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RHEOLOGICAL CHARACTERISTICS OF ASSAI AND PASSION FRUIT SMOOTHIES FORTIFIED WITH UNRIPE BANANA PULP

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ABSTRACT The determination of the food rheology is required in modeling and optimization of plant processes. In the food industry, juices are the most important liquids derived from fruits, so the characteristics of their flows have been a major topic of study in recent years. Ready-to-drink fruit beverages showed a growth of about 12% per year in Brazil, this increase was stimulated by the will to consume healthy drinks. Passion fruit juice has gained a special place in the juice market due to its intense exotic flavor, strong aroma (typically tropical), high acidity and efficient processed pulp. The assai, an exotic fruit from the Amazon, is rich in antioxidants and contains a variety of compounds associated to health benefits. Therefore, this project aims at determining the rheological characteristics of assai and passion fruit smoothies enriched with unripe banana pulp. Rheological properties and viscosity were determined by using a BROOKFIELD programmable rheometer, model DVIII. Results were evaluated using the software *STATISTICA version 8.0*. The evaluation of viscosity as a function of temperature corresponds to the Arrhenius model, which made it possible to determine the E_a (Ativation Energy). The rheological behavior of smoothies followed the model of Herschel-Bulkley (HB).

Keywords: Ready-to-drink fruit beverages, Rheological characteristics, Assai, Passion fruit, Viscosity.

INTRODUCTION Brazil is the third largest fruit producer in the world, and the food industry, conscious of Brazil's potential, is using technology to invest in a growing market: that of ready-to-drink fruit juices (Monteiro, 2006).

The passion fruit juice has reached within the juice market due to intense exotic flavor, strong aroma (typically tropical), high acidity and pulp yield (Garruti, 1989). These features made passion fruit juice interesting for the preparation of mixed drinks, fruit juices, ice cream, cream and other confectionery products (Medina et al., 1980). Even if added in small proportions, passion fruit juice is capable of giving intense aroma and flavor in various products. Moreover, the passion fruit juice is rich in citric acid, minerals and carotenoids.

The assai, exotic fruit from the Amazon, is rich in antioxidant components and composes a variety of products associated with the benefit of health. It also applies to energy and soft drinks. Kuskoski et al. (2006) found high values of total polyphenols in frozen pulp of assai.

The fruit juice added to the unripe pulp banana is introduced as an important source of macro and micro nutrients (vitamins A, B1, B2, nicotinic acid, sodium, potassium, magnesium, manganese, copper, phosphorus, sulfur, chlorine and iodine) (Valle & Camargos, 2004), and contain resistant starch.

The current positive trend of the fruit juice industry, which stems from the non-alcoholic beverage market, is to improve and automate fruit juice production plants. During processing, the fruit juice industry deals with juice in a variety of concentrations and temperatures and is submitted to unit operations such as pumping, heat exchange, evaporation, spray-drying and others. In order to have a suitable process design, operation and control, knowledge of thermophysical and rheological behavior of the fruit juice as affected by water fraction and temperature are of fundamental importance (Cabral et al., 2007).

According to the Gratão et al. (2005), the rheological properties of most of the liquid foods exhibit substantial changes during the processing stages due to their dependence upon temperature and concentration. In general, the viscosity of liquids decreases with an increase in temperature, and a measure of the temperature influence on the rheological parameters is usually obtained from the Arrhenius-type equation (Saravacos, 1970; Ibarz et al., 1996).

Many fluids of interest in industrial practice are non-Newtonian in nature, being characterized by viscous polymeric emulsions, such as those encountered in polymer and plastic extrusion, pharmaceuticals, cosmetics, food, petrochemical and hygiene product processing. Different empirical equations are available for the description of their rheological behavior, such as the Herschel-Bulkley model (Saravacos and Kostaropoulos, 1995) and the Ostwald-de-Waele model, also known as the Power-Law, which is one of the most extensively used to describe the rheological behavior of fruit juices (Rao et al., 1984).

The objective of this work was to evaluate the viscosity and the rheological characteristics of assai and passion fruit smoothies fortified with unripe banana pulp during 180 days of shelf life.

MATERIALS AND METHODS The beverage was bottled in 300 mL glass bottles and led to the exhaustion tunnel, closed hermetically with metallic lids and pasteurized for 15 minutes in boiling water. After cooling, the bottles were stored at room temperature for 180 days. The rheological properties and the viscosity were determined in the 0, 30, 60, 90 and 180 days by using a BROOKFIELD programmable rheometer, model DVIII, with an small samples adapter and a cylindrical spindle (specification: S15). A BROOKFIELD thermostatic bath, model TC – 500 (-10 °C a +130 °C; ±0,03 °C) was used in order to maintain the temperature of the product as needed for each test.

Viscosity To analyze the relationship between the temperature and the viscosity, the rheometer was programmed to the constant shear rate at 20 rpm for 120 seconds at each temperature. The thermostatic bath temperatures were adjusted at 8 °C, 25 °C, 35 °C, 65 °C and 85 °C.

In order to evaluate the viscosity behavior as a function of temperature, the Arrhenius-type equation (Equation 1) was used for determination of the parameters η_0 e E_a.

$$\ln\eta = \ln\eta_0 + \frac{E_a}{RT} \qquad \text{(Equation 1)}$$

Whereas: η is the viscosity ($Kg.m^{-1}.s^{-1}$); η_0 is a parameter of the Equation 1 ($Kg.m^{-1}.s^{-1}$); E_a is the flow activation energy ($kJ.mol^{-1}$); R is the ideal gas constant ($8{,}314.10^{-3}$ $kJ.mol^{-1}.K^{-1}$) and T is the absolute temperature (K).

Rheological Characteristics To analyze the relationship between the shear rate and the shear stress, the rheometer was programmed as follows: 0,5 rpm (60 seconds); 1,0 rpm (60 seconds); 2,5 rpm (60 seconds) ; 5,0 rpm (60 seconds); 10,0 rpm (60 seconds); 20,0 rpm (60 seconds); 50,0 rpm (60 seconds); 100,0 rpm (60 seconds); 100,0 rpm (60 seconds); 50,0 rpm (60 seconds); 20,0 rpm (60 seconds); 10,0 rpm (60 seconds); 5,0 rpm(60 seconds); 2,5 rpm(60 seconds); 1,0 rpm(60 seconds); 0,5 rpm(60 seconds). The rheological characterization was carried out at 8 ºC and 25 ºC and the results evaluated by *STATISTICA version 8.0* software, using Power-Law and Herschel-Bulkley (HB) models.

Real fluids deform irreversibly and when stresses are applied to these materials, fluids flow. The strain energy is dissipated within the fluid as heat and cannot be recovered if the applied stress is suspended. Due to the flow, these materials are studied by the rheology through the relationship between the shear rate and shear stress (Steffe, 1996).

Several models have been proposed to correlate the shear rate and shear stress. This article presents a study of the following models:

$$\sigma = K(\gamma)^n \qquad \text{Power-Law Model} \qquad \text{(Equation 2)}$$

$$\sigma = \pm\sigma_0 - K(\gamma)^n \qquad \text{Herschel-Bulkley-HB Model} \qquad \text{(Equation 3)}$$

Whereas: σ is the shear stress (Pa) and γ is the shear rate (s^{-1}). The parameters found by the software *STATISTICA version 8.0* were: K is the consistency index ($Pa.s^n$), n is the flow behavior index (dimensionless) and σ_0 is the initial shear stress (Pa).

RESULTS

Viscosity The viscosity analysis was carried out twice for each temperature. The mean values and the standard deviation (SD) of the results are presented in the Table 1 below.

Table 1. Viscosity of the smoothie during 180 days

Time (days)	Viscosity ($Kg.m^{-1}.s^{-1}$)				
	8 ºC	25 ºC	35 ºC	65 ºC	85 ºC
0	6,78±0,05	5,64±0,09	5,00±0,09	3,77±0,25	2,53±0,04
30	6,59±0,04	5,18±0,04	4,51±0,00	3,26±0,04	2,81±0,04
60	7,45±0,05	5,46±0,04	4,90±0,02	3,52±0,04	3,04±0,05
90	5,74±0,14	4,38±0,09	3,63±0,01	2,63±0,04	2,01±0,14
180	6,56±0,11	4,79±0,07	4,65±0,02	3,34±0,04	2,50±0,07

According to the results above, the viscosity of smoothie decreases with an increase in temperature. During the smoothie's shelf life, the viscosity exhibited a small variation.

The Figure 1 below shows the curves ln η versus 1/T for the smoothie during the shelf life. The Table 2 presents the parameters of the Equation 1 and the correlation coefficient of linearization.

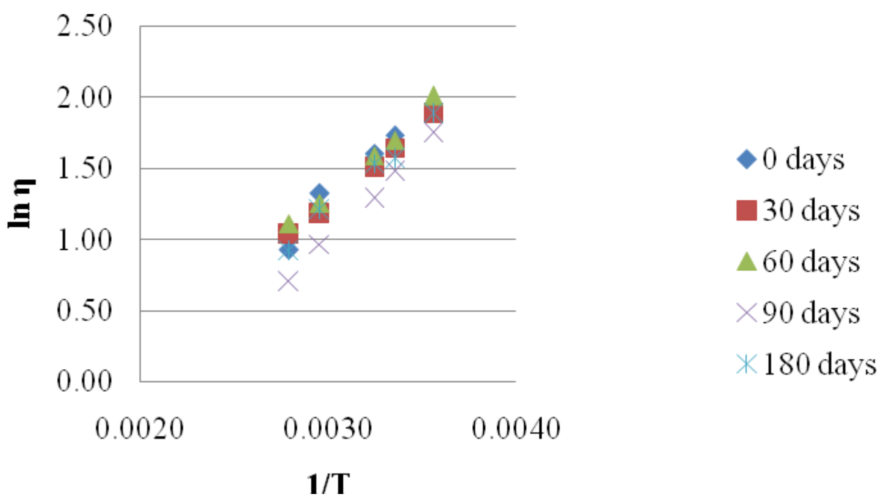

Figure 1. Curve ln η versus 1/T for the smoothie of assai and passion fruit

Table 2. Equation 1 parameters for the smoothie of assai and passion fruit

Time (days)	η_0 ($Kg.m^{-1}.s^{-1}$)	E_a ($kJ.mol^{-1}$)	R^2
0	0,089	10,238	0,961
30	0,120	9,325	0,998
60	0,116	9,624	0,992
90	0,048	11,156	0,996
180	0,093	9,928	0,982

According to the Table 2 below, Arrhenius is a good model to describe the relationship between the viscosity and the temperature, because the correlation coefficients present high values (higher than 0,9).

Gratão et al. (2005) found an average activation energy (E_a) equals 11.39 $J.mol^{-1}$ for soursop juice. Therefore, this value is a thousand times smaller than the value found for the smoothie of assai and passion fruit.

The viscosity decreases with increase in temperature and the highest E_a values indicate a greater influence of temperature on the viscosity (Gratão et al., 2004).

Rheological Characteristics The Tables 3, 4, 5, 6 and 7 below present the parameters found for each rheological model to the smoothie at 8ºC and 25ºC in 0, 30, 60, 90 and 180 days. The best proposed model has to present the correlation coefficient (R) close to unity.

Table 3. Rheological parameters for the smoothie of assai and passion fruit in 0 days

T (ºC)	Model	Rate*	σ_0 (Pa)	K (Pa.s^n)	n	R
8	Power-Law	Increasing	-	344,6	0,2964	0,99984
8	HB	Increasing	437515,4	437146,5	-0,0004	0,97647
8	Power-Law	Descending	-	306,2	0,3150	0,99771
8	HB	Descending	117,8	-193,5	0,4078	0,99974
25	Power-Law	Increasing	-	288,9	0,2866	0,99969
25	HB	Increasing	-46,7	-334,9	0,2606	0,99987
25	Power-Law	Descending	-	254,2	0,3060	0,99873
25	HB	Descending	351197,7	350920,6	-0,0003	0,96529

* The term "increasing" refers to the parameters found with the shear rate ranging from 0.5 rpm to 100 rpm and the term "descending" from 100 rpm to 0.5 rpm.

Table 4. Rheological parameters for the smoothie of assai and passion fruit in 30 days

T (ºC)	Model	Rate	σ_0 (Pa)	K (Pa.s^n)	N	R
8	Power-Law	Increasing	-	346,4	0,2786	0,99973
8	HB	Increasing	-58,2	-403,9	0,2520	0,99992
8	Power-Law	Descending	-	302,5	0,3017	0,99824
8	HB	Descending	106,7	-199,4	0,3840	0,99989
25	Power-Law	Increasing	-	260,2	0,2889	0,99950
25	HB	Increasing	-60,1	-319,4	0,2530	0,99984
25	Power-Law	Descending	-	239,1	0,2995	0,99822
25	HB	Descending	82,4	-159,4	0,3794	0,99977

Table 5. Rheological parameters for the smoothie of assai and passion fruit in 60 days

T (ºC)	Model	Rate	σ_0 (Pa)	K (Pa.s^n)	n	R
8	Power-Law	Increasing	-	403,9	0,2741	0,99952
8	HB	Increasing	531834,6	531409,0	-0,0003	0,98396
8	Power-Law	Descending	-	357,0	0,2895	0,99685
8	HB	Descending	144,2	-217,1	0,3874	0,99910
25	Power-Law	Increasing	-	263,0	0,2988	0,99745
25	HB	Increasing	-176,3	-437,1	0,2132	0,99938
25	Power-Law	Descending	-	255,3	0,2928	0,99815
25	HB	Descending	46,2	-210,1	0,3296	0,99848

Table 6. Rheological parameters for the smoothie of assai and passion fruit in 90 days

T (ºC)	Model	Rate	σ_0 (Pa)	K (Pa.s^n)	n	R
8	Power-Law	Increasing	-	325,8	0,2813	0,99752
8	HB	Increasing	451695,5	451354,3	-0,0003	0,98760
8	Power-Law	Descending	-	280,4	0,3018	0,99793
8	HB	Descending	92,01	-191,4	0,3770	0,99927
25	Power-Law	Increasing	-	217,6	0,2930	0,99840
25	HB	Increasing	301457,4	301228,2	-0,0003	0,98556
25	Power-Law	Descending	-	198,5	0,3039	0,99764
25	HB	Descending	215931,2	215716,3	-0,0004	0,96900

Table 7.Rheological parameters for the smoothie of assai and passion fruit in 180 days

T (ºC)	Model	Rate	σ_0 (Pa)	K (Pa.s^n)	n	R
8	Power-Law	Increasing	-	319,0	0,3044	0,99982
8	HB	Increasing	-27,0	-345,4	0,2898	0,99988
8	Power-Law	Descending	-	284,3	0,3217	0,99835
8	HB	Descending	93,6	-194,9	0,3979	0,99973
25	Power-Law	Increasing	-	233,8	0,3018	0,99867
25	HB	Increasing	-90,6	-322,9	0,2451	0,99951
25	Power-Law	Descending	-	221,0	0,3049	0,99893
25	HB	Descending	51,3	-171,4	0,3544	0,99953

The proposed models (Power-Law and HB) have been made suitable to describe the behavior of smoothie of assai and passion fruit enriched with unripe banana pulp, because the correlation coefficient (R) was higher than 0.9 in all cases described above.

However, the Herschel-Bulkley model (HB) fits better than the Power-Law model because it showed the highest R values in most cases. The Figures 2, 3, 4, 5 and 6 below illustrate the rheograms for HB model in 0, 30, 60, 90 and 180 days at 8 ºC and the Figures 7, 8, 9, 10 and 11 show the rheograms at 25 ºC.

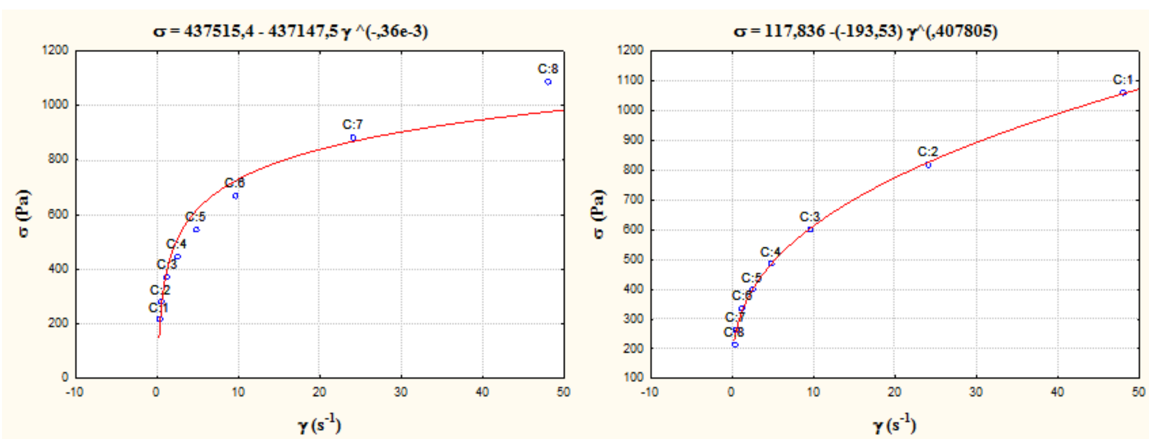

Figure 2. Rheogram of HB model at 8ºC in 0 days with increasing shear rate (left) and descending shear rate (right)

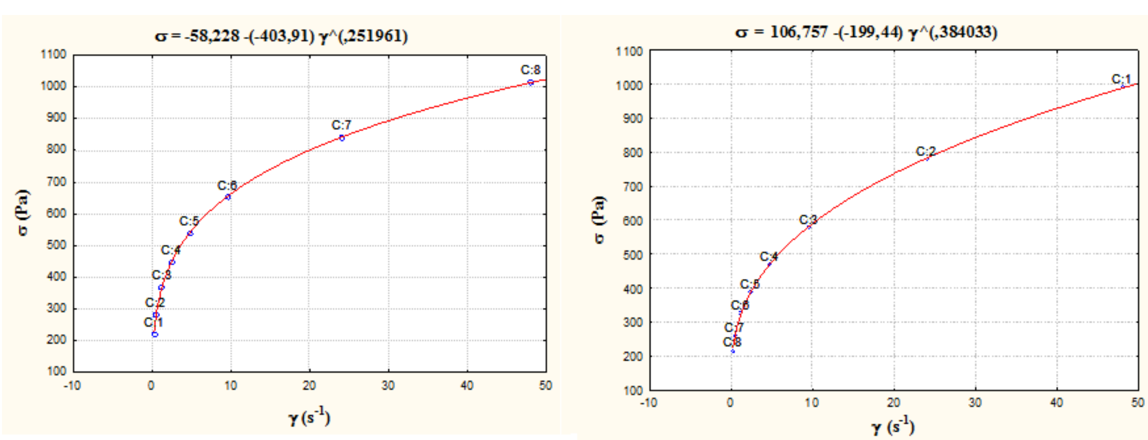

Figure 3. Rheogram of HB model at 8ºC in 30 days with increasing shear rate (left) and descending shear rate (right)

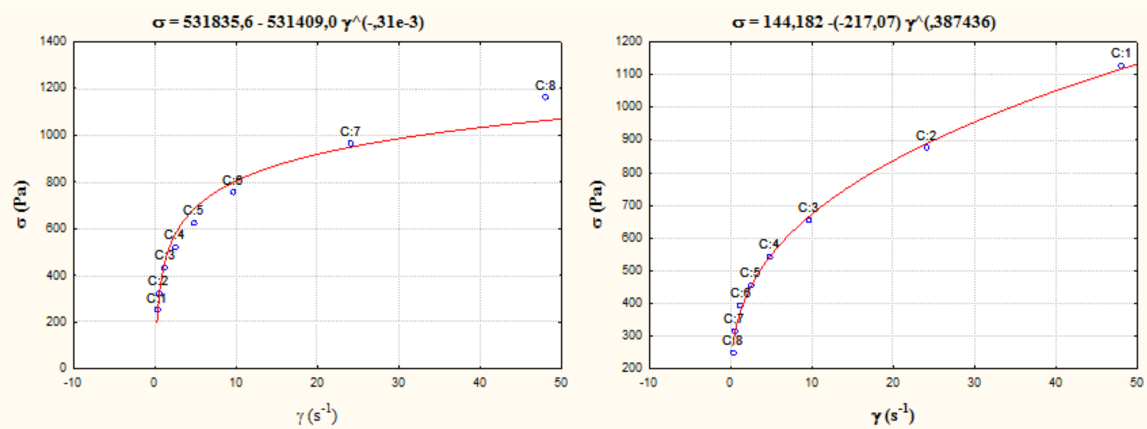

Figure 4. Rheogram of HB model at 8ºC in 60 days with increasing shear rate (left) and descending shear rate (right)

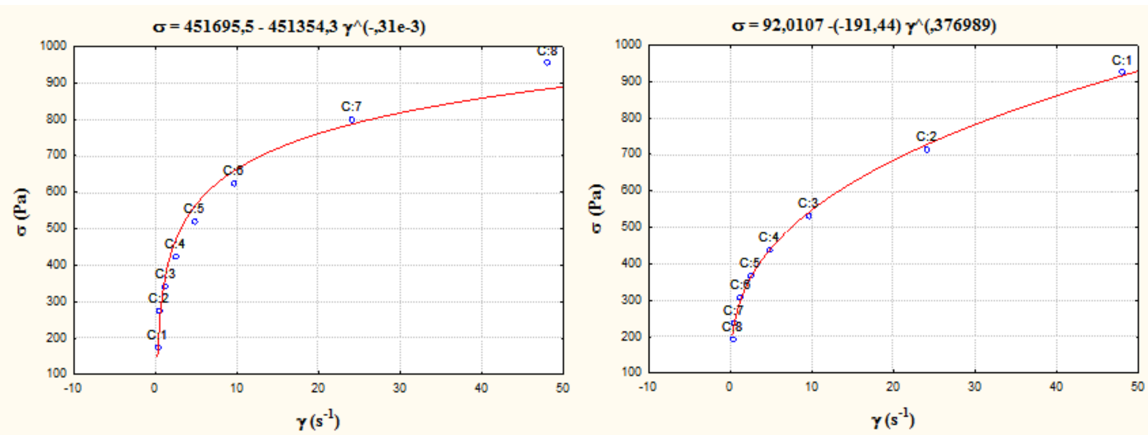

Figure 5. Rheogram of HB model at 8ºC in 90 days with increasing shear rate (left) and descending shear rate (right)

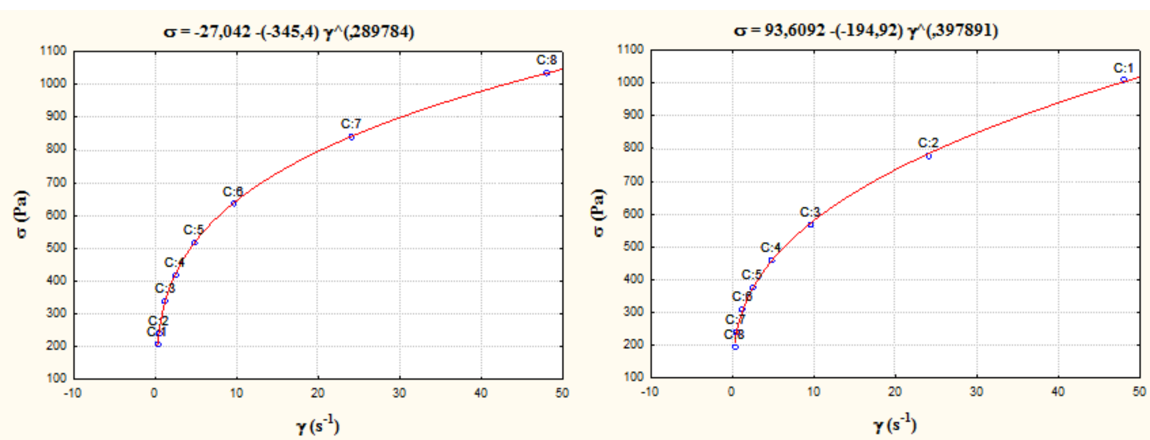

Figure 6. Rheogram of HB model at 8ºC in 180 days with increasing shear rate (left) and descending shear rate (right)

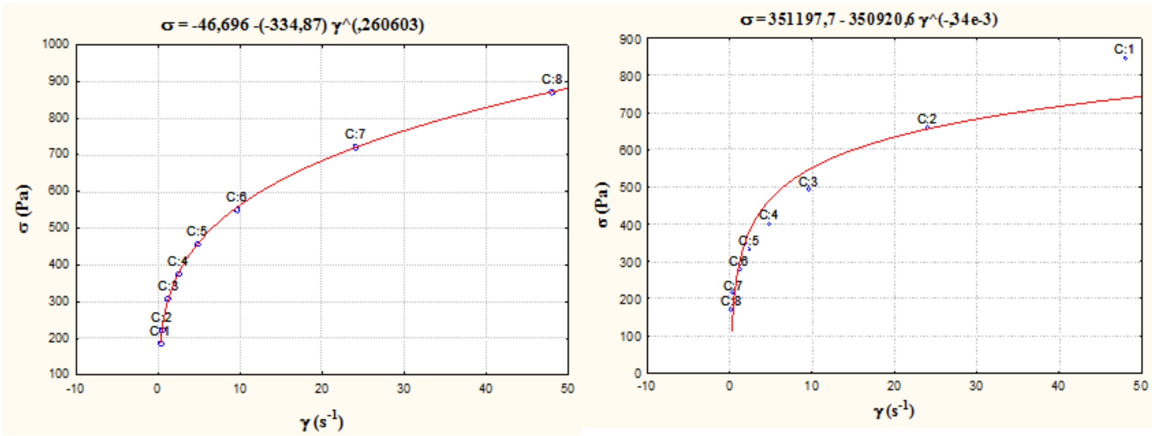

Figure 7. Rheogram of HB model at 25ºC in 0 days with increasing shear rate (left) and descending shear rate (right)

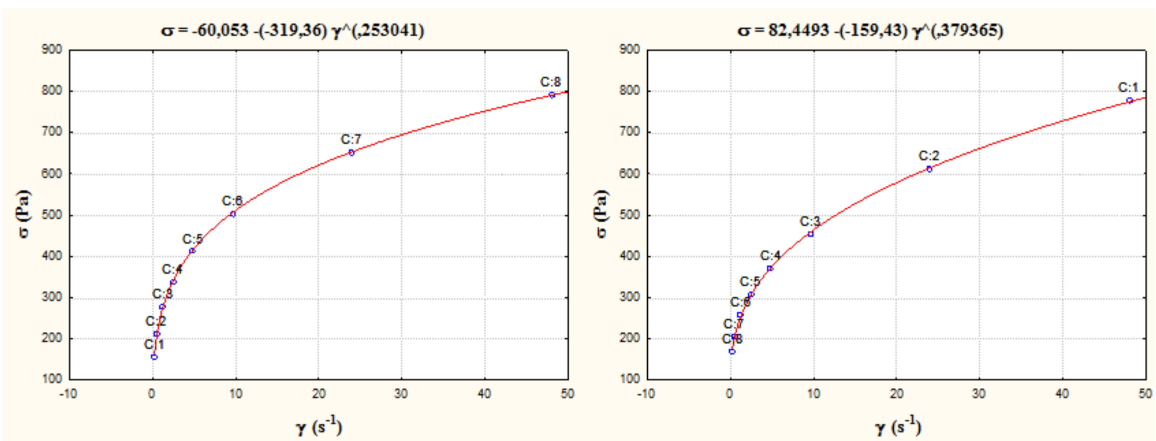

Figure 8. Rheogram of HB model at 25ºC in 30 days with increasing shear rate (left) and descending shear rate (right)

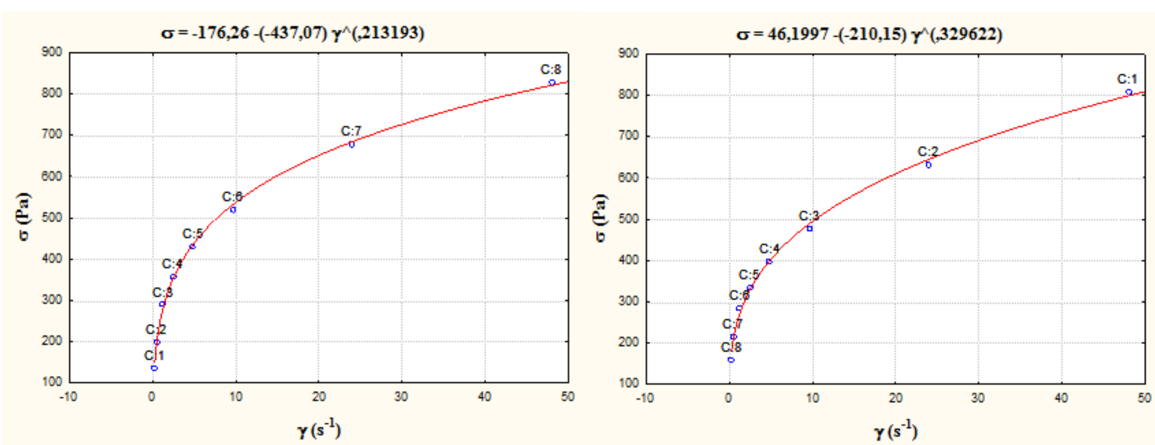

Figure 9. Rheogram of HB model at 25ºC in 60 days with increasing shear rate (left) and descending shear rate (right)

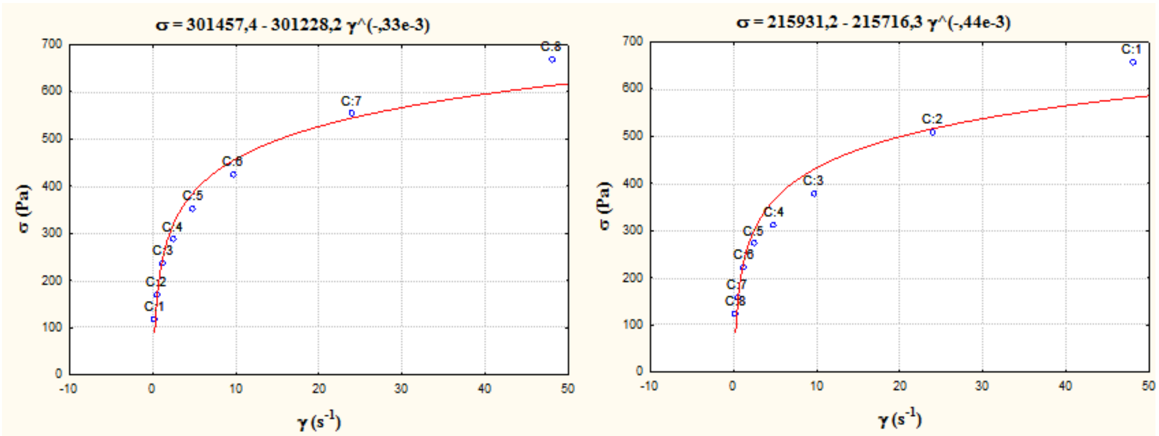

Figure 10. Rheogram of HB model at 25ºC in 90 days with increasing shear rate (left) and descending shear rate (right)

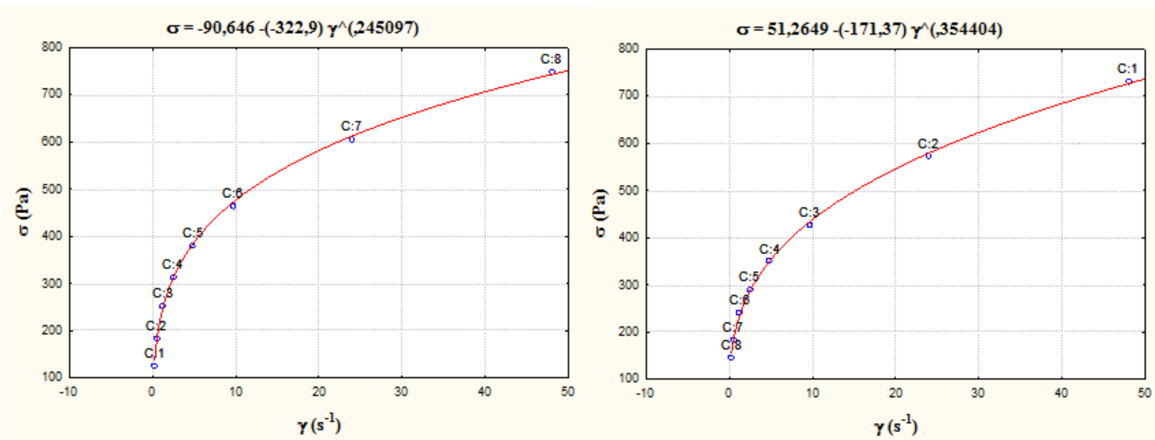

Figure 11. Rheogram of HB model at 25ºC in 180 days with increasing shear rate (left) and descending shear rate (right)

The Smoothie behavior observed in the rheograms above, with increasing and descending shear rates, shows that smoothie behaves as a thixotropic fluid.

Fluids in this group present a rheological behavior dependent on the time and are known to contain small particles (crystals or polymers) that are held together by weak forces. The shear of the material separates the aggregated particles and then decreasing the resistance to the flow and the viscosity decreases with the time until a constant value. (McClements, 1999). Among the foods which have thixotropic behavior, can be cited: pectin gels, alginate gels, gels, creams, butters, salad dressings, among others. The thixotropy can be attributed to the presence of hydrogen bonds present between the colloidal micelles and, when the bonds are broken by shaking, the micelles can form themselves again in the system at rest (Sharma et al., 2000).

CONCLUSION The viscosity evaluation as a function of temperature sets perfectly to the Arrhenius model, and it was possible to determine the parameters η_0 and E_a. The rheological behavior of smoothie of assai and passion fruit enriched with unripe banana pulp followed the Herschel-Bulkley model (HB) and it can be considered as thixotropic fluid.

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