PHYSICAL PROPERTIES OF RASPBERRY AND ORANGE FLAVOURED FRUIT SYRUPS

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Short running title: **PHYSICAL PROPERTIES OF FRUIT SYRUPS**

Abstract

In case of fruit syrups consumer prefer thicker, deep colored ones, because it reminds them to good old homemade ones. Our current work focuses first of all on the viscosity and color of fruit syrups with different sugar and fruit content.

An Anton-Paar MCR302 rheometer with Couette-geometry (CC27) was used to determine the apparent viscosity. The used test program had 3 intervals, upward shear rate ramp from 0.1 to 250 1/s in 120s, high shear phase at 250 1/s for 120s and downward shear rate ramp from 250 to 0.1 1/s in 120s. Samples were measured in triplicates at 25±0.1°C. There were significant differences between the apparent viscosities of raspberry and orange flavored syrups containing 2 to 79g sugar and 33% fruit juice, showing the highest values with the highest sugar content. Surprisingly, there were considerable differences as well in the apparent viscosities of syrups with 33% fruit juice and 79±2g sugar content, depending on the used fruits in juice content. Using fruit juices other than pure raspberry or pure orange respectively caused a lower apparent viscosity. Preliminary tests showed that the fruit combination of the used fruit juice in tested syrups had a higher effect on the viscosity than the amount of added sugar.

Color, refractive index and soluble solid content of the samples were evaluated in triplicates as well. The ColorLite sph850 spectrophotometer was used to measure L*, a*, b* values and Abbe refractometer was applied to determine refractive index and soluble solid content. Besides dielectric measurements were carried out in frequency range from 30 Hz up to 30 MHz. Results gained with these instruments show differences between the samples as well, together with the viscosity values the characteristics of different syrups could be described.

Keywords: fruit syrups, viscosity, color, refractometry, electrical impedance

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Introduction

Decades ago, homemade fruit syrups prepared of raspberry or red currant were exceedingly popular in Hungary. Served with icy water this drink was the children's favourite in sizzling summer days and it is still popular. Luckily, there is a wide range of fruit squashes available in local supermarkets to choose from. Customers usually prefer nice thick syrups with a deep colour and a smell of the fruit it is made of. So, in our work we have focused mainly on viscosity and colour characteristics of fruit syrups. This kind of drinks belong to soft drinks in the concentrated drink category, namely squashes and cordials. (Ashurst et al, 2017). While homemade squashes have fruits, sugar, and a small amount of tartaric acid as ingredients, store-bought ones they contain less fruit, and more additives to replace the missing fruit content. Many researchers investigated the effect of different additives on quality and on customers' acceptance of fruit juices. Pongsawatamit et al (2011) analyzed blueberry syrup with added citric acid, sorbic acid, color, flavor and different amount of xanthan gum. The upward stage of flow curve was detected and apparent viscosity were determined. The syrups with xanthan gum content had higher apparent viscosity. In Ghafari et al's (2013) experiment glucose syrup was substituted with bleached date syrup in non-alcoholic and flavorless beer applying four levels of substitution: w/w 25, 50, 75, and 100 percent of glucose syrup. The apparent viscosity and color were measured. It was found that regarding the results of physical and sensory experiments, the sample with 50 percent date syrup stands to be acceptable having maintained and or improved the physical characteristics. Al-Dabbas and Al-Qudsi (2012) pasteurized orange nectars measured with the composition of saccharose syrup, citric acid, beta carotene and orange syrup (60% SS). The samples were sweetened with different ratios from sucrose and sucralose. The replacement of large proportion of sucrose with low amount of sucralose produced a decrease in the viscosity of nectars and this reduction in viscosity is proportional to the decreases in the produced nectars water activities.

The objective of our work was to evaluate the effect of sugar content and fruit composition in fruit juice content on the physical properties -mainly viscosity and color- of store-bought raspberry and orange flavored squashes.

Materials and methods

Materials

Raspberry and orange flavoured syrups with different sugar and sweetener contents and with different fruit content composition were purchased from local groceries. All the samples had 33% fruit juice content in total, but some of them had other fruit juices than

raspberry and orange respectively, such as apple, grape or elderberry. Three sets of experiment were carried out. The used samples and they properties are summarized in Tables 1. The orange squashes contained stabilizers (E414, E445, and E1450) except the O_757_33 sample. As for the stabilizers, sample O_600_33 contained xanthan gum, while sample O_769_15 had corn oil as an extra additive.

Table 1 Experiments of fruit syrups

Sample	sugar g/100ml	sweetener content	raspberry in juice, %	Sample	sugar g/100ml	sweetener content	orange in juice, %
Experiment 1 *evaluating the effect of sugar and sweetener content*							
R_032_1	3.2	YES	1	***O_020_33***	2	YES	33
R_340_1	34	YES	1	***O_330_8***	33	YES	8
R_550_3	55	YES	3	***O_550_2***	55	YES	2
R_600_33	60	NO	33	***O_600_33***	60	NO	33
R_790_33	79	NO	33	***O_790_33***	79	NO	33
Experiment 2 *evaluating the effect of fruit juice content composition (sugar content 77±2g/100ml)*							
R_772_2	77.2	NO	2	***O_810_2***	81	NO	2
R_810_3	81	NO	3	***O_769_15***	76.9	NO	15
R_790_33	79	NO	33	***O_790_33***	79	NO	33
Experiment 3 *with evaluating the effect of sugar with pure raspberry/orange content*							
R_575_33	57.5	NO	33	***O_600_33***	60	NO	33
R_600_33	60	NO	33	***O_740_33***	74	NO	33
R_740_33	74	NO	33	***O_757_33***	75.7	NO	33
R_790_33	79	NO	33	***O_790_33***	79	NO	33

Methods

In our work the focus was on the rheological and colour characteristics of the samples, but refractive index soluble solid content and some dielectric parameters was evaluated as well.

MCR302 modular compact rheometer (Anton Paar, Austria) with Couette-geometry (CC27) was applied to describe the rheological characteristics of the samples. The three stages of the test were as follows: upward shear rate ramp from 0.1 to 250 1/s in 120s, high shear phase at 250 1/s for 120s and downward shear rate ramp from 250 to 0.1 1/s in 120s. Flow curves were recorded with the Rheo Compass software delivered with the rheometer. Apparent viscosity was determined at a shear rate of 50 1/s, and the viscosity of the samples was calculated by the average of the values recorded in the constant speed phase at 250 1/s. The colour of the samples was evaluated with ColorLite sph850 (ColorLite, Germany) spectrophotometer, where L*, a*, b* values was measured. Abbe refractometer was applied to determine refractive index and soluble solid content. The flow curve, colour, refractive index and soluble solid content of samples were measured in triplicates at 25±0.1°C.

As for the dielectric properties the magnitude (Z) and the phase angle (ϕ) of electrical impedance in frequency range from 30 Hz up to 1 MHz and from 75 kHz up to 30 MHz were

measured with precision LCR meters HP4284A and HP4285A, respectively. Home-made stainless-steel electrodes were inserted into the liquid sample of 15ml volume. The distance between the electrodes was 10.5mm. The measuring voltage was 1V. LabVIEW program was used for collecting measured data and curves were created using Microsoft Excel.

Results and discussion

Figure 1 shows the results of viscosity measurements of Experiment 1. Apparently, the sugar content strongly influences the values. As supposed, higher sugar content caused higher viscosities, and the use of sweeteners caused a dramatic drop of viscosity.

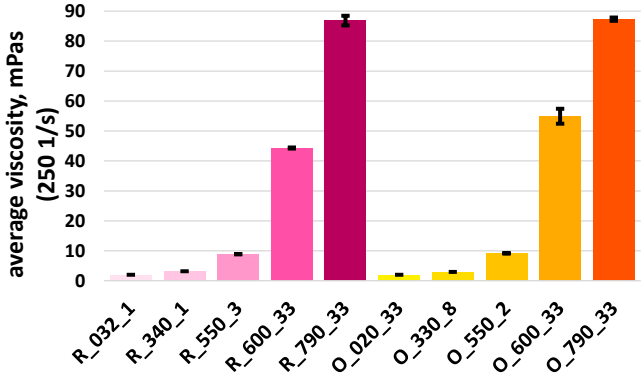

Figure 1 Average viscosity values of Experiment 1

According to the results of colour measurements (Figure 2), orange syrups with the highest sugar and orange juice content have a nice, reddish-yellow colour, like the peel of the orange fruit itself. Samples prepared with sweeteners and barely any orange juice have a light yellowish artificial colour and do not really meets the consumers' expectations. In case of raspberry syrups, the two samples (R_600_33 and R_790_33) containing purely raspberry juice has quite different values. While R_790_33 has a warm red colour, R_600_33 is slightly purple. Both have anthocyanins as colorant.

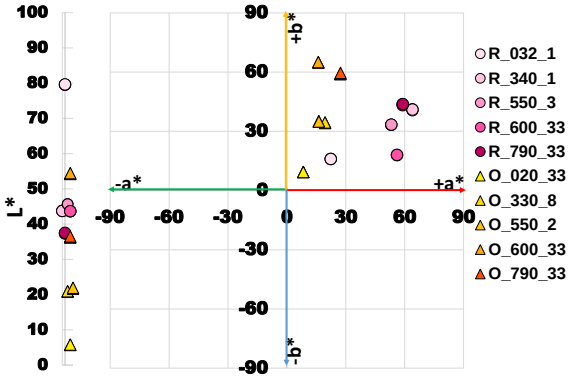

Figure 2 CIE Lab values of Experiment 1

Anthocyanins are water soluble natural dyes and are responsible for a wide variety of colours, such as red, purple and blue, in plants. The colours of anthocyanins change at

different pH. This colour change is related to the structural transformations, which are reversible in a certain range of pH values.

Tang et al (2019) used UV–vis absorption spectroscopy to observe the spectral features of anthocyanin solutions at different pH values, in the visible light range of 400–700. At pH 2 they found a strong single absorption band at 528 nm, corresponding to the red colour. When the pH was changed from 2 to 3 the absorption band reduced in intensity and red-shifted to 531 nm. Increasing the pH further to 6, the absorption band became broader and further shifted to 551 nm which means the colour turns to purple/violet. In our case, R_790_33 contains citric acid as acidulant and ascorbic acid as antioxidant, while R_600_33 contains only citric acid, so the pH was higher causing the purplish colour. Refractive index and soluble solid content (SSC) values show similar tendencies for both flavours. The higher the sugar content the higher the mentioned two values. This result exactly meets our expectations, sugar content obviously influences both the refractive index and SSC.

The results of dielectric measurements underlines, that fruit juices with different sugar content and sweeteners have characteristic, well distinguished properties (Figure 3).

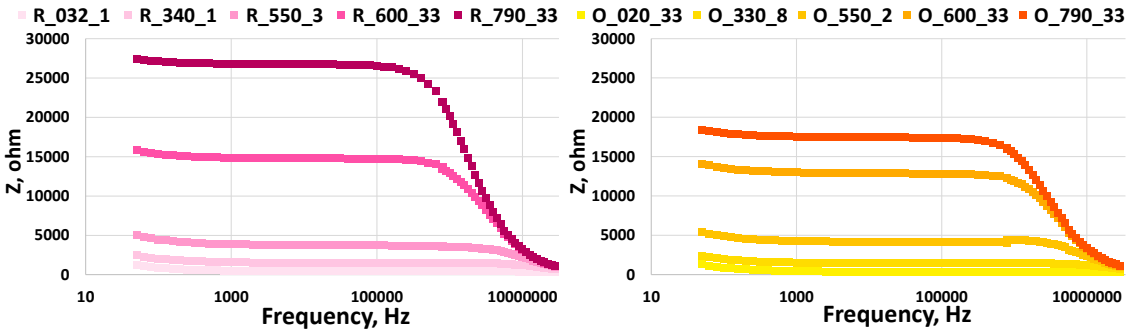

Figure 3 Impedance magnitudes of raspberry and orange syrups in the Experiment 1

Because in the first set of experiment not only the sugar content but the composition of fruit juice content was different in the samples, we wanted to investigate the effect of fruit composition as well. In the second experimental setup, samples with 77±2g sugar content but different fruit composition in the 33% fruit juice content were evaluated. The exact fruit composition is summarized in Table 2.

Table 2: Fruit composition of juice content of raspberry and orange squashes (Experiment 2)

Fruit composition	**R_810_3**	**R_772_2**	**R_790_33**	**O_810_2**	**O_769_15**	**O_790_33**
raspberry	3%	2%	33%	-	-	-
orange	-	-	-	2%	15%	33%
apple	24.5%	24.5%	-	24.5%	18%	-
grape	5.5%	6%	-	6.5%	-	-
elderberry	-	0.5%	-	-	-	-

Figure 4 shows the result of viscosity measurements for Experiment 2. In case of raspberry squashes, viscosity increased with flavour specific fruit juice content. Surprisingly, it seems that fruit composition has a stronger effect on the viscosity than sugar content, because despite the similar sugar content viscosity values show quite high differences.

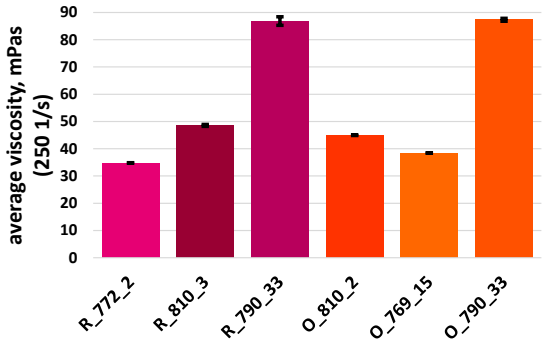

Figure 4 Average viscosity values of Experiment 2

Orange syrups have similar characteristics, but they show a slightly different trend. The sample containing relatively high 15% orange juice has the lowest viscosity. However, it is the only one which contains maize oil as an additive and this may influence the viscosity, but further investigation is needed.

Results of colour measurements does not show real correlation between the fruit content and L, a*, b* values. All of the samples contained some kind of colorants, so the colour does not represent the fruit content. In case of orange syrups, O_790_33 and O_810_2 have similar a* and b* values causing the reddish-yellow colour but O_810_2 contains only 2% orange juice however both contains carotenes and Beta-apo-8'-carotenal while the lighter yellow O_769_15 with 15% orange juice only carotenes. Raspberry samples differ from each other and all of them contains different colorants. R_790_33 with 33% raspberry juice contains only anthocyanins and has a red colour like raspberry fruit. R_810_3 contains anthocyanins and Sulphite ammonia caramel represents a cool red colour while R_772_2 is coloured with black carrot juice and caramel besides has 0.5% elderberry in fruit juice content and its colour moves towards purply pinks.

Refractive index and SSC values show similar trend to changes in viscosity. Because of nearly the same sugar content of the samples, remarkably similar values were expected despite there are remarkable differences in the parameters. Samples with pure raspberry and orange juice content have the highest values both for refractive index and SSC.

The magnitude of the electrical impedance depended somewhat on the composition of the fruit, the value of the phase angle remained essentially the same for the different compositions. This shows that the nature of the electrical conduction did not depend on the composition of the fruit (Figure 5).

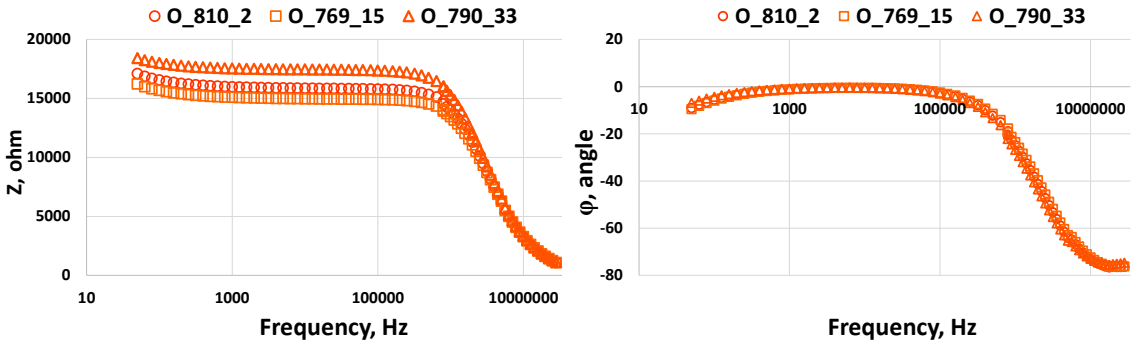

Figure 5 Impedance magnitudes and phase angles of raspberry and orange syrups in the Experiment 2

To eliminate the effect of sweeteners and of different fruit juices, samples made with sugar and 33% of pure raspberry or pure orange juice respectively were tested as well in Experiment 3. The results of viscosity measurements are shown in Figure 6. Surprisingly, samples with 74g/100ml sugar content (R_740_33 and O_740_33) had the lowest viscosity both in raspberry and orange flavoured squashes. Both had the same producer, sample R-740_33 contained elderberry syrup as colorant, and O_740_33 was the only orange flavoured sample containing ascorbic acid as antioxidant. The sample O_600_33 has slightly higher viscosity than expected presumably because of its xanthan gum content.

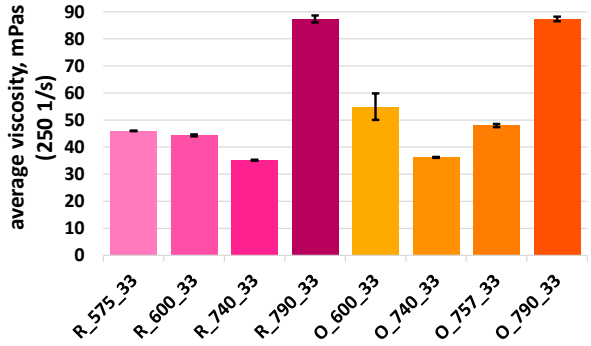

Figure 6 Average viscosity values of Experiment 3

All the syrups in this experimental setup contained 33% of pure raspberry or orange juice respectively. Thus, the CIE L*, a*, b* values are similar (Figure 7). Raspberry squashes have deep red colour except R_600_33 with slightly higher pH value and most of them have anthocyanins as colorant, R_740_33 contained elderberry juice instead as mentioned above. The orange flavoured ones are slightly different. Here O_790_33 and O_740_33 contains the same colorants namely carotenes and beta-apo-8-carotenal causing a reddish-yellow colour. O_600_33 with carotenes and sulphite ammonia caramel is brighter yellow. Uniquely sample O_757_33 does not contain any added colorant, representing the colour of real fruit juice.

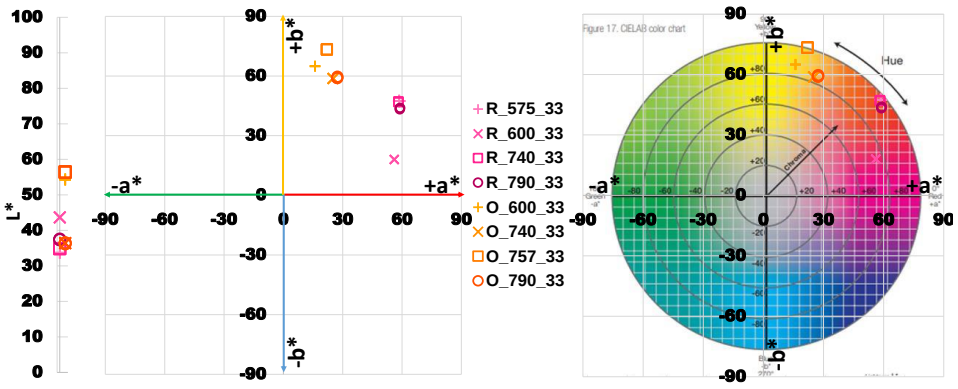

Figure 7 CIE Lab values of Experiment 3

Refractive index and SSC show slightly confusing results. In case of orange syrups both parameters change the same way (SSC from 60.06±0.05% to 66.81±0.1%, RI from 1.4410±0.0001 to 1.4549±0.0002). They increased with sugar content as expected. Surprisingly, raspberry syrups do not follow any rules. R_575_33 has the lowest sugar content but the second highest refractive index (1.4477±0.0002) and SSC (63.31±0.1%) while R_740_33 with the second highest sugar content has the lowest values of RI (1.4423±0.0001) and SSC (60.91±0.05%). We have to mention that in case of R_575_33 sugar content was added as 57.5g/100ml on the product label but 75.7g/100ml in the product description on the producer's website.

As for the results of dielectric measurements (Figure 8), as Juanash and Yulianti (2016) and Widodo et al (2016) stated, impedance should increase with sugar content.

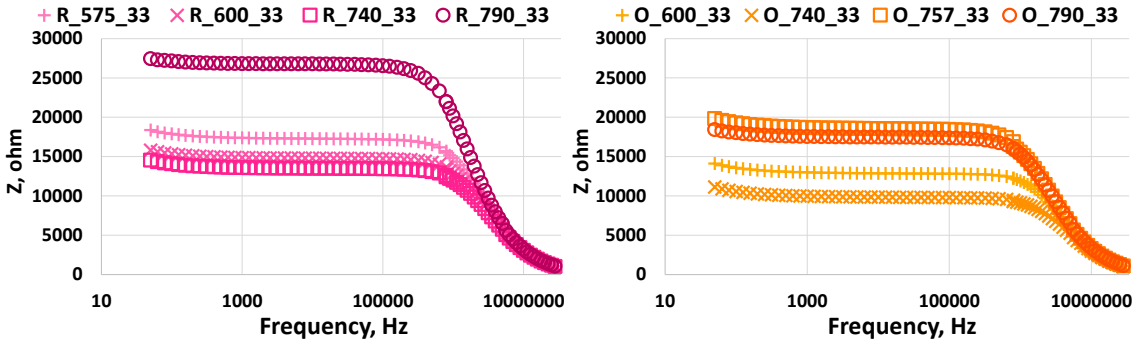

Figure 8 Impedance magnitudes of raspberry and orange syrups in the Experiment 3

According to this, the second highest impedance values of sample R_575_33 shows, that its sugar content may be higher than suggested. Chemical analysis is needed to check the real sugar content. In case of orange flavoured samples O_757_33 had the highest impedance values while those of O_790_33 is slightly lower despite the higher sugar content. Worthy of notice, that O_757_33 is the only sample without any stabilizers, colorants, flavourings, or

preservatives. O_600_33 contains E445 and E415 (xanthan gum) as stabilizer and has higher impedance values than O_740_33 with higher sugar content and E445 and E414 as stabilizer. These confirm that additives have a definite effect on the physical properties of squashes.

Conclusion

Fruit content of used fruit juice and sugar content has a definite effect on the physical properties of squashes. Although color characteristics is defined mostly by the colorant added to the squash, are the other parameters are influenced by the amount of added sugar and used fruit juice. Sweeteners decreased viscosity, refractive index, SSC values and impedance magnitude shows similar tendencies as well. Keeping sugar content on the same level as using different fruit juices in the 33% fruit content caused changes in viscosity, refractive index, and SSC values but the magnitude of impedance showed little changes for all samples. The characteristics of squashes with pure raspberry and orange juice respectively and different sugar content does not follow any trends which emphasizes, that additives have a significant effect on the physical properties.

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