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RHEOLOGICAL BEHAVIOR OF SENGA SENGANA STRAWBERRY MASH
REOLOŠKO PONAŠANJE KAŠE JAGODE SORTE SENGA SENGANA

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ABSTRACT

The objectives of the research presented in this paper are rheological properties of a mash made of Senga Sengana strawberries. Organically grown strawberries were washed in cold water, blended and in order to be conserved, treated with sodium benzoate. Rheological properties of the mash with solids concentration of 10.53% were examined at a rotational rheometer at the temperatures of 20oC, 30oC and 40oC. The aim of the research was to investigate the rheological properties (rheological behavior) of a strawberry mash with emphasis on the effects of temperature. It was found that the strawberry mash behaves as non-Newtonian, pseudoplastic fluid, where the apparent viscosity decreases with increasing of shear rate (velocity gradient). The strawberry mash has thixotropic properties, where the apparent viscosity changes with time slowly and where the strawberry mash has no gel properties. Dependence of shear stress and the velocity gradient is modeled by Ostwald de-Waele equation. It was stated that the increase of a mash temperature leads to consistency index reduction and flow behavior index increase. The dependence of the apparent viscosity and temperature is modeled by Arrhenius equation, where the activation flow energy increases with shear rate reduction.
Key words: *rheology, mash, strawberry, Senga Sengana.*

REZIME

Istraživanje prikazano u ovom radu odnosi se na reološke karakteristike kaše jagode sorte Senga Sengana. Jagode dobijene iz organske proizvodnje su nakon pranja hladnom vodom izblendovane, a zatim je dobijena kaša konzervisana natrijum - benzoat. Reološke osobine kaše koncentracije suve materije 10.53 % ispitivane su na rotacionom viskozimetru na temperaturama 20°C, 30°C i 40°C. Cilj istraživanja je da se ispitaju reološke osobine kaše jagode sa akcentom na istraživanju uticaja temperature. Utvrđeno je da se kaša jagode ponaša kao nenjutnovski, pseudoplastični fluid, gde se prividna viskoznost smanjuje sa povećanjem gradijenta brzine. Kaša jagode ima tiksotropnu prirodu, gde je promena prividne viskoznosti sa vremenom veoma mala i gde kaša jagode nema osobine gela. Zavisnost tangencijalnog napona i gradijenta brzine modelirana je Ostwald de Wael jednačinom. Utvrđeno je da sa porastom temperature kaše dolazi do smanjenja vrednosti koeficijenta koezistencije i povećanja vrednosti indeksa strujnog ponašanja. Zavisnost prividne viskoznosti i temperature modelirana je Arhenijusovom jednačinom, gde se aktivaciona strujna energija povećava sa smanjenjem gradijenta brzine.
Ključne reči: *reologija, kaša, jagoda, Senga Sengana.*

INTRODUCTION

Knowledge about the rheological properties of fruit is of great importance in the design of process equipment, product development, storage, transportation and quality control (Omah et al., 1999). The last three decades is the period of intensive research in this field with primary objective to examine the properties that influence rheological behavior of strawberry products. Rheological properties of strawberry products are dependent on several influential factors. It is now well known that the viscosity of a fluid can generally be affected by following properties: shear rate, temperature, pressure, humidity, composition and duration of storage (Giap, 2010).

The dependence of the rheological behavior of fruit products on temperature has been researched by many authors in the past (Saravacos, 1970; Vitali and Rao, 1982, Rao, 1999; Ibarz et al., 1992, 1994, 1996; Eipeson and Singh, 2000; Juszczak and Fortuna , 2003; Belibagli and Dalgic, 2007). The influence of the temperature on the viscosity of the fluid can be so large that in some instances changes the rheological behavior of fluids. For example, it is documented that sea buckthorn juice has different rheological behavior at different temperatures; below 10 °C acts as pseudoplastic fluid, at temperature of 10 °C behaves as a Newtonian fluid, while above 10 °C behaves as a dilatant fluid (Oomach et al., 1999).

The rheological behavior of strawberry jam at temperatures between 20°C and 40°C has non-Newtonian, pseudoplastic behavior, where suspended matter affects the consistency index (Alvarez et al., 2006). Fruit purees consist of serum, usually Newtonian, and particles of different sizes and shapes scattered across it, where the pulp, together with pectin, is component that contributes to non-Newtonian behavior (Balestra et al., 2011). The rheological behavior of fruit juices and concentrates depends on their composition, especially the type of fruit and treatment that is carried out in its production process (Ibarz et al., 1996). For example, concentrated strawberry juice at temperatures of 10 to 60°C and humidity of the sample from 50 to 65% showed Newtonian behavior, where the viscosity strongly depends on the temperature and humidity of the sample (Juszczak et al., 2003).

The Complex interactions between soluble sugars, pectin substances and suspended solids significantly affect the rheological behavior of fruit purees (Balestra et al., 2011). The rheological properties of strawberry jam are significantly affected by the presence of sugar (Javanmard and Endan, 2010), resulting in strawberry jam having a higher apparent viscosity than fresh strawberry mash. This is supported by analysis of the rheological behavior of various products made from strawberries, where the sacharose is replaced with healthy sugar (sucrose, isomaltulose, sucrose-glucose, and fructose-isomaltulose). All products have non-Newtonian, pseudoplastic behavior and complied well with Herschel-Bulkley model. The consistency index K and yieldstress $\tau 0$ are influenced by the type of sugar, the way of preparation and the level of pectin. Flow behavior index n does not depend on the type of sugar, but it depends on the level of preparation and pectin (Peinado et al., 2012).

It has been explored (Aguayo et al., 2009) how the treatment of strawberry juice during storage (63 days) affects the viscosity. The two treatments were considered: heating of strawberry juice to a temperature of 90°C (for 60 s and 30 s) and exposure of strawberry juice to high-intensity pulsed electric field (HIPEF) (35 kV/cm for 1700 ms applying 4-ms pulses at 100 Hz in bipolar mode). The highest initial value of viscosity has a sample treated with HIPEF (19.7 mPa), then the sample heated to temperature of 90°C for 60 s (17.6 mPa), while the lowest viscosity has a sample heated to temperature of 90°C for 30 s (10.2 mPas). During the storage period, in all three treatments, a reduction in viscosity has the same trend. It is interesting to note research on the effect of storage to flavor and rheological properties of fat free strawberry yogurt. Storage of yogurt is maintained at 10°C, while the measurements are performed at room temperature of 21°C after 7, 14 and 28 days. Apparent viscosity increased significantly during storage. The main influence on the rheological properties of yogurt has bacterial activity, which reduces the pH value during storage and increases the strength of the protein grid due to living bacteria in yogurt (Lubbers et al., 2004).

The ohmic heater was tested (Castro at all, 2004) for the aseptic processing of pulp and strawberry jam. The aim of the study were hydrodynamics and fluid residence time distribution (RTD) of water as a Newtonian fluid representative, and for the pulp and strawberry jam as non-Newtonian fluid representatives and for seven different flow rates at the inlet. The flow pattern was obtained using CFD, where the numerical model was verified using the experimental parameters for the pulp and strawberry jam (consistency index and flow behavior index for temperatures from 40°C to 90°C). The results showed that the flow rate affects the RTD, while the process temperature slightly affects the RTD. The CFD analysis indicated "the shortcuts" and dead zones, especially for non-Newtonian fluid (pulps and strawberry jam).

Since the scope of research in this paper is Senga Sengana strawberry mash, a particular attention was directed to research of previous studies about the subject. Based on the literature review, it is founded that the strawberry mash is rarely the subject of rheological research. The objectives of rheological studies are mainly focused on other strawberry products: juices, concentrates, purees and jams. Even as early as 1977, Rao (Rao, 1977) found that in general pulp and purees made from fruits and vegetables act as non-Newtonian, pseudoplastic fluids. Later rheological studies of strawberry products mostly confirmed the conclusion of Rao's research. In that sense the hypothesis is set, that the strawberry mash is non-Newtonian, pseudoplastic and thixotropic fluid.

Nomenclature:

E_a (J/mol) - activation flow energy
$K\left(\mathrm{Pa \cdot s^n}\right)$- consistence index
$n(-)$ - flow behavior index
$n(\mathrm{r/min})$ - number of rotation
$R(\mathrm{J/kgK})$ - gas constant
R^2 (-) - coefficient of determination
$R_c(\mathrm{m})$ - radius of container
$R_b(\mathrm{m})$ - radius of spindle
$T(\mathrm{K})$- absolute temperature
$t(\mathrm{s})$ - time
$x(\mathrm{m})$ - radius at which shear rate is being calculated

Greek symbols
$\dot{\gamma}\left(s^{-1}\right)$- shear rate
$\eta(\mathrm{Pa \cdot s})$- viscocity
$\eta_{T\infty}(\mathrm{Pa \cdot s})$- viscosity at temperature tends to infinity
$\tau(\mathrm{Pa})$- shear stress
$\omega(\mathrm{rad/s})$ - angular velocity of spidle

Subscripts
a – activation
c – container
b – bob or spindle
T_∞ - infinitive temperature

MATERIAL AND METHOD

The scope of research presented in this paper is strawberry mash made of old German sort Senga Sengana. The mash was prepared from fresh strawberry fruits that are grown in organic conditions. Fresh strawberries were hand-chosen, and only ripe and healthy fruits were used. Then, the strawberries were washed under a gentle stream of cold water, to remove dirt. The stems were removed, and the fruits were then blended with hand mixer to obtain a mash of homogenic appearance.

The sample of 700 ml was made from obtained pure mash and conserved with sodium - benzoate. The concentration of the dry matter of the sample was determined next, using moisture analyzer "Kern and Sohn" model MLB50-3N. The measuring range of the device is up to 50 g, with 0.001 g resolution / 0.01%, repeatability (sample weight 2 g) and 0.5% (10 g sample weight) 0.02%. Three measurements of part of the dry matter were performed for the sample, where the concentration of dry matter in the sample was determined as the arithmetic mean and calculated to be 10.53%. In order to determine the effect of temperature on the rheological behavior of mash, the viscometer manufactured by "Myr" model "V2-R" (Brookfield viscometer) was used. The accuracy of the viscometer is 0.5% of the measured value; the measuring range is 20 ÷ 13 million mPas, while the accuracy of measurement is ± 1% for the entire measuring range. The sample was heated in a water bath, and the temperature was controller using PT 100 temperature probe of the viscometer. Measuring range of the temperature probe is -15 ÷ 180˚C, resolution 0.1˚C, accuracy ± 0.1˚C, while the accuracy is ± 1% for the entire measuring range. Rheological tests of strawberry mash samples were performed at different temperatures: 20˚C, 30˚C and 40˚C. For each sample, at particular temperature, two rheological curves were recorded, one by increasing of cylinder rotation speed (spindle) and the other by reducing the cylinder rotation speed. Rheological curve was obtained as the arithmetic average of the two measured rheological curves. The range of cylinder spindle is from 0.3 to 200 rpm. In order to determine the time dependence, the rheological characteristics of strawberry mash were measured at room temperature of 20˚C for 5 h. The measurements were performed at constant spindle of the rotating cylinder of 60 rpm, 20 rpm and 6 rpm. The rotational viscometer is controlled by computer and software package for the viscometer Viscosoft Plus V2 version v1.05 was used to determine where to enter, display, processing and storage of data was used.

According to the recommendations for the viscometer type "Brookfield" (Brookfield Engineering), based on measured cylinder rotation speeds *n*, the shear rate $\dot{\gamma}$ was calculated as:

$$\dot{\gamma} = \frac{2 \cdot R_c^2 R_b^2}{x^2 \left(R_c^2 - R_b^2\right)} \omega , \tag{1}$$

where angular velocity ω is:

$$\omega = \frac{2\pi n}{60} \tag{2}$$

Shear stress is defined as the product of the measured apparent viscosity and shear rate:

$$\tau = \eta \cdot \dot{\gamma} , \tag{3}$$

where rheological behavior of strawbery mash was moddeled by Ostwald – de Wael (Power Law) model:

$$\tau = K \dot{\gamma}^n . \tag{4}$$

Dependence of apparent viscosity on temperature of strawberry mash is modeled by Arhenius equation, which is used to describe the effect of temperature on the flow behavior of food (*Saravacos, 1970; Vitali and Rao, 1982, Rao, 1999; Ibarz et al., 1992, 1994, 1996; Eipeson and Singh, 2000; Juszczak and Fortuna, 2003; Belibagli and Dalgic, 2007)*:

$$\eta = \eta_{T\infty} \exp\left(\frac{E_a}{RT}\right) . \tag{5}$$

RESULTS AND DISCUSSION

Figure 1 shows the graphical dependence of the apparent viscosity on the shear stress recorded by increasing and decreasing cylinder spindle. It can be noticed that the strawberry mash act as non-Newtonian, pseudoplastic fluid, where the apparent viscosity decreases with increasing of shear stress. Pseudoplastic fluid behavior is explained by cracking of the molecule structure when exposed to hydrodynamic forces and increasing the alignment of the constituent molecules *(Balestra et al., 2011)*.

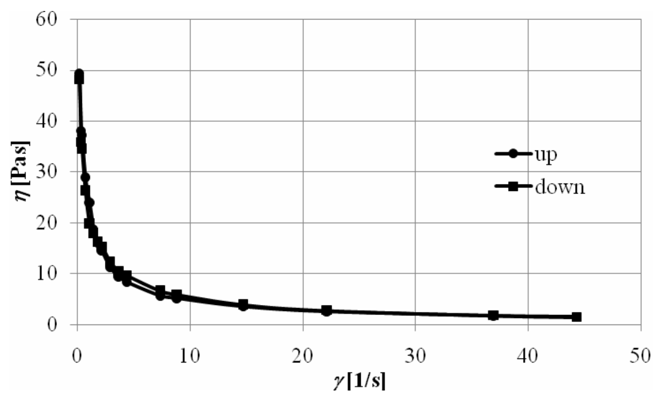

Fig. 1. The dependence of the apparent viscosity and shear stress at a mash temperature of 20°C and mash solids concentration of 10:53oBx

Hysteresis loop between the curves is explained by the change of mash viscosity over time. Generally, fruit mashes have thixotropic behavior, where the viscosity of mash at a constant shear rate decreases with time *(Falguera et al., 2012)*. Therefore, it is recommended that the rheological curves are recorded by increasing and decreasing cylinder spindle, and then the rheological curve is obtained as the arithmetic mean of the two recorded curves *(Falguera et al., 2012)*. It is observed that strawberry mash has thixotropic behavior, where the viscosity decreases over time. Figure 2 shows a log - linear dependence of the apparent viscosity over a period of 300 min for three different values of the shear rates of 4.24, 14.74 and 44.24 s^{-1}, the slurry temperature of 20 °C and the mash concentration of solids of 10.53%.

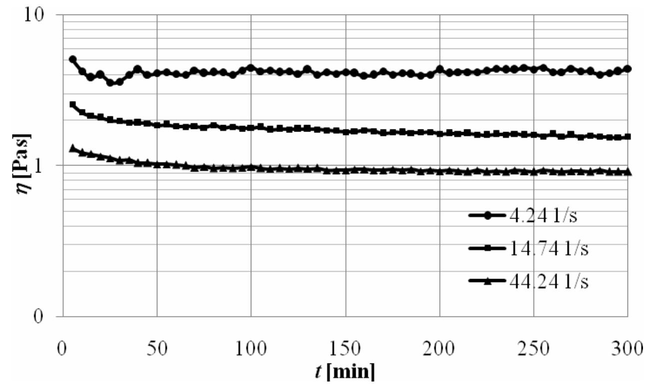

Fig. 2. The thixotropic behavior of the mash at temperature of 20°C and the mash concentration of solids of 10.53%

Small hysteresis between the curves in Figure 1 indicated that the changes of apparent viscosity over time are very low. If the first half an hour is excluded, while the measurement is not stabilized, in Figure 2 it can be seen that the slope of the curves is very small, so it can be considered that the strawberry mash is time nondependent. In presented log - linear graph the apparent viscosity dependence of time can be estimated if the mash has gel properties (Brookfield Engineering). As the curves shown in Figure 2 do not have a steep slope, i.e. slope flattens out gradually, it can be concluded that strawberry mash doesn't have gel properties.

Several mathematical models are used for modeling of the rheological behavior of fruit products. The rheological behavior of four kinds of fruit puree (raspberry, strawberry, peach and prune) is very accurately modeled by Ostwald de Waele and Herschel - Bulkey model *(Maceiras et al., 2007)*. Rheological behavior of four kinds of fruit jam (Kewpie strawberry, Marmalade, Blueberry and ST Dalfour) was modeled as Herschel - Bulkey model *(Gao et al., 2011)*. Interestingly, the successful modeling of each fruit jam (Strawberry, Peach, Prune, Raspberry and Apricot) was achieved by the following models: Ostwald de Waele, Carreau, Herschel-Bulkley and Cross models *(Alvarez et al., 2006)*.

In Figure 1, it is evident that the apparent viscosity of strawberry mash was measured even at very low shear stress. The minimum value of the shear rate was 0.22 s^{-1} which corresponds to 0.3 rpm cylinder spindle. At such low shear rates recorded, rheological curve is obtained, which can easily be extrapolated to estimate the yield stress τ_0. Figure 3 shows the rheological curves obtained for the mash temperatures of 20°C, 30°C and 40°C, and the concentration of solids of 10.53%. Extrapolation of rheological curves led to the conclusion that the yield stress is negligible. For this reason, the modeling of the rheological behavior of strawberry mash was done by Ostwald de Waele model, equation (4), which contains no yield stress unlike other mathematical models used to model the rheological behavior of fruit. For example, *(Gao et al., 2011)* modeled the rheological behavior of Kepwie strawberry jam by Herschel-Bulkley model, where the yield stress was even 99.14 Pa at a temperature of 25°C of jam. Practically, strawberry jam behaved as Bingham plastic.

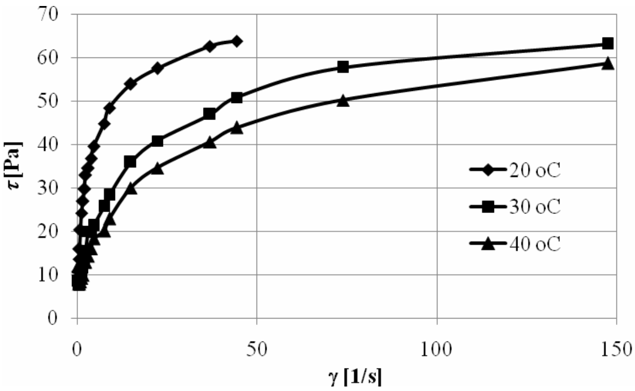

Fig. 3. Mash rheological curves measured at 20oC, 30oC and 40oC, and the mash concentration of solids of 10.53%

Table 1 shows the dependence of the parameters of Ostwald de Waele model from the temperature of strawberry mash, which has a concentration of solids of 10.53%. Ostwald de Waele model fits well the measured values which can be seen according to the value of coefficient of determination R^2. With strawberry mash temperature increase a consistence index K decreases and flow behavior index n increases. The same trends were obtained by Maceiras *(Maceiras, et al., 2007)* and Alvarez *(Alvarez et al., 2006)*. Maceiras at al. researched the rheological properties of strawberry puree; they fitted data of rheological behavior of Ostwald de Waele and Herschel-Bulkley with probability even R^2> 0.998. Alvarez *(Alvarez et al., 2006)* studied the rheological behavior of strawberry jam.

Table 1. Dependence of parameters of Ostwald de Waele model on temperature for strawberry mash with solids concentration of 10.53%

$t\left(^{\circ}\mathrm{C}\right)$	$K\left(\mathrm{Pa}\cdot\mathrm{s^n}\right)$	$n(-)$	R^2
20	24	0.277	0.964
30	13.03	0.337	0.953
40	11.12	0.344	0.971

The dependence of the apparent viscosity on temperature is modeled by Arhenius equation (5), where the parameters of the equation are shown in Table 2. Since at constant temperature activation flow energy depends also on the concentration of solids in fruit product *(Shamsudin et al., 2009)*, the parameters of Arhenius equations are given for the sample of strawberry mash with solids concentration of 10.53%.

Table 2. The parameters of the Arhenius equation for *mash with* solids concentration of 10.53%

$\dot{\gamma}\left(\mathrm{s}^{-1}\right)$	$\eta_{T\infty}\left(\mathrm{Pa}\cdot\mathrm{s}\right)$	E_a (J/mol)	R^2 (-)
0.737	0.021	33941.3	0.759
1.843	0.028	32049.8	0.807
3.686	0.019	31880.2	0.938
7.373	0.018	30805.9	0.961
8.848	0.040	28674.9	0.950
14.74	0.349	22474.0	0.959
22.12	0.968	19501.6	0.968
36.86	1,836	16595.7	0.972
44.24	3.960	14344.1	0.988

It is noticed that the apparent viscosity at infinite temperature $\eta_{T\infty}$ decreases, while the activation flow energy increases with decreasing of shear rate. Since the activation flow energy is a measure of viscosity changes with the temperature sensitivity, it can be concluded that the effect of temperature on the viscosity of strawberry mash is much more pronounced at lower values of velocity gradients. The results are consistent with Krokida *(Krokida et al., 2001)* where it was determined that the Newtonian fluid has lower activation energy than non-Newtonian fluid. For example, activation flow energy of water is 14.4 kJ/mol, while of the solution of sugar and juice concentrate is 60 kJ/mol. For pseudoplastic fluids, nonlinearity of rheological curve occurs at lower values of shear rate, while for the higher values of shear rate, rheological curve is linear (Figures 1 and 3). It is for this reason in the field of higher shear rates, where pseudoplastic strawberry mash behaves like a Newtonian fluid, there are lower values of the activation flow energy. In accordance with Giap *(Giap, 2010)*, at higher shear rates more accurate measurement of viscosity are obtained. This is due to fact that at the lower temperature gradient at higher fluctuation of the measured viscosity occurs. This is evident by the values of R^2 in Table 3, where a decrease in the shear stress lead to decrease R^2, which is used to verify Arhenius model. At higher values of the shear rate Arhenius equation coincides well with the measured data (R^2> 0.98), while for the values of the shear rate $\dot{\gamma}$<1 change of apparent viscosity with temperature cannot be sufficiently accurately described by Arhenius equation.

CONCLUSION

The mash is prepared by blending of fresh strawberry sort Senga Sengana got from organic production. The mash was conserved with sodium benzoate and measured solids concentration was 10.53%. Rheological properties of strawberry mash were researched on rotational rheometer at temperatures of 20°C, 30°C and 40°C. It was found that the strawberry mash behaves as non-Newtonian, pseudoplastic fluid, where the apparent viscosity η decreases with shear rate $\dot{\gamma}$ increase. The strawberry mash has thixotropic behavior, where the apparent viscosity change in time is relatively small. Analysis of the log - linear graph of the apparent viscosity dependence on time found that strawberry mash has no gel properties. Dependence of tangential stress τ and shear rate $\dot{\gamma}$ was modeled by Ostwald de Waele model with probability R^2=0.97. Parameters of Ostwald de Waele model show that with mash temperature increase, consistency index K decreases and flow behavior index n increases. The dependence of the apparent viscosity and temperature is modeled by Arhenius equation. The activation flow energy E_a increases, and the apparent viscosity at infinite temperature decreases with shear stress decrease. Since, the activation flow energy is a measure of sensitivity of viscosity change with the temperature, it can be concluded that the effect of temperature on the viscosity of strawberry mash will be much more pronounced at lower values of velocity gradients.

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