724).

KORHONEN, H. PIHLANTO-LEPPÄLÄ, A., RANTAMÄKI, P., TUPASELA, T. Impact of processing on bioactive proteins and peptides. Trend in Food Science & Technology, v. 9, p.307-319, 1998.

LEITE, D. M. C.; JONG, E. V.; NOREÑA, C. P. Z. BRANDELLI, A. Nutritional evaluation of *Araucaria angustifolia* seed flour as a protein complement for growing rats. Journal of the Science of Food and Agriculture, 88, p.1166-1171, 2008.

LIU, H. J.; CHANG, B. Y. et al. Journal of AOAC International, v.78, n.3, p.736-744, 1995.

OLIVERA, D. M. C.; JONG, E. V de; NOREÑA, C. P. Z.; BRANDELLI, A. Nutritional evaluation of *Araucaria angustifólia* seed flour as a protein complemente for growing rats. Journal of the Science of Food and Agriculture. v. 88, p. 1166-1171, 2008.

PIRES, C. V.; OLIVEIRA, M. G. A.; ROSA, J. C.; COSTA, N. M. B. Qualidade nutricional e escore química de aminoácidos de diferentes fontes protéicas. Ciência e Tecnologia de Alimentos, Campinas, v. 26, n 1, p.179-187, jan.-mar.,2006.

SLUPSKI, J. Effect of cooking and sterilisation on the composition of amino acids in immature seeds of flageolet bean (*Phaseolus vulgaris L.*) cultivars. Food Chemistry. v. 121, p.1171-1176, 2010.

VIEIRA DA SILVA, C.; MIGUEL, L.A.; REIS, M.S. A comercialização do pinhão de *Araucaria angustifolia* no Distrito de Taquara Verde, município de Caçador-SC. Revista Brasileira de Agroecologia, v.4, n.2, nov. 2009.

## Acknowledgement

This paper was supported by the Embrapa Food Tecnology and Scholl of Chemical-UFRJ/TPQB.