RESEARCH ARTICLE

Effect of temperature on the rheological behavior of sugary cassava

Leiliane do Socorro Sodré Souza¹, Tatiane Pereira de Souza², Rafael Lopes e Oliveira³, Sérgio Duvoisin Junior³, Ari de Freitas Hidalgo¹, Anderson Mathias Pereira^{1*}

¹Faculty of Agricultural Sciences, Universidade Federal do Amazonas (UFAM), LABPROS (Separation Processes Laboratory), Av. General Rodrigo Octavio, CEP 69080-900, Manaus, Amazonas, Brazil, ²Faculty of Pharmaceutical Sciences, Universidade Federal do Amazonas (UFAM), Av. General Rodrigo Octavio, CEP 69080-900, Manaus, Amazonas, Brazil, ³School of Technology, Universidade do Estado do Amazonas (UEA), Av. Darcy Vargas, CEP 69050-020, Manaus, Amazonas, Brazil

ABSTRACT

The rheological behavior of the juice extracted from sugary cassava roots, a type of cassava that stored the largest amount of sugars and the starch as it was, at various temperatures (9-65°C) and in concentrations of 5°Brix, 10.5°Brix, and 18.5°Brix. The experiments were performed on a Brookfield viscometer in a shear rate range of 0.01-237.6 s⁻¹. The rheological models of Newton, Bingham, and Ostwald-De-Waele were fitted to the experimental results. The Newton model describes well the rheological behavior of the three samples evaluated. The effect of temperature on viscosity was evaluated using an Arrhenius equation; the viscosity value is influenced by the same temperature. The activation energy values for the concentrations of 5°Brix, 10.5°Brix and 18.5°Brix correspond to 3.14 kcal mol⁻¹, 3.53 kcal mol⁻¹ and 3.71 kcal mol⁻¹. This type of cassava can be used in the production of ethanol, fermented beverages and syrups. It is also an important alternative for food production, as the cultivation of cassava can be classified as less aggressive to the environment, in comparison with sugarcane.

Keywords: Rheological model; Cassava; Sugary cassava; Activation energy, Rheological parameters

INTRODUCTION

Cassava originates in the Amazon and belongs to the Euforbiacea family (Fao, 2013), this root is rich in starch and its use is the most used industrial application for this raw material. Among the advantages of cassava production are resistance to drought and pest attacks, in addition to the need for few inputs (Faostat, 2018). different type of cassava has been identified and has been investigated by researchers, it is popularly known as sugary cassava or mandiocaba. There are no large amounts of starch in these roots, but sugars, especially reducing sugars, such as fructose and glucose (Vieira et al., 2011; Souza et al., 2013a). These species can also be differentiated by the amount of moisture present in the roots, sugared cassava has around 90%, whereas non-sugared cassava has an average of 60%. The broth, called manicuera, is obtained from the roots of sugary cassava after peeling the roots are pressed and then the manicure is collected. This liquid can be applied for various purposes in the food industry, such as syrups and fermented drinks (Carvalho et al., 2004; Souza et al., 2013a; Souza et al., 2013b). Identifying the rheological behavior of new raw materials and products is important, as the fluid flow depends on both the quantitative and qualitative composition and, consequently, leads to the correct realization of projects and equipment sizing, plus another tool for quality control (Fischer & Windhad, 2011; Vandressen et al., 2009; Augusto et al., 2012; Telis-Romero et al., 1999, Bhandari et al., 2002). Knowing the rheological parameters of a sample at different temperatures and concentrations is essential for food processing, pois a matéria-prima é submetida a diferentes operações, como pasteurização, bombeamento, evaporação, resfriamento e outros, logo é necessário realizar ensaios para entender como a amostra irá se comportar em condições distintas (Ibarz et al., 1987; Fischer & Windhad, 2011; Khalil et al., 1987). The rheological properties can be obtained from various mathematical models, these models

*Corresponding author:

Anderson Mathias Pereira, Faculty of Agricultural Sciences, Universidade Federal do Amazonas (UFAM), LABPROS (Separation Processes Laboratory), Av. General Rodrigo Octavio, CEP 69080-900, Manaus, Amazonas, Brazil. **E-mail:** ampereira.eng@gmail.com

Received: 01 July 2019; Accepted: 11 January 2020

facilitate the interpretation of basic shear diagrams. The Newtonian model is used to describe the behavior of fluids that have a linear relationship between shear stress (σ) and shear rate (γ), for non-Newtonian fluids, several models can be applied, including Ostwald-De-Waele, Herschel-Bulkley and Bingham. The temperature directly influences the variation in the viscosity of fluids, for liquids the higher the temperature, the lower the viscosity value, a intensidade dessa variação pode ser avaliada através da equação de Arrhenius, onde a energia de ativação é usada como parâmetro para esta medida (Dak et al., 2007; Shamsudin et al., 2013). This work aims to evaluate the rheological behavior of manicures extracted from sweetened cassava (Manihot Esculenta Crantz), verify the influence of temperature and concentration on viscosity, taking into account the importance of providing data on new raw materials for the food processing and ethanol production industry.

MATERIALS AND METHODS

The sugary cassava roots were harvested at the Experimental Farm of the Federal University of Amazonas, in the city of Manaus, after 12 months of cultivation. The roots were washed in running water to remove dirt, then peeled, cut and pressed in a hydraulic squeezer (SOLAB, SL-10, Brazil) for the removal of the broth, known as a manicuera, and then vacuum filtered. The obtained liquid had a soluble solids content of 5°Brix, then was concentrated by evaporation in a water bath (Quimis, Q-215M, Brazil) to obtain two samples, one with 10.5°Brix and another with 18.5°Brix. The concentration values worked are close to those found in the samples of sugarcane juice according to the work developed by Astolfi-Filho et al. (2011). Soluble solids content was monitored using an Abbé refractometer (BEL, RMT, Italy) at 20°C, according to AOAC method 932.12 (1997).

Rheological measurements

The rheological properties were determined using a Brookfield viscometer in Small Sample Adapter (LVDV-II + Pro, Brookfield Engineering Laboratories, USA). In the temperature control a thermostatic bath (Quimis, Q-214M, Brazil) was used. The measurements were carried out at temperatures of 9,15, 25, 35, 45, 55 and 65°C, for the different concentrations (5, 10.5 and 18.5°Brix). The data of viscosity (η), shear stress (σ) and deformation rate (γ) were obtained using Rheocalc® software (Version V2.4, Brookfield Engineering Laboratories, USA). The shear rate range was 0.01 to 237.6 s⁻¹, and both ascending and descending tests were performed in triplicate for each temperature at the concentrations evaluated, in each replicate a new sample was used to avoid possible time effects. The mean and standard deviation were calculated using Microsoft Excel 2007 (XP Edition, Microsoft Corporation, USA). The experiments were carried out according to Ibarz et al. (1987) and Vandresen et al. (2009). Fig. 1 shows the peeled sweet cassava root (on the left) and the filtered juice (on the right).

Flow models

The rheological models evaluated were: Newton, Bingham, and Ostwald-De-Waele or Power Law (Eq.1-3) (Ibarz et al., 1996); the rheological data for the three concentrations at different temperatures were obtained using software, and the best fit was evaluated by the correlation coefficient (R²).

Newton:
$$\sigma = \eta(\gamma)$$
 (Eq. 1)

Bingham: $\sigma = \sigma_0 + \eta_\infty \gamma$ (Eq. 2)

Ostwald-De-Waele: $\sigma = k(\gamma)^n$ (Eq. 3)

According to the definition of a Newtonian fluid (Eq. 1), the shear stress, σ and the shear rate, γ , are proportional to each other, through the parameter η , called Newtonian viscosity (Rao, 2014; Heldman & Lund, 2006).

A fluid that behaves like a solid until a limit stress (σ_0) is exceeded, and subsequently presents a linear relationship between shear stress and shear rate, has its rheological behavior called Bingham (Eq. 2) (Fox et al., 2006). In the Ostwald-De-Waele model (Eq. 3), where k e n correspond to the consistency coefficient and the flow behavior index, respectively, it is possible to understand whether the fluid is shear thinning or pseudoplastic when n <1, or shear thickening or diluting when n> 1; in the case of Newtonian fluid n = 1 (Rao, 2014).

The effect of the temperature on the viscosity was evaluated through the Arrhenius equation (Rao et al., 1984) (Eq. 4):

$$\eta_a = \eta_0 \exp\left(\frac{E_a}{RT}\right) \tag{4}$$

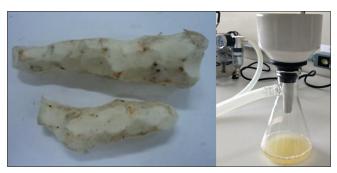


Fig 1. Sugary cassava peeled root (on the left) and the filtered juice extracted (on the right).

Where corresponds to the apparent viscosity (mPa.s), to an empirical constant (mPa.s), R = universal gas constant (1,987 × 10⁻³ kcal.mol⁻¹.K⁻¹); $E_a =$ activation energy for viscous flow (kcal.mol⁻¹), T = absolute temperature (K).

RESULTS AND DISCUSSIONS

The flow curves (Fig. 2A, Fig. 2B and Fig. 2C) were obtained for the manicuera samples of sugary cassava with concentrations of 5, 10.5 and 18.5° Brix, in the temperature range of 9-65°C.

Fig. 2 shows the shear stress reograms and shear rates of the sugary cassava juice in three different concentrations in the temperature range from 9 to 65 $^{\circ}$ C. As the shear

stress and shear rates of the reograms have a linear relationship, the behavior of the sweetened cassava juice in the studied concentration range can be considered as Newtonian. Fig. 3 (A, B and C) shows the viscosity at different temperatures as a function of the shear rate, at concentrations of 5, 10.5 and 18.5°Brix, respectively. Fig. 3 complements the analysis of Fig. 2 and presents the constant viscosity at each temperature of analysis, the higher values are related to the lower temperatures and lower to the higher temperatures, typical characteristics of a newtonian fluid.

Fig. 3 (A, B and C) show the viscosity at different temperatures as a function of the shear rate, at concentrations of 5, 10.5 and 18.5 °Brix, respectively.

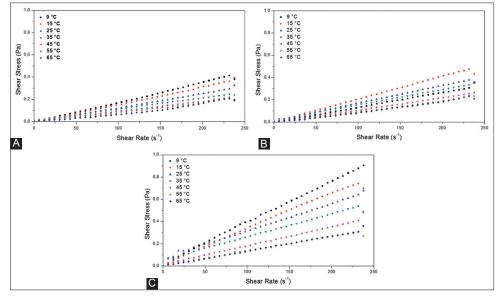


Fig 2. Manicuera flow curves for concentration at (A) 5, (B) 10.5 and (C) 18.5 °Brix at different temperatures.

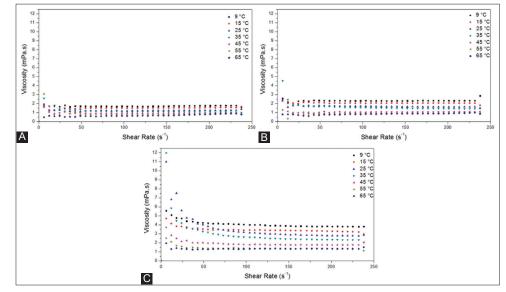


Fig 3. Viscosity as a function of the shear rate of the manicuera with (A) 5, (B) 10.5 and (C) 18.5 Paria t different temperatures.

The rheological parameters are presented in Table 1, adjustments were made for the models, Ostwald-dewaale (Power Law), Newton, and Bingham, for the manicuera extracted from sugary cassava roots at different concentrations and temperatures (9°C, 15°C, 25°C, 35°C and 45°C, 55°C, 65°C). Selection of the rheological model that best describes the flow behavior of the samples was performed by comparing the correlation coefficients, R². Knowing the rheological data is necessary for the knowledge of the relationship between rheology and food processing, as well as process optimization and simulation (Fischer & Windhad, 2011). The experimental results showed that the flow characteristics of the manicuera at 5°Brix, 10.5°Brix and 18.5°Brix obtained better data adjustment to the model of Power Law with values of R² in the range of 0.9878-0.9996, however the values of n for this models are close to 1 in most of the analyzed points, just as in the Bingham model the limit stress value is approximately zero, so the Newton model can well describe the rheological behavior of the three samples analyzed. Astolfi-Filho et al. (2011) studied the rheological behavior of three samples of sugarcane juice, with soluble solids concentration of 19.1%, 18.8% and 18.2%; the model that presented the best fit to the experimental data was the Newtonian one, and the dynamic viscosity had its value reduced with the temperature increase.

Table 2 shows the parameters of the Arrhenius equation obtained from the adjustment to the data obtained in the experiments carried out, in which variations of temperature and concentration occurred. The correlation coefficients for the manicuera samples (5°Brix, 10.5°Brix and 18.5°Brix) are in the range of 0.9573 - 0.9954; which represents that the evaluation of the influence of the temperature on the apparent viscosity through the Arrhenius equation is considered satisfactory for this study. The activation energy values determined for the manicuera in the concentrations of 5°Brix, 10.5°Brix and 18.5°Brix correspond, respectively, to 3.1437 kcal mol⁻¹, 3.5258 kcal mol⁻¹, and 3.7110 kcal mol⁻¹, it is observed that for the range of concentration studied, Ea values increase with increasing concentration, according to Souza et al. (2013b), the activation energy for syrup produced from manicuera extracted from sugary cassava, with a soluble solids content of 80 °Brix, is 69.65 kJ.mol⁻¹; this result is proportional to that obtained in this study, for 18.5°Brix the activation energy corresponds to 15.53 kJ mol⁻¹. According to Chin et al. (2009), where they evaluated the rheological behavior of pummelo juice at different concentrations and

Table 1: The rheological parameters obtained through the Power Law, Newton and Bingham models for manicuera in the concentrations of 5°Brix, 10.5°Brix and 18.5°Brix and in the temperatures of 9, 15, 25, 35, 45, 55 and 65°C

Concentration	Temperature	Power Law		Newton		Bingham			
(°Brix)	(°C)	k	n	R ²	η	R ²	σ	η	R ²
5	9	0.0015±0.0001	1.0271±0.0135	0.9970	0.0018±0.0000	0.9967	-0.0029±0.0022	0.0018±0.0000	0.9968
	15	0.0012±0.0001	1.0572±0.0089	0.9987	0.0016±0.0000	0.9975	-0.0055±0.0015	0.0016±0.0000	0.9981
	25	0.0009±0.0001	1.0609±0.0118	0.9978	0.0013±0.0000	0.9964	-0.0038±0.0016	0.0013±0.0000	0.9968
	35	0.0019±0.0001	0.8889±0.0091	0.9980	0.0011 ± 0.0000	0.9916	0.0116±0.0008	0.0010 ± 0.0000	0.9987
	45	0.0011±0.0001	0.9602±0.0169	0.9945	0.0009 ± 0.0000	0.9941	0.0031±0.0014	0.0009 ± 0.0000	0.9946
	55	0.0005±0.0000	1.0719±0.0001	0.9910	0.0008±0.0000	0.9893	-0.0005±0.0020	0.0008 ± 0.0000	0.9891
	65	0.0001±0.0000	1.3770±0.0302	0.9919	0.0007±0.0000	0.9571	-0.0154±0.0032	0.0008 ± 0.0000	0.9723
10.5	9	0.0017±0.0002	1.0557±0.0279	0.9878	0.0014±0.0000	0.9949	-0.0067±0.0061	0.0024±0.0000	0.9870
	15	0.0023±0.0001	0.9723±0.0143	0.9962	0.0020±0.0000	0.9960	0.0034±0.0028	0.0020 ± 0.0000	0.9960
	25	0.0023±0.0001	0.933±0.0112	0.9974	0.0016±0.0000	0.9953	0.0082±0.0020	0.0016 ± 0.0000	0.9966
	35	0.0024±0.0001	0.9029 ± 0.0086	0.9983	0.0015±0.0000	0.9936	0.0140 ± 0.0010	0.0014±0.0000	0.9989
	45	0.0008±0.0001	1.0423±0.0071	0.9991	0.0011 ± 0.0000	0.9985	-0.0026±0.0008	0.0011 ± 0.0000	0.9987
	55	0.0006±0.0001	1.0828±0.0114	0.9981	0.0009 ± 0.0000	0.9956	-0.0047±0.0012	0.0010 ± 0.0000	0.9967
	65	0.0004±0.0000	1.1571±0.0179	0.9959	0.0009 ± 0.0000	0.9877	-0.0095±0.0018	0.0010 ± 0.0000	0.9926
18.5	9	0.0055±0.0001	0.9296±0.0041	0.9996	0.0038 ± 0.0000	0.9973	0.0232±0.0022	0.0037±0.0000	0.9993
	15	0.0050±0.0002	0.9171±0.0110	0.9974	0.0033±0.0000	0.9941	0.0204±0.0043	0.0032±0.0000	0.9962
	25	0.0089±0.0007	0.7797±0.0156	0.9922	0.0029±0.0000	0.9622	0.0633±0.0037	0.0025±0.0000	0.9954
	35	0.0076±0.0006	0.7747±0.0157	0.9921	0.0024±0.0000	0.9600	0.0511±0.0043	0.0021±0.0000	0.9913
	45	0.0021±0.0002	0.9704±0.0216	0.9910	0.0018±0.0000	0.9909	0.0084±0.0035	0.0017±0.0000	0.9919
	55	0.0019±0.0001	0.9286±0.0180	0.9932	0.0013±0.0000	0.9910	0.0083±0.0024	0.0013±0.0000	0.9930
	65	0.0011±0.0001	1.0339±0.0171	0.9952	0.0013±0.0000	0.9948	-0.0025±0.0022	0.0014±0.0000	0.9949

Table 2: Parameters obtained from the Arrhenius model and
the corresponding correlation coefficients

Parameters	Soluble solids (°Brix)					
	5	10.5	18.5			
Ea (kcal mol-1)	3.1437±0.0905	3.5258±0.2244	3.7110±0.3432			
η ₀ (mPa.s ⁿ)	0.0063±0.0009	0.0044±0.0017	0.0054±0.0032			
R ²	0.9954	0.9787	0.9573			

Table 3: Mean and standard deviation values for the viscosity (η) of samples at different concentrations and temperatures

Temperature	η (110 s⁻¹)					
(°C)	5°Brix	10.5°Brix	18.5°Brix			
9	1.7238±0.0127	2.3195±0.0382	3.9983±0.0638			
15	1.5162±0.0540	2.0578±0.0000	3.4116±0.0255			
25	1.2275±0.0510	1.7058±0.0382	3.1047±0.0510			
35	1.0830 ± 0.0000	1.5253±0.3701	2.5993±0.0000			
45	0.9206 ± 0.0255	1.0650±0.0255	1.8231±0.0255			
55	0.8033±0.0382	0.9025±0.0000	1.3583±0.0064			
65	0.6498 ± 0.0000	0.8484±0.0765	1.3358±0.0511			

temperatures, the maximum activation energy was found in association with the 30 °Brix concentration in a study range of 20-50 °Brix, however, according to Quek et al. (2013), where the influence of temperature and concentration on the rheological parameters of soursop juice is studied, a reduction in E_a values is observed accompanying an increase in the concentration (10 – 40 °Brix), only in 50°Brix the activation energy value increases. In the evaluation of the rheological properties of samples of sugarcane juice with different concentrations, higher values of activation energy are related to lower concentration values (Astolfi-Filho et al., 2011).

The values of viscosity, η , determined for the manicuera samples studied (5, 10.5 and 18.5°Brix), measured in triplicate, are reported in Table 3, where it is possible to observe that the viscosity values decrease with the addition of temperature, and are elevated as the concentration of soluble solids of the manicuera increases, for the study range of 5 - 18.5°Brix. In the case of Arrhenius equation, it is possible to observe a general tendency of the decrease of the apparent viscosity with the temperature increase (Vandresen et al., 2009), in relation to the soluble solids content, according to Deshmukh and Raju, (2015), where they deal with Sapota's juice rheological behavior, the viscosity of liquid foods depends heavily on temperature and concentration, an increase in the amount of soluble solids leads to an increase in the viscosity of the juice.

CONCLUSIONS

The manicuera, in the concentrations of 5°Brix, 10.5°Brix and 18.5°Brix presented Newtonian behavior. Viscosity values decrease with increasing temperature (9°C, 15°C, 25°C, 35°C, 45°C, 55°C and 65°C), and are elevated as the soluble solids concentration of manicuera increases (5°Brix, 10.5°Brix and 18.5°Brix). The Arrhenius equation was successfully applied to describe the effect of temperature on the viscosity of the samples analyzed. The activation energy values found for the concentrations of 5°Brix, 10.5°Brix and 18.5°Brix corresponded respectively to 3.14 kcal mol⁻¹, 3.53 kcal mol⁻¹, and 3.71 kcal mol⁻¹, respectively, so that the effect of temperature on viscosity was maintained concentrations. The design and dimensioning of equipment for Newtonian fluids is simple, which classifies the studied raw material as interesting for industrial processing, focusing on the production of syrups and fermented drinks.

Author contributions

Authors contributed equally to this study.

REFERENCES

- AOAC. 1997. Official Methods of Analysis. 16th ed. Association of Official Analytical Chemists, Arlington, Virginia.
- Astolfi-Filho, Z., V. R. N. Telis, E. B. Oliveira, J. C. R. Coimbra and J. Telis-Romero. 2011. Rheology and fluid dynamics properties of industrial sugarcane juices. Biochem. Eng. J. 53: 260-265.
- Augusto, P. E. D., M. Cristianini and A. Ibarz. 2012. Effect of temperature on dynamic and steady-state shear rheological properties of Siriguela (*Spondias purpurea* L.) Pulp. J. Food Eng. 108: 283-289.
- Bhandari, P. N., R. S. Singhal and D. D. Kale. 2002. Effect of succinylation on the rheological profile of starch pastes. Carbohydr Polym 47: 365-371.
- Carvalho, L. J. C., C. R. B. Souza, J. C. M. Cascardo and L. Campos. 2004. Identification and characterization of novel cassava (*Manihot esculenta* Crantz) clone with high free sugar content and novel starch. Plant Mol. Biol. 56: 643-659.
- Chin, N. L., S. M. Chan, Y. A. Yusof, T. G. Chuah and R. A. Talib. 2009. Modelling of rheological behaviour of pummelo juice concentrates using mastercurve. J. Food Eng. 93: 134-140.
- Dak, M., R. C. Verma and S. N. A. Jaaffrey. 2007. Effect of temperature and concentration on rheological properties of "Kesar" mango juice. J. Food Eng. 80: 1011-1015.
- Deshmukh, P. S., S. S. Manjunatha and P. S. Raju. 2015. Rheological behaviour of enzyme clarified sapota (*Achras sapota* L) juice at different concentration and temperatures. J. Food Sci. Technol. 52: 1896-1910.
- FAOSTAT Database, Food and Agriculture Organization of the United Nations. 2018. FAO, Rome, Italy. Available from: http://www.fao. org/3/a-i3278e.pdf. [Last accessed on 2018 Feb 10].
- Fischer, P. and E. J. Windhad. 2011. Rheology of food materials. Curr. Opin. Colloid Interface Sci. 16: 36-40.
- FAO. 2013. Save and Grow: Cassava a Guide to Sustainable Production Intensification. p. 140. Available from: http://www.fao. org/ag/save-and-grow/cassava/pdf/sg-cassava-brief.pdf. [Last accessed on 2018 Feb10].
- Fox, R. W., A. T. Mcdonald and P. J. Pritchard. 2006. Introduction to Fluid Mechanics. 6th ed., Rio de Janeiro.

- Heldman, D. R. and D. B. Lund. 2006. Handbook of Food Engineering. 2th, CRC Press, Boca Raton, Flórida.
- Ibarz, A., A. Garvin and J. Costa. 1996. Rheological behaviour of sloe (*Prunus spinosa*) fruit juices. J. Food Eng. 27: 423-430.
- Ibarz, A., M. Vicente and J. Graell. 1987. Rheological behaviour of apple and pear juices and the concentrates. J. Food Eng. 6: 257-267.
- Khalil, K. E., P. Ramakrisna, A. M. Nanjundaswamy and M. V. Patwardhan. 1987. Rheological behaviour of clarified banana juice: Effect of temperature and concentration. J. Food Eng. 10: 231-240.
- Quek, M. C., L. N. Chin and Y. A. Yusof. 2013. Modelling of rheological behavior of soursop juices concentrates using shear rate temperature-concentration superposition. J. Food Eng. 118: 380-386.
- Rao, M. A. 2007. Rheology of Fluid and Semisolid Foods: Principles and Applications. 2th ed. Springer Science, USA.
- Rao, M. A., H. J. Cooley and A. A. Vitali. 1984. Flow properties of concentrated juices at low temperature. Food Technol. 38: 113-119.

- Shamsudin, R., C. S. Ling, N. M. Adzahan and W. R. W. Daud. 2013. Rheological properties of ultraviolet-irradiated and thermally pasteurized Yankee pineapple juice. J. Food Eng. 116: 548-553.
- Souza, H. A. L., T. C. L Souza, A. S. Lopes and R. S. Pena. 2013b. Production and characterization of sugary cassava syrup. Int. J. Food Eng. 9: 39-44.
- Souza, H. A. L., A. S. Bentes, T. M. S. Ladeira, A. S. Lopes and R. S. Pena. 2013a. Physicochemical properties of three sugary cassava landraces. Ciênc. Rural. 43: 792-796.
- Telis-Romero, J., V. R. N. Telis and F. Yamashita. 1999. Friction factors and rheological properties of orange juice. J. Food Eng. 40: 101-106.
- Vandresen, S., M. G. N. Quadri, J. A. R. Souza and D. Hotza. 2009. Temperature effect on the rheological behaviour of carrot juices. J Food Eng. 92: 269-274.
- Vieira, E. A., J. F. Fialho, F. G. Faleiro, G. Bellon, K. G. Fonseca and L. J. C. Carvalho. 2011. Molecular characterization of sugary and non-sugary cassava accessions. Ciênc. Agrotecnol. 35: 455-461.