Oroian, MA.; Amariei, S.; Escriche Roberto, MI.; Leahu, A.; Damian, C.; Gutt, G. (2014).
Chemical composition and temperature influence on the rheological behaviour of honeys.
International Journal of Food Properties. 17(10):2228-2240.
doi:10.1080/10942912.2013.791835.

Chemical composition and temperature influence on the rheological behaviour of honeys

Mircea Oroian[1*], Sonia Amariei[1], Isabel Escriche[2], Ana Leahu[1], Cristina Damian[1], Gheorghe Gutt[1]

[1]Faculty of Food Engineering, Stefan cel Mare University of Suceava (Romania)
[2]Institute of Food Engineering for Development (IUIAD), Food Technology Department (DTA), Universidad Politécnica de Valencia, Valencia, Spain

[*]Corresponding author.Tel.:+40-0744524872; fax: +40-0230520267;
e-mail address *m.oroian@fia.usv.ro* (Mircea Oroian)

Abstract

The purpose of this work was to examine the viscoelastic properties of Spanish honeys with various sugar contents [fructose (32 - 42 g/100 g honey), glucose (24 - 35 g/100 g honey), sucrose (0.0 - 3.4 g/100 g honey)]; concentrations (79 – 83 °Brix) and moisture levels (16 - 19 g/100 g honey) at different temperatures (5, 10, 15, 20, 25, 30 and 40°C). Honey showed Newtonian behaviour, presenting a highly viscous part (loss modulus was much greater than the elastic modulus). The loss modulus (G’’) and viscosity increased with moisture content and a decrease with temperature. Exponential and power law models were applied to fit loss modulus and viscosity data. Polynomial models were proposed to describe the combined effect of

temperature, fructose, glucose, sucrose content, other sugars, non-sugar substance and moisture content.

Key words: honey, viscosity, viscoelasticity, polynomial model

INTRODUCTION

Knowledge about the rheological behaviour of viscous food stuff is useful in: quality and process control, the calculation of energy requirements, and the selection of suitable processing equipment [1]. Recently, the influence of temperature on the flow behaviour of honey varieties has been studied [2-17] however there are few articles related to the effect of temperature on the viscoelastic behaviour of honeys [18]. In particular, little information is available on the viscoelastic properties of Spanish honeys with different botanical origins.

The purpose of this study was on one hand to observe the influence of temperature and total soluble content on viscosity and the loss modulus of different honeys, and on the other hand to obtain a polynomial model that could explain the behaviour of viscosity and the loss modulus as a function of the chemical composition (sugars, moisture, etc.) and temperature.

MATERIALS AND METHODS

Materials

11 different types of Spanish honey were used in this study. Before being used, they were warmed to 55°C to dissolve any crystals, and kept in flasks at 30°C to remove air bubbles that could interfere in rheological studies. This was done because rheological properties can be influenced by the presence of crystals and air bubbles [2, 19, 20].

Moisture content

The moisture content of the honey samples was obtained by measuring the refractive index at 20 °C using a digital refractometer (3T Atago Abbe refractometer, Atago Co., Tokyo, Japan). The water content and °Brix concentration were determined based on a Chataway table [21]. Each measurement was taken in duplicate.

Sugar determination

Glucose, fructose and sucrose in honey samples were measured using a HPLC 10ADVP-SHIMADZU, with RI-detector, according to a method described by Bogdanov [21]. The linear regression factor of the calibration curves was higher than 0.9982 for all sugars. Sugars were quantified by comparison of the peak area obtained with those of standard sugars. The results for each sugar were expressed as g/100g. Values of parameters were expressed as the mean and standard deviation to a confidence interval of 95%for the mean.

Viscoelastic measurement

The dynamic rheological properties of honey samples were obtained with a RheoStress 1 rheometer (Thermo Haake, Germany) at different temperatures (5, 10, 15, 20, 25, 30 and 40°C), using a parallel plate system (Ø 60 mm) at a gap of 500 µm. A batch of each composition was prepared and at least two measurements were performed on each batch, using a fresh sample for each measurement. After loading the sample, a waiting period of 5 min was used to allow the sample to recover itself and to reach the desired temperature. In order to determine the linear viscoelastic region, stress sweeps were run at 1 Hz first. Then, the frequency sweeps were performed over the range w=0.62–62.83Hz at 1 Pa stress. The 1 Pa stress was in the linear viscoelastic region. Rheowin Job software (v. 2.93, Haake) was used to obtain the experimental data and to calculate storage (or elastic) modulus (G'), loss (viscous) modulus (G''), and complex viscosity (η^*).

Statistical analysis

The variables were weighted with the inverse of the standard deviation of all objects in order to compensate for the different scales of the variables. The proposed models have been made up using SPSS trial version, Excel 2007, Statgraphics trial version and Design Expert trial version.

To verify the suitability of the models, the mean relative deviation modulus D (eq. 1) was calculated:

$$D = \frac{100}{n}\sum_{i=1}^{n}\left|\frac{A_{\exp} - A_{pred}}{A_{\exp}}\right| \qquad (1)$$

RESULTS AND DISCUSSIONS

Physicochemical parameters of honey are summarised in Table 1. The moisture content ranged between 15.60-19.10 g/100 g and met the threshold requirement of moisture content required by the Codex Alimentarius (max. 20g/100 g) [22]. Sugars represent the main components of any type of honey. Reducing sugars (invert sugar), mainly fructose and glucose, are the major constituents of honey but small quantities of sucrose are also present [23].The actual proportion of fructose to glucose, in any particular honey, depends largely on the source of the nectar [7-9].The total content of glucose and fructose was over 60 g/100 g of honey, in accordance with the 2001/110/CE Directive. The fructose/glucose ratio was calculated for all samples. This ratio gives information about the crystallization state of honey, when fructose is higher than glucose honey is fluid. In all the cases this ratio was higher than 1 (Table 1), which was confirmed by the crystallization state of the mentioned honey sample; all the honeys were in a liquid state. For the rheological characterization of honey the F/G ratio must be higher than 1, if not the rheological parameters could not be determined due to crystallization of the honey.

Figure 1 presents a typical rheogram of a honey sample in a 0.10–10 Hz frequency domain at 5-40 °C; it shows the changes in storage modulus (G’) and loss modulus G’’ with the frequency, while the viscosity is not influenced by the shear stress. All the samples analysed exhibited a Newtonian behaviour (fig. 1c). The rheological parameters (G’, G”, η) increased with the increment of the frequency applied to the sample, showing that G’’ had a greater magnitude than G’. All the viscoelastic parameters are positively influenced by the °Brix concentration. In general, G’ is less important than G’’ due to its low value with respect to G’’ (G’’ > G’) as indicated by Doubly and Cavalier [24]. Therefore, the elastic behaviour of honey seems to be less important than its viscous behaviour, as noted by Yoo[18]. The rheological properties of honey can also be affected by additional factors, such as sugars and other polymeric compounds in the honey [4, 8]. In particular, the sugar content (glucose and fructose) can greatly affect the rheological properties because these sugars have different rheological behaviours. The models used for predicting the loss modulus and viscosity (with respect to temperature, concentration), presented below, use the magnitude of the two parameters at 1 Hz.

Viscosity modelling

Influence of Temperature: The influence of temperature on honey viscosity is described by the Arrhenius model (equation 2):

$$\eta = \eta_0 \cdot \exp\left[-\frac{E_a}{RT}\right] \qquad (2)$$

where η_0 is a constant, R is the gas constant [$\mathrm{kJ \cdot mol^{-1} \cdot K^{-1}}$], and E_a activation energy (is an energy barrier to flow) [$\mathrm{kJ \cdot mol^{-1}}$], T – absolute temperature [K]. The activation energies (E_a) values (tab.2), calculated by the Arrhenius model ranged between 90.78 – 100.28 kJ/mol. The magnitude of η influenced the activation energy magnitude.

Effect of Concentration: The increase of honey viscosity with soluble solid content (C, °Brix) can be described by power-law (eq. 3):

$$\eta = \eta_1 C^{a_1} \qquad (3)$$

and exponential models (eq.4) [24, 25]:

$$\eta = \eta_2 \exp(a_2 C) \qquad (4)$$

where η_1, η_2, a_1, a_2 are constants, and C is the concentration in °Brix. In order to calculate the model constants, the viscosity data were fitted to equations 2-3 by non-linear regression. The resulting values of the constants are presented in table 3. The coefficients of regression (R^2) are fairly similar, so the two models are suitable for describing the effect of the soluble solids on honey viscosity.

Taking into account the mean relative deviation, it seems that the exponential models are suitable for predicting the influence of the concentration on the magnitude of viscosity. For a given temperature, the activation energy for flow depends on the soluble solid content which can be described by several models [26]. Two models, similar to equations5 and 6 were used.

$$E_a = A_1 C^{B_1} \qquad (5)$$

$$E_a = A_2 \exp(B_2 C) \qquad (6)$$

where A_1, A_2, B_1 and B_2 are constants. The E_a values and their respective concentrations were fitted to equations 5 and 6 by non-linear regression to determine the model parameters. The calculated parameters for these models are given in table 4. The coefficients of regression (R^2) of the two models proposed above are the same. Computing the mean relative deviation (eq. 1) of the activation energies, it was observed that the exponential model was better than the power law model in describing the dependency of E_a on °Brix concentration.

Combined effect of Temperature and Concentration

For practical applications, it is useful to obtain an equation describing the combined effect of temperature and concentration on viscosity [27]. The combined influence of temperature and concentration on honey viscosity is represented in figure 2. The following models for viscosity (eq. 7 and 8) were investigated:

$$\eta = \eta_3 \exp(E_1 C + E_a / RT) \qquad (7)$$

$$\eta = \eta_4 C^{E_2} \exp(E_a / RT) \qquad (8)$$

The viscosity, concentration, and temperature data were fitted to these models by non-linear regression and the values of the model constants were determined. The values of these constants are summarised in Table 5. The viscosity predictions with temperature and °Brix concentration achieve coefficients of regression between 0.67 and 0.77. The mean relative deviation *D* certifies that the suitable model corresponds to eq. 7. Therefore, for the interval of ^{0}Brix concentrations and temperatures (T) were studied the following equation (equation 9) is proposed to evaluate honey viscosity:

$$\eta = 7.14 \cdot 10^{-19} \cdot \exp(0.16 * C + 76406 / RT) \qquad \text{(eq. 9)}$$

Polynomial modelling of viscosity

The data model regarding the prediction of honey viscosity according to its chemical composition (fructose, glucose, sucrose, sugars (the difference between °Brix concentration – reported as dry matter – and the sum of fructose, glucose and sucrose), non-sugars components (the difference, reported to 100 g, between 100 g and the sum of moisture content and °Brix concentration), moisture content and temperature was made using a 3rd grade polynomial equation with seven variables. The measured and predicted values have been compared to check the suitability of the model. The equation of the model is shown below (eq. 10):

$$\eta_{pred} = b_0 + \sum_{i=o}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} x_i^2 + \sum_{i=1}^{n} b_{iii} x_i^3 + \sum_{i<j<k} b_{ijk} x_i x_j x_k + \sum_{i<j}^{n} b_{ij} x_i x_j + \sum_{i<j}^{n} b_{ij} x_i^2 x_j + \sum_{i<j}^{n} b_{ij} x_i x_j^2 \quad (10)$$

where η_{pred} is the loss modulus predicted, b_0 is a constant that fixes the response at the central point of the experiments, b_i – regression coefficient for the linear effect terms, b_{ij} – interaction effect terms, b_{ii} – quadratic effect terms and b_{iii} – cubic effect terms. The operating region and the levels of the design variables (key factors) are given in actual and coded values as shown in Table 6. Based on the design variables (Table 6) a 3rd order polynomial equation with 7 variables for viscosity was obtained as follows (eq.11):

$$\begin{aligned} \log(\eta) &= 2.15 - 1.07 \cdot X_1 - 1.11 \cdot X_2 - 0.85 \cdot X_3 - 0.70 \cdot X_4 - 0.55 \cdot X_5 \\ &- 0.26 \cdot X_7 - 1.60 \cdot X_7^2 - 0.68 \cdot X_1 \cdot X_7 - 0.71 \cdot X_2 \cdot X_7 - 0.65 \cdot X_3 \cdot X_7 - 0.36 \cdot X_4 \cdot X_7 \\ &- 0.07 \cdot X_5 \cdot X_7 + 0.01 \cdot X_7^3 + 1.65 \cdot X_1 \cdot X_7^2 + 1.68 \cdot X_2 \cdot X_7^2 + 1.27 \cdot X_3 \cdot X_7^2 + 1.07 \cdot X_4 \cdot X_7^2 \\ &+ 0.53 \cdot X_5 \cdot X_7^2 \end{aligned} \quad (11)$$

The coefficient of regresion of the proposed model represents 99.91% (R^2adjusted 99.84%). The model is a significant one ($P=0.001$). In figure 3 the measured and predicted values of viscosity are plotted.

Loss modulus modelling

Influence of Temperature: The influence of temperature on honey loss modulus is described by the Arrhenius model (equation 12):

$$G'' = G_0'' \cdot \exp\left[-\frac{E_a}{RT}\right] \qquad (12)$$

where G_0 is a constant, R is the gas constant [kJ·mol^{-1}·K^{-1}], and E_a activation energy (it is an energy barrier to flowing) [kJ·mol^{-1}], T – absolute temperature [K].The activation energy (E_a) values (tab.7), calculated by the Arrhenius model ranged between 80.82 – 95.05 kJ/mol. The magnitude of G'' influenced the activation energy magnitude. The activation energy is negatively correlated with moisture (r = - 0.85).

Effect of Concentration

The increase of honey loss modulus with soluble solid content (C, °Brix) can be described by power-law (eq. 13):

$$G'' = G_1'' C^{b_1''} \qquad (13)$$

and exponential models (eq.14) [24, 25]:

$$G'' = G_2'' \exp(b_2'' C) \qquad (14)$$

where $G_1'', G_2'', b_1'', b_2''$ are constants, and C is the concentration in °Brix. In order to calculate the model constants, the loss modulus data were fitted to equations13-14 by non-linear regression. The resulting values of the constants are presented in table 8. The coefficients of regression (R^2)

are fairly the same so the two models are suitable for describing the effect of the soluble solids on honey loss modulus.

Taking into account the mean relative deviation, it seems that the exponential models are suitable for predicting the influence of the concentration on the magnitude of loss modulus. For a given temperature, the activation energy for flow depends on soluble solid content which can be described by several models [26]. Two models similar to equations 15 and 16 were used.

$$E_a = A_1'' C^{B_1''} \qquad (15)$$

$$E_a = A_2'' \exp(B_2'' C) \qquad (16)$$

where A_1'', A_2'', B_1'' and B_2'' are constants. The E_a values and their respective concentrations were fitted to equations 15 and 16 by non-linear regression to determine the model parameters. The calculated parameters for these models are given in table 9. The coefficients of regression (R^2) of the two models proposed above are the same. Computing the mean relative deviation (eq.1) of the activation energies, it was observed that the exponential model was better than the power law model in describing the dependency of E_a on °Brix concentration.

Combined effect of Temperature and Concentration

For practical applications, it is useful to obtain an equation describing the combined effect of temperature and concentration on honey loss modulus [27]. The combined influence of temperature and concentration on honey loss modulus is presented in figure 4. The following models for loss modulus (equations17 and 18) were investigated:

$$G'' = G_3'' \exp(E_1'' C + E_a / RT) \qquad (17)$$

$$G'' = G_4'' C^{E_2''} \exp(E_a / RT) \qquad (18)$$

The loss modulus, concentration, and temperature data were fitted to these models by non-linear regression and the values of the model constants were determined. The values of these constants are summarised in Table 10. The loss modulus predictions with temperature and °Brix concentration achieve coefficients of regression between 0.65 and 0.75. The mean relative deviation *D* certifies that the suitable model corresponds to eq. 17. Therefore, for the interval of ^{0}Brix concentrations and temperatures (T) studied, the following equation (eq. 19) is proposed to evaluate the loss modulus (G’’) of honeys:

$$G'' = 2.23 \cdot 10^{-10} \cdot \exp(0.19 * C + 71630 / RT) \qquad \text{(eq. 19)}$$

Polynomial modelling of loss modulus

The data model regarding the prediction of honey loss modulus (G’’) according to its chemical composition (fructose, glucose, sucrose, sugars (the difference between °Brix concentration – reported as dry matter – and the sum of fructose, glucose and sucrose), non-sugars components (the difference, reported to 100 g, between 100 g and the sum of moisture content and °Brix concentration), moisture content and temperature was made using a 3rd grade polynomial equation with seven variables (according to table 6). The equation of the model is as follows (eq. 20):

$$G^{"}_{pred} = b_0 + \sum_{i=o}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} x_i^2 + \sum_{i=1}^{n} b_{iii} x_i^3 + \sum_{i<j<k} b_{ijk} x_i x_j x_k + \sum_{i<j}^{n} b_{ij} x_i x_j + \sum_{i<j}^{n} b_{ij} x_i^2 x_j + \sum_{i<j}^{n} b_{ij} x_i x_j^2 \tag{20}$$

where $G^{"}_{pred}$ is the loss modulus predicted, b_0 is a constant that fixes the response at the central point of the experiments, b_i – regression coefficient for the linear effect terms, b_{ij} – interaction effect terms, b_{ii} – quadratic effect terms and b_{iii} – cubic effect terms. Based on the design variables (Table 6) a 3rd order polynomial equation with 7 variables for loss modulus was obtained as follows (eq. 21):

$$\begin{gathered}\log(G'') = -887.14 + 1498.77\cdot X_1 + 1381.78\cdot X_2 + 466.51\cdot X_3 + 1714.68\cdot X_4 + 27.09\cdot X_5 \\ + 476.13\cdot X_6 + 2962.67\cdot X_7 + 1.38\cdot X_1^2 - 1.89\cdot X_2^2 + 1.77\cdot X_3^2 - 1.64\cdot X_4^2 - 3.77\cdot X_5^2 \\ - 2075.60\cdot X_7^2 - 4993.87\cdot X_1\cdot X_7 - 4604.92\cdot X_2\cdot X_7 - 1555.18\cdot X_3\cdot X_7 - 5714.61\cdot X_4\cdot X_7 \\ - 91.68\cdot X_5\cdot X_7 + 0.07\cdot X_7^3 - 3.21\cdot X_1^2\cdot X_7 + 3492.46\cdot X_1\cdot X_7^2 + 4.57\cdot X_2^2\cdot X_7 \\ + 3221.87\cdot X_2\cdot X_7^2 - 4.11\cdot X_3^2\cdot X_7 + 1088.83\cdot X_3\cdot X_7^2 + 3.72\cdot X_4^2\cdot X_7 + 3998.68\cdot X_4\cdot X_7^2 \\ + 8.90\cdot X_5^2\cdot X_7 + 66.75\cdot X_5\cdot X_7^2 + 1114.11\cdot X_6\cdot X_7^2\end{gathered} \tag{21}$$

The coefficient of regresion of the proposed model represents 99.71 (R^2adjusted 99.50). The model is a significant one (P=0.001). In figure 5 the measured and predicted values of loss modulus are plotted.

CONCLUSIONS

Spanish honeys present a Newtonian behaviour, while from the viscoelastic point of view it behaves like a liquid with loss modulus much greater than the elastic modulus in the domain of the temperature used (5-40 °C). The viscosity, loss and modulus are influenced negatively by the increasing of the temperature, and positively by °Brix concentration. The exponential models are much suitable for predicting the influence of °Brix concentration on loss modulus and viscosity. In the case of viscosity and loss modulus a model of the influence of temperature and °Brix concentration was obtained. Based on the experimental design results, the cubic polynomial models with 7 variables were developed for predicting the loss modulus as a combination of design variables, namely fructose, glucose, sucrose, sugars, non-sugars, moisture content and temperature. The polynomial models were statistically validated by F-ratio test.

REFERENCES

[1] Kaya, A., Ko, S., Gunasekaran, S.,. Viscosity and color change during in situ solidification of grape pekmez, Food Bioprocess Technology., 2008, 4(2), 241-246

[2] Bhandari, B., D'Arcy, B., & Chow, S.. Rheology of selected Australian honeys. Journal of Food Engineering, 1999, 41(1), 65–68

[3] Chen, Y.W., Lin, C.H., Wu, F.Y., Chen, H.H., Rheological properties of crystallized honey prepared by new type of nuclei. Journal of Food Processing Engineering, 2009, 32, 512–527

[4] Kang, K.M., Yoo, B., Dynamic rheological properties of honeys at low temperatures as affected by moisture content and temperature. Food Science and Biotechnology, 2008, 17 (1), 90–94.

[5] Yanniotis, S., Skaltsi, S., Karaburnioti, S., Effect of moisture content on the viscosity of honey at different temperatures. Journal of Food Engineering, 2006,72(4), 372–377

[6] Kumar, J.S., Mandal, M., Rheology and thermal properties of marketed Indian honey. Nutrition Food Sci., 2009, 39 (2), 111–117

[7] Oroian, M., Amariei, S., Escriche, I., Gutt, G., Rheological aspects of Spanish Honeys, Food Bioprocess Techology, 2013, 6(1), 228-241

[8] Oroian, M., Physicochemical and rheological properties of Romanian honeys, Food Biophysics., 2012, 7(4), 296-307

[9] Oroian M., Amariei, S., Escriche, I., Gutt, G., A viscoelastical model for honey using the time-temperature superposition principle (TTSP), Food Bioprocess Technology, 2012, DOI 10.1007/s11947-012-0893-7

[10] Cohen, I., Weihs, D., Rheology and microrheology of natural and reduced-calorie Israeli honeys as a model for high-viscosity Newtonian liquids, Journal of Food Engineering, 2010, 100(2), 366-371

[11] Witczak, M., Juszcak L., Galkowska D., Non-Newtonian behaviour of heather honey, Journal of Food Engineering, 2011, 104 (1), 532–537

[12] Gómez-Díaz, D., Navaza, J.M., Quintáns-Riveiro, L. C., Rheological behaviour of Galician honeys, European Food Research and Technology, 2006, 222, 439-442

[13] Gómez-Díaz, D., Navaza, J.M., Quintáns-Riveiro, L. C., Physicochemical characterization of Galician honeys, International Journal of Food Properties, 2012, 15, 292-300

[14] Mora-Escobedo, R., Moguel-Ordonez, Y., Jaramillo-Flores, M.E., Gutierrez-Lopez, G.F., The Composition, Rheological and Thermal Properties of Tajonal (ViguieraDentata) Mexican Honey, International Journal of Food Properties, 2006, 9(2), 299-316

[15] Bhandari, B., D'Arcy, B., Kelly, C., Rheology and crystallization kinetics of honey: Present status, International Journal of Food Properties., 1999, 2(3), 217-226

[16]Mossel, B., Bhandari, B., D'Arcy, B., Caffin, N., Determination of Viscosity of Some Australian Honeys Based on Composition, International Journal of Food Properties, 2003, 6(1), 87-97

[17] Zaitoun, S., Ghzawi, A. A., Al-Malah, K.I.M., Abu-Jdayil, B., Rheological properties of selected light colored Jordanian honey, International Journal of Food Properties, 2001, 4(1), 139-148

[18] Yoo B., Effect of temperature on dynamic rheology of Korean honeys, Journal of Food Engineering, 2004, 65, 459–463

[19] Abu-Jdayil, B., Al-MajeedGhzawi, A., Al-Malah, K. I. M., &Zaitoun, S. J.,Heat effect on rheology of light and darkcolored honey. Journal of Food Engineering, 2002, 51(1), 33–38

[20] Mossel, B., Bhandari, B., D'Arcy, B., Caffin, N. Use of Arrhenius model to predict rheological behaviour in some Australian honeys. Lebensmittel-Wissenschaft und-Technologie, 2000,33, 545–552.

[21] Bogdanov S., (2002) Harmonised methods of the international honey commission. Swiss Bee Research Centre, FAM, Liebefeld, CH-3003 Bern, Switzerland.

[22] Codex Alimentarius. Standard for Honey, Ref. no. CL 1993/14, SH, Codex Alimentarius Commission FAO/WHO, 1993, Rome.

[23] Kucuk, M., Kolayh, S., Karaoglu, S., Ulusoy, E., Baltaci, C., &Candan, F. Biological activities and chemical composition of three honeys of different types from Anatolia. Food Chemistry, 2007, 100, 526–534.

[24]Doublier, J. L., &Cuvelier, G. Gums and hydrocolloids: functional aspect. In A. C. Eliasson (Ed.), Carbohydrates in Food (pp. 283–318), 1996, New York: Marcel Dekker Inc.

[25] Rao, M.A., Cooley, H.J., Vizali, A.A., Flow properties of concentrated juices at low temperatures. Food Technology, 1984, *38*, 113-119

[26] Giner, J., Ibarz, A., Garza. S., Xhian-Quan, S., Rheology of Clarified Cherry Juices, Journal of Food Engineering, 1996, 30, 147-154

[27] Ibarz, A., Pagán, J., Miguelsanz, R. Rheology of clarified fruit juices. II. Blackcurrant juices. Journal of Food Engineering, 1992,15,63-67. Doi:10.1016/0260-8774(92)90040-D

Tab. 1. Physicochemical parameters of honey

Parameter	Value Mean (standard deviation)
Fructose (g/100 g honey)	36 (4)
Glucose (g/100 g honey)	30 (3)
Sucrose (g/100 g honey)	2 (1)
F/G	1.2 (0.1)
Sugars (g/100 g honey)	14 (4)
Moisture content (g/100 g honey)	18 (1)
Non-sugar substances (g/100 g honey)	1.69 (0.06)

Tab.2. Influence of temperature on honey viscosity

Sample	η_0 [mPa·s]	Ea [kJ/mol]	R2
H1	$9.26\cdot10^{-16}$	94.59	0.99
H2	$6.41\cdot10^{-15}$	92.10	0.99
H3	$9.98\cdot10^{-15}$	91.60	0.99
H4	$2.02\cdot10^{-15}$	92.41	0.99
H5	$1.43\cdot10^{-15}$	93.60	0.99
H6	$3.29\cdot10^{-15}$	98.56	0.98
H7	$7.56\cdot10^{-15}$	101.87	0.99
H8	$6.59\cdot10^{-15}$	93.08	0.99
H9	$9.73\cdot10^{-16}$	100.28	0.99
H10	$2.82\cdot10^{-15}$	90.78	0.99
H11	$1.57\cdot10^{-15}$	99.86	0.99

Tab.3. Effect of °Brix concentration (C) on the honey's viscosity at different temperature (T)

	Power law				Exponential model			
	η_1	a_1	R^2	D	η_2	a_2	R^2	D
5	$2\cdot10^{-11}$	60.12	0.98	6.28	$1\cdot10^{-24}$	0.74	0.98	5.90
10	$2\cdot10^{-11}$	60.96	0.98	6.97	$2\cdot10^{-25}$	0.75	0.98	5.52
15	$2\cdot10^{-96}$	50.84	0.98	4.13	$2\cdot10^{-21}$	0.63	0.98	4.09
20	$1\cdot10^{-91}$	48.18	0.98	3.75	$2\cdot10^{-20}$	0.59	0.98	3.45
25	$9\cdot10^{-91}$	47.59	0.98	2.06	$2\cdot10^{-20}$	0.59	0.98	2.02
30	$7\cdot10^{-86}$	44.93	0.99	3.51	$1\cdot10^{-19}$	0.55	0.99	3.32
40	$7\cdot10^{-89}$	46.27	0.97	1.48	$1\cdot10^{-20}$	0.57	0.98	0.95

D-mean				4.03				3.61

Tab.4. Influence of the °Brix concentration on the viscosity's activation energy

Model	**η**			
	A_i^*	**B_i^***	**R^2**	***D***
$E_a = A_1 \cdot C^{B_1}$	$1.01 \cdot 10^{-4}$	2.85	0.98	0.52
$E_a = A_2 \cdot \exp(B_2 C)$	5.39	$3.50 \cdot 10^{-3}$	0.98	0.54

Tab.5. Combined effect of °Brix concentration and temperature on the honey's viscosity

Model	**η[mPa·s]**	**E_i**	**E_a**	**R**	***D***
$\eta = \eta_3 \exp(E_1 C + E_a / RT)$	$7.14 \cdot 10^{-19}$	0.16	76.41	0.77	20.26
$\eta = \eta_4 C^{E_2} \exp(E_a / RT)$	$3.90 \cdot 10^{-14}$	-0.89	91.15	0.68	30.15

Tab.6. Correspondence between actual and coded values of design variables

Design variables	Symbol	Actual values of coded levels	
		-1	+1
Fructose (g/100g)	X_1	31.50	42.47
Glucose (g/100g)	X_2	24.40	34.52
Sucrose (g/100g)	X_3	0.00	3.42
Sugars (g/100g)	X_4	3.26	15.82
Moisture content (g/100g)	X_5	15.60	19.10
Non-sugar substances (g/100g)	X_6	1.59	1.80
Temperature (°C)	X_7	5	40

Tab.7. Influence of temperature on honey loss modulus

Sample	G’’		
	Go’’ [mPa]	E_a [kJ/mol]	R^2
H1	$9.20\cdot10^{-14}$	89.00	0.99
H2	$4.10\cdot10^{-14}$	84.99	0.99
H3	$8.80\cdot10^{-14}$	83.24	0.99
H4	$2.10\cdot10^{-14}$	86.86	0.99
H5	$1.30\cdot10^{-14}$	88.09	0.99
H6	$5.90\cdot10^{-15}$	92.15	0.99
H7	$2.52\cdot10^{-14}$	95.05	0.99
H8	$1.09\cdot10^{-13}$	87.73	0.99
H9	$1.22\cdot10^{-12}$	80.82	0.99
H10	$6.41\cdot10^{-14}$	89.76	0.99
H11	$3.34\cdot10^{-14}$	93.02	0.99

Tab.8. Effect of °Brix concentration (C) on the honey loss modulus at different temperature (T)

	Power law model $G'' = G_1'' C^{b_1''}$				**Exponential model** $G'' = G_2'' \cdot \exp(b_1'' C)$			
	G_1'' **[mPa]**	b_1''	R^2	**D**	G_2'' **[mPa]**	b_2''	R^2	**D**
5	$3\cdot10^{-114}$	60.99	0.97	12.48	$3\cdot10^{-24}$	0.75	0.97	12.90
10	$2\cdot10^{-114}$	60.94	0.99	26.97	$1\cdot10^{-24}$	0.75	0.99	23.52
15	$1\cdot10^{-95}$	50.84	0.98	24.13	$1\cdot10^{-20}$	0.62	0.98	26.69
20	$9\cdot10^{-91}$	48.17	0.99	3.75	$1\cdot10^{-19}$	0.59	0.99	3.45
25	$8\cdot10^{-90}$	47.54	0.99	6.06	$1\cdot10^{-19}$	0.58	0.99	5.40
30	$5\cdot10^{-85}$	44.89	0.99	2.51	$9\cdot10^{-19}$	0.55	0.99	3.32
40	$5\cdot10^{-88}$	46.27	0.98	6.48	$9\cdot10^{-20}$	0.57	0.98	3.95
D - mean				11.76				11.32

Tab.9. Influence of the °Brix concentration on the loss modulus’s activation energy

Model	**G’’**			
	A_1''	B_1''	R^2	***D***
$E_a = A_1'' C^{B_1''}$	$5\cdot10^{-6}$	3.78	0.94	3.41
$E_a = A_2'' \exp(B_2'' C)$	2.021	0.05	0.94	1.65

Tab.10. Combined effect of °Brix concentration and temperature on the honey’s loss modulus

Model	G_i''**[mPa]**	E''_i	E_a **(kJ/mol)**	R^2	***D***
$G'' = G_3'' \exp(E_1'' C + E_a / RT)$	$2.23\cdot10^{-10}$	0.19	71.63	0.78	1723.40

$G'' = G''_3 \cdot C^{E''_2} \exp(E_a / RT)$	$1.49 \cdot 10^{-12}$	-0.78	99.87	0.67	2893.30