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# *Rheology of redcurrant juices*

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*Reología de zumos de grosella*

*Reologia de sucs de grosella*

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## **RESUMEN**

Se ha estudiado el comportamiento reológico de dos zumos diferentes de grosella. El zumo con contenido en pectinas exhibió comportamiento no newtoniano. El zumo al que se le han extraído las pectinas exhibió comportamiento newtoniano. El modelo de la ley de la potencia describió la relación entre el esfuerzo cortante y el gradiente de velocidad para el primer tipo de zumo y el modelo newtoniano describió el comportamiento del segundo tipo de zumo. El efecto de la temperatura en la viscosidad aparente a 100 s<sup>-1</sup> queda descrito por la ecuación de Arrhenius.

**Palabras clave:** Reología, grosella, zumo, viscosidad

## **ABSTRACT**

The rheological behaviour of two different redcurrant juices was studied. Juices containing pectins exhibited non-Newtonian behavior. Juices from which pectins were removed exhibited Newtonian behavior. The power law model described the relationship between shear stress and shear rate for the first type of juice, and the Newtonian model described the second type. The effect of temperature on the apparent viscosity at 100 s<sup>-1</sup> was described by Arrhenius equation.

**Keywords:** Rheology, redcurrant, juices, viscosity

## **RESUM**

S'ha estudiat el comportament reòlogic de dos sucs diferents de grosella. El suc amb contingut en pectines va exhibir comportament no newtonià. El suc al que se li van extreure les pectines va mostrar un comportament newtonià. El model de la llei de la potència va descriure la relació entre el esforç tallant i el gradient de velocitat pel primer tipus de suc i el model newtonià va descriure el comportament del segon tipus de suc. L'efecte de la temperatura en la viscositat apparent a 100 s<sup>-1</sup> es pot descriure per l'equació d'Arrhenius.

**Paraules clau:** Reologia, grosella, suc, viscositat

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## INTRODUCTION

The redcurrant (*ribes rubrum*) is original of Western Europe. These fruits can be consumed freshly, although its concentrated juice is often used in the elaboration of jams, jellies, liquors, syrups and sauces. It contributes to acidify the products due to its high content in organic acids, and to improve their consistency because of its high content in pectins.

The flow behavior of fruit juices and their fluid derivatives is strongly affected by both juice and fruit characteristics. The presence of pulp solids, as in the dispersed phase of fruit juice, contributes to their non-Newtonian nature (Ramos & Ibarz 2006, Falguera et al 2010). Clarified and depectinated juices usually show a rheological behavior that may be described either by Newton's viscosity equation or by power-law equation. Juices with pectins and pulp in suspension usually show yield stress, and their rheological behavior may be described by Herschel-Bulkley's model. In non-Newtonian fluids the quotient between shear stress and shear rate is not a constant as it occurs with Newtonian fluids. Therefore, the concept of apparent viscosity ( $h_a$ ) is used at a given shear rate, which for fluids which follow the power-law equation will be expressed according to the following equation:

$$h_a = K \cdot \dot{\gamma}^{n-1} \quad (1)$$

and fluids which follow the Herschel-Bulkley model will be expressed according to this one:

$$h_a = \frac{S_0}{\gamma} + k \cdot \dot{\gamma}^{n-1} \quad (2)$$

The main purpose of this work has been to analyze the rheological behavior of redcurrant juices studying its flow response as a function of the temperature and soluble solids concentration. Although there are many studies with similar fruits: raspberry, strawberry and blackberry (Alvarez et al 2006, Haminiuk et al 2006, 2007, 2009, Ramaswamy and Basak 1992, Sousa et al 2006) and blackcurrant (Ibarz et al 1992b), the rheology of redcurrant juices has not been studied yet.

## MATERIALS AND METHODS

### Obtaining Samples

The redcurrant juices were obtained in the laboratory from natural fruits purchased in a local market in Lleida (Spain). The juice was obtained by squeezing the fruits and filtering the liquor obtained. The obtained paste was clarified by centrifugation at 3600 rpm for 20 minutes (Medifriger, Selecta, Abrera, Spain). The clarified juice had no pulp in suspension, but it did have pectins. Approximately half the juice without pulp was subjected to an enzymatic clarification in order to eliminate the pectins, using Pectinex and Ultrazym 100-C (Novo). The enzymes were left to act for two hours at 25°C, and the juice was then vacuum filtered. Two types of juices were therefore obtained, the first one clarified and depectinated (type I) and the other one clarified with pectins (type II).

From these two types of juices, different samples with different soluble solids contents were obtained by evaporation at approximately 25°C, temperature that corresponds

to a pressure of 24 mm Hg (Labo-rota C-311, Resonatechnics, Buchs, Switzerland).

Samples were extracted during the time of the concentration process, which allowed obtaining juices with different soluble solids contents: 68, 65, 60, 55, 50, 45 and 40°Brix for type I, and 63, 58, 53, 44 and 38°Brix for type II. All experiments and analysis were carried out by triplicate.

### Physical and Chemical Analysis

- The physicochemical analysis carried out to the redcurrant juices were:
- Soluble solids. These were determined using a digital refractometer at 20°C (Atago RX-1000, Tokyo, Japan).
- Density. A picnometer was used at 20°C (PROTON, Barcelona, Spain).
- Total acidity. This was determined by titrating the juice with NaOH 0.1 N, using phenolphthalein as indicator.
- pH. It was determined by using a pH-meter (MicropH2001, Crison Instruments, Alella, Spain).
- L-malic acid. This was determined by using the enzyme L-malate dehydrogenase. The absorbance was measured at 340 nm (Boehringer Mannheim 1984) using a spectrophotometer (PU 8720 UV/VIS, Philips, Eindhoven, Netherlands).
- Citric acid. This was determined by using the enzymes citrate lyase, malate dehydrogenase and L-malate dehydrogenase. The absorbance was measured at 340 nm (Boehringer Mannheim 1984).
- Ascorbic acid. This was determined by using the enzyme ascorbate oxidase. The absorbance was measured at 578 nm (Boehringer Mannheim 1984).
- Glucose, fructose and sucrose. These were determined by using the enzymes hexokinase and glucose-6-phosphate dehydrogenase. The absorbance was measured at 340 nm.
- Pectins. This content was determined by degradation in sulphuric acid medium. The absorbance was measured at 525 nm (De Giorgi et al 1985) and the result was expressed as g of galacturonic acid (AGA) per kg of juice.

### Rheological measurements.

The rheological measurements of the different samples were carried out on a concentric cylinder viscometer (Rottovisco RV 12, Haake, Karlsruhe, Germany), equipped with M-500-type measurement attachment, which can transmit a torque of 4.9 N·cm. A thermostatic bath (Digitherm 30000613, Selecta, Abrera, Spain) controls the working temperature within the range 5-65°C.

Rotor speeds were variable in the range 0.01-512 rpm. Readings were taken at decreasing rotor speeds until a minimum speed was reached, after which it was gradually increased. In order to eliminate the possible effects of thixotropy, the sample was previously sheared at maximum speed for three minutes.

The rheological behavior of the juices at different temperatures (5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55 and 60°C.) was studied.

### Statistical analysis

The experimental results obtained were fitted to mathematical models by using the Statgraphics Plus 5.1 software (STCSC Inc. Rockville, Md, USA) for data processing. All the fittings and the estimates were calculated at a 95% significant level.

## RESULTS AND DISCUSSION

First of all, thixotropy was not observed.

The results of the physical and chemical analysis of red-currant juice are shown in Table 1.

**Table 1.- Characteristics of centrifuged juice**

Density	1.044	g/mL
pH	2.64	
Soluble solids	11.2	°Brix
Total acidity	0.41	eq/L
L-Malic acid	1.2	g/L
Citric acid	26.8	g/L
Ascorbic acid	60	mg/L
Glucose	10.1	g/L
Fructose	13.6	g/L
Sucrose	0.9	g/L
Pectins (Type I – 68°Brix)	2.2	g AGA/kg
Pectins (Type II – 63°Brix)	6.8	g AGA/kg

### Rheological behavior of type I juice.

Figure 1 shows the experimental results obtained for the depectinized juice of 68 °Brix at the different temperatures tested. Similar rheograms were obtained for the other concentrations.

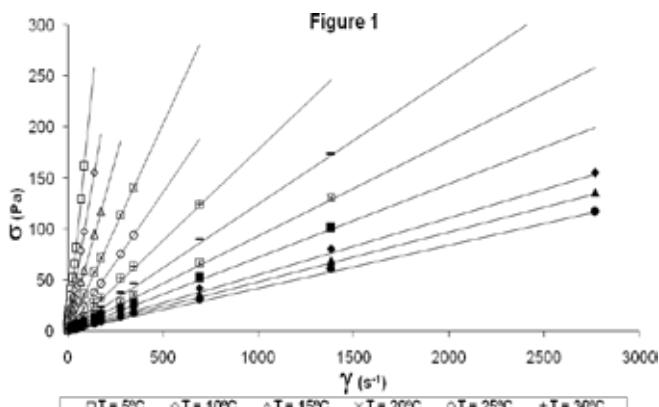


Table 2 shows the parameters obtained with Newton and power-law models. Herschel-Bulkley model was discarded because the yield stress obtained for all the concentrations and temperatures was smaller than 1 Pa (Vitali and Rao 1984).

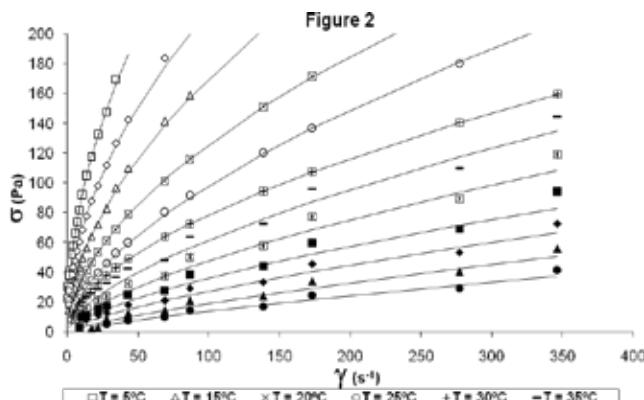
In all cases, Newton model and power-law model show good fits. The behavior of type I juice can be considered as Newtonian due to its bigger simplicity. Newton model fittings show that the viscosity decreases with temperature and increases with soluble solids content.

Power-law model always shows a flow behavior index smaller than the unit, but near to it. As expected, the consistency index ( $k$ ) decreases with temperature and increases with soluble solids content. The flow behavior index ( $n$ ) is relatively constant with temperature for soluble solids content below 65°Brix, similarly to previous works (Falguera and Ibarz 2010, Falguera et al 2010). For soluble solids content above 65°Brix, the flow behavior index ( $n$ ) show a slight decrease with temperature, as it was observed by Ibarz et al. (1993).

### Rheological behavior of type II juice.

Figure 2 shows the experimental results obtained for the concentrated sample of 63°Brix at the different tested temperatures. Similar rheograms were obtained for the other concentrations. The rheogram shows the non-linear fit; therefore, experimental data were fitted to the power-law and Herschel-Bulkley models.

Table 3 shows the parameters obtained with power-law and Herschel-Bulkley models. The values of the apparent viscosity at a shear rate of 100 s⁻¹ are included for each model.



In Table 3 it can be observed that rheological behavior of this type of juice fits better to power-law model. The flow behavior index is always clearly smaller than the unit, thus the rheological behavior is pseudoplastic, and it shows an upward trend with decreasing concentration and increasing temperature. The consistency coefficient increases as the concentration increases and temperature decreases. The apparent viscosity increases as the concentration rises up, temperature decreases and the pectins content increases. The obtained values and tendencies are similar to those described in the literature (Falguera and Ibarz 2010, Falguera et al 2010, Ibarz et al 1993, Haminuk et al 2006, 2007, 2009, Sato and Cunha 2009, Tonon et al 2009, Vandresen et al 2009).

### Temperature effect.

The variation in apparent viscosity or viscosity with temperature can be described by an Arrhenius-type equation (Saravacos 1970; Rao et al 1984; Ibarz et al 1992a; 1992b; 1996; Falguera et al, 2010):

$$h \text{ or } h_a = h_\psi \exp \left[ \frac{E_a}{RT} \right] \quad (3)$$

The parameters of the equation are shown in tables 4 and 5. The activation energy increases with the soluble solids content; therefore, temperature had a greater effect on the samples with higher soluble solids. For fixed soluble solids content, the value of activation energy of flow for clarified and depectinized juice is greater than the activation energy for juice containing pulp and pectin.

The activation energy values obtained for the clarified and depectinized juice were very similar to those for the depectinized apple and grape juices (Rao et al 1984), clarified banana juice (Khalil et al 1989), depectinized pear juice (Ibarz et al 1987), depectinized peach juice (Ibarz et al 1992a) and depectinized blackcurrant juice (Ibarz et al 1992b). For the juice containing pulp and pectins, the values obtained were similar to those obtained in tomato

**Table 2.- Clarified and depectinated redcurrant juices parameters**

C °Brix	T °C	Newton Model				Power-law Model			
		h mPa·s		r	k Pa·sn		n	r	
		h	r		k	Pa·sn			
68	5	1866	± 15	0.9999	2.06	± 0.14	0.98	± 0.02	0.9998
	10	1116	± 10	0.9999	1.43	± 0.11	0.95	± 0.02	0.9999
	15	674	± 8	0.9999	0.92	± 0.07	0.94	± 0.02	0.9997
	20	406	± 6	0.9999	0.56	± 0.03	0.94	± 0.01	0.9998
	25	272	± 3	0.9999	0.35	± 0.02	0.96	± 0.02	0.9975
	30	177.6	± 2.0	0.9999	0.33	± 0.02	0.90	± 0.04	0.9997
	35	124.6	± 1.5	0.9999	0.27	± 0.03	0.89	± 0.02	0.9995
	40	93.2	± 1.0	0.9999	0.22	± 0.02	0.87	± 0.02	0.9997
	45	72.0	± 1.0	0.9999	0.17	± 0.02	0.88	± 0.02	0.9997
	50	57.0	± 0.9	0.9999	0.14	± 0.02	0.88	± 0.03	0.9996
	55	45.1	± 0.7	0.9999	0.13	± 0.01	0.87	± 0.02	0.9999
	60	43.1	± 0.7	0.9999	0.11	± 0.02	0.87	± 0.02	0.9982
65	5	682	± 7	0.9999	0.67	± 0.05	1.00	± 0.02	0.9999
	10	396	± 4	0.9999	0.59	± 0.04	0.93	± 0.01	0.9998
	15	144.4	± 1.3	0.9999	0.51	± 0.03	0.89	± 0.01	0.9996
	20	176.6	± 1.6	0.9999	0.29	± 0.04	0.93	± 0.03	0.9985
	25	120.3	± 1.4	0.9999	0.27	± 0.03	0.88	± 0.09	0.9992
	30	86.9	± 1.0	0.9999	0.21	± 0.02	0.87	± 0.02	0.9996
	35	66.1	± 0.7	0.9999	0.17	± 0.02	0.87	± 0.02	0.9991
	40	52.6	± 0.6	0.9999	0.13	± 0.01	0.88	± 0.02	0.9991
	45	41.2	± 0.5	0.9999	0.11	± 0.01	0.88	± 0.01	0.9998
	50	35.2	± 0.4	0.9999	0.10	± 0.02	0.86	± 0.03	0.9991
	55	29.6	± 0.3	0.9999	0.07	± 0.01	0.89	± 0.02	0.9993
	60	27.1	± 0.3	0.9999	0.06	± 0.01	0.89	± 0.02	0.9996
60	5	194.7	± 2.0	0.9999	0.36	± 0.03	0.90	± 0.02	0.9998
	10	123.2	± 1.4	0.9998	0.33	± 0.03	0.85	± 0.02	0.9995
	15	86.2	± 0.9	0.9997	0.28	± 0.03	0.83	± 0.02	0.9993
	20	63.9	± 0.7	0.9998	0.20	± 0.03	0.84	± 0.03	0.9996
	25	48.2	± 0.5	0.9999	0.16	± 0.02	0.84	± 0.02	0.9997
	30	36.3	± 0.3	0.9999	0.13	± 0.02	0.83	± 0.02	0.9992
	35	29.5	± 0.4	0.9988	0.11	± 0.02	0.83	± 0.02	0.9992
	40	25.5	± 0.3	0.9989	0.10	± 0.01	0.82	± 0.02	0.9996
	45	21.90	± 0.20	0.9974	0.08	± 0.01	0.84	± 0.03	0.9999
	50	19.6	± 0.3	0.9976	0.08	± 0.01	0.82	± 0.02	0.9998
	55	17.2	± 0.3	0.9968	0.06	± 0.02	0.84	± 0.04	0.9998
	60	15.30	± 0.20	0.9967	0.06	± 0.01	0.82	± 0.03	0.9996
55	5	70.6	± 1.0	0.9998	0.17	± 0.02	0.87	± 0.02	0.9993
	10	52.5	± 0.6	0.9997	0.14	± 0.01	0.86	± 0.02	0.9997
	15	38.0	± 0.7	0.9997	0.11	± 0.01	0.86	± 0.02	0.9997
	20	28.5	± 0.5	0.9995	0.08	± 0.01	0.87	± 0.02	0.9991
	25	24.2	± 0.3	0.9993	0.08	± 0.01	0.84	± 0.02	0.9994
	30	18.1	± 0.3	0.9989	0.07	± 0.01	0.83	± 0.02	0.9995
	35	15.10	± 0.20	0.9986	0.05	± 0.01	0.85	± 0.04	0.9999
	40	13.00	± 0.20	0.9985	0.05	± 0.02	0.81	± 0.06	0.9972
	45	11.70	± 0.20	0.9978	0.04	± 0.01	0.84	± 0.02	0.9996
	50	9.40	± 0.20	0.8788	0.03	± 0.03	0.86	± 0.09	0.9991
	55	9.40	± 0.10	0.9975	0.03	± 0.01	0.86	± 0.05	0.9982
	60	8.30	± 0.10	0.9978	0.02	± 0.01	0.88	± 0.06	0.9996
50	5	36.7	± 0.5	0.9998	0.12	± 0.02	0.84	± 0.02	0.9992
	10	27.4	± 0.4	0.9996	0.08	± 0.03	0.86	± 0.03	0.9992
	15	21.9	± 0.3	0.9992	0.07	± 0.02	0.86	± 0.01	0.9993
	20	17.4	± 0.3	0.9975	0.06	± 0.02	0.83	± 0.01	0.9997
	25	14.9	± 0.3	0.9975	0.05	± 0.01	0.84	± 0.02	0.9993
	30	9.00	± 0.20	0.9943	0.04	± 0.01	0.85	± 0.03	0.9999
	35	10.70	± 0.20	0.9962	0.03	± 0.01	0.85	± 0.04	0.9998
	40	9.40	± 0.10	0.9973	0.03	± 0.01	0.86	± 0.04	0.9998
	45	8.30	± 0.10	0.9978	0.02	± 0.01	0.87	± 0.04	0.9992
	50	7.20	± 0.10	0.9998	0.02	± 0.01	0.87	± 0.04	0.9996
	55	7.90	± 0.10	0.9997	0.02	± 0.01	0.90	± 0.06	0.9995
	60	6.80	± 0.10	0.9982	0.02	± 0.01	0.88	± 0.06	0.9995
45	5	21.3	± 0.3	0.9986	0.54	± 0.22	0.71	± 0.06	0.9918
	10	17.00	± 0.20	0.9961	0.08	± 0.12	0.79	± 0.13	0.9992
	15	14.20	± 0.20	0.9942	0.07	± 0.01	0.80	± 0.03	0.9993
	20	12.10	± 0.20	0.9932	0.06	± 0.01	0.79	± 0.03	0.9997
	25	10.40	± 0.20	0.9948	0.05	± 0.01	0.80	± 0.04	0.9996
	30	9.00	± 0.10	0.9948	0.04	± 0.01	0.82	± 0.05	0.9997
	35	8.20	± 0.10	0.9956	0.04	± 0.01	0.81	± 0.05	0.9997
	40	7.00	± 0.10	0.9973	0.03	± 0.01	0.80	± 0.02	0.9994
	45	6.70	± 0.10	0.9972	0.03	± 0.08	0.82	± 0.04	0.9993
	50	6.30	± 0.07	0.9974	0.02	± 0.02	0.82	± 0.08	0.9982
	55	5.60	± 0.07	0.9948	0.02	± 0.02	0.82	± 0.10	0.9996
	60	4.90	± 0.06	0.9923	0.04	± 0.01	0.83	± 0.05	0.9993
40	5	12.90	± 0.15	0.9987	0.04	± 0.01	0.87	± 0.05	0.9994
	10	11.00	± 0.13	0.9962	0.04	± 0.03	0.85	± 0.05	0.9983
	15	9.10	± 0.11	0.9965	0.04	± 0.02	0.83	± 0.05	0.9991



**Table 5.- Parameters of Arrhenius Equation for Type II redcurrant juices**

C °Brix	Power Law			Herschel-Bulkley		
	E <sub>a</sub> kJ/mol	h <sub>Y</sub> ·10 <sup>7</sup> mPa·s	r	E <sub>a</sub> kJ/mol	h <sub>Y</sub> ·10 <sup>7</sup> mPa·s	r
63	41.42	56.15	0.9940	56.49	0.02	0.9819
58	40.17	37.75	0.9986	44.77	6.16	0.9977
53	37.66	63.54	0.9536	38.49	39.97	0.9981
44	29.71	362.50	0.9987	31.38	72.56	0.9969
38	23.85	2332.04	0.9304	27.20	422.40	0.9834

derivates (Saravacos 1970; Ibarz et al 1988) and plum and peach pulp (Ibarz and Lozano 1992). The h<sub>Y</sub> values obtained of the clarified and depectinized juice were within the same order as those for depectinized peach, blackcurrant and banana juice above mentioned.

## CONCLUSION

From the experimental results obtained from depectinized and non-depectinized redcurrant juices in the temperature range of 5-60°C and soluble solids content between 38 an 68°Brix, the following conclusions may be drawn: Redcurrant juices containing pectins showed rheological behavior which was better described by the power-law model. Herschel-Bulkley model also fitted experimental data.

Clarified and depectinized redcurrant juices showed rheological behavior which can be described by the Newtonian model. The parameters obtained for power-law model also fit well.

For both depectinized and non-depectinized redcurrant juices, the effect of temperature in apparent viscosity at 100s<sup>-1</sup> can be described by an exponential Arrhenius-type equation.

## NOTATION

C	Concentration (°Brix)
E <sub>a</sub>	Activation energy (kJ/mol)
k	Consistency index (Pa·s <sup>n</sup> )
n	Flow behavior index (dimensionless)
R	Gas constant (8.314 J/mol K)
T	Temperature (°C or K)
ẏ	Shear rate (s <sup>-1</sup> )
h	Viscosity (mPa·s)
h <sub>a</sub>	Apparent viscosity (mPa·s)
h <sub>Y</sub>	Apparent viscosity at great temperatures (mPa·s)
σ	Shear stress (Pa)
S <sub>0</sub>	Yield stress (Pa)

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