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CHANGE OF JUICE COLOR DURING RASPBERRY PROCESSING IN FRUIT JUICE AND FRUIT JUICE CONCENTRATE

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Abstract: A change of anthocyanins under different conditions of enzymatic treatments, clarification and concentration was determined. A pectin preparation Klerzyme®120, manufactured by DSM, France, specific for "sour fruits" with pH below 3.2, was used for maceration and depectinization. Experiments were carried out by a laboratory hydraulic press. Raw raspberry juice was clarified either by membranes separation processes or by traditional treatments using gelatin and bentonite. For microfiltration and ultrafiltration processes, membrane cut-off should not be below 30,000 g/mol to prevent any color loss. Experiments with membrane separations processes were carried out with five different membranes. A raw depectinized raspberry juice was clarified by cross-flow microfiltration and ultrafiltration using ceramic tubular membranes and hollow fiber polymeric membranes of a molecular weight cut-off of 300, 50 and 30 kg /mol or with a mean pore size of 0.2 μm in the case of microfiltration. Fruit juice concentrations were carried out by a laboratory equipment for vacuum evaporation. Extraction yield by a laboratory hydraulic press was the same in case of single-stage maceration and two-stage maceration. However, due to a lower viscosity, it was observed that single-stage process provides raspberry juice with more color and high efficiency of extraction. It was noticed that thermal breaks of raspberry pulp provide juice containing more total anthocyanins. The clarification using gelatin and bentonite removed about 50% total anthocyanins, while a clarification by a cross-flow ultrafiltration using Carbosep M9, M8 and M7 membranes achieved the highest level of color loss. Total color loss after concentration was 70%. The best results in color protection were observed by a microfiltration through Kerasep membrane, due to its relatively large pores (0.2μm).

Key words: anthocyanins, raspberry, clarification, concentration, microfiltration, ultrafiltration.

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Introduction

The color compounds (anthocyanins) in raspberry (*Rubus idaeus* L.) play an important role in fruits industry. They are natural colored compounds, responsible for nonenyimatic browning and appearance of sediment in fruit juices. Raw material containing water-soluble pigments, such as anthocyanins are particularly suitable for production of juices (especially clear ones). Raspberry belongs to those fruits. Anthocyanins are found in vacuoles of plant cells, as a neutral to slightly acid water solution. They are responsible for red, purple, blue hues in flowers, fruits and other parts of various plants. They are found most in skin or near-to-skin cells, their biological function being to attract other living organisms that will set seed free and thus enable plant reproduction. In some cherry, plum, grape fruits anthocyanins are found in skin, but not in other part of fruit, or they are present only in small amounts.

Anthocyanins belong to the group of plant compounds called flavonoids. In their chemical composition flavonoids are compounds having the structure C_6C_3-C_6 i.e. they have two built in benzole nuclei linked by three-carbon bond condensed via oxygen into an intermediary ring. The basic structure of all anthocyanins is 3, 5, 7, 4′ tetrahydroxyflavilium cation with basic carbon skeleton as other flavonoids, structures C_6C_3-C_6. (fig.1.). Glycosylation of anthocyanins takes place most frequently at C_3 atom whereby they are mostly in the form of monoglucosides. Diglucosides are less frequently on C_3 and C_5 atoms, and triglucosides are very rarely on C_3, C_5 and C_7 atoms. Glucosation is most frequent with glucose, but less frequent with galactose, xylose, arabinose, ramnose and other carbohydrates. Carbohydrates are often esterified on C_4 or C_6 atoms with some organic acids (p-cumaric, caffeic, ferulic or sinapine acid, but less often with p-hydroxybenzoic, malonic and acetic acid).

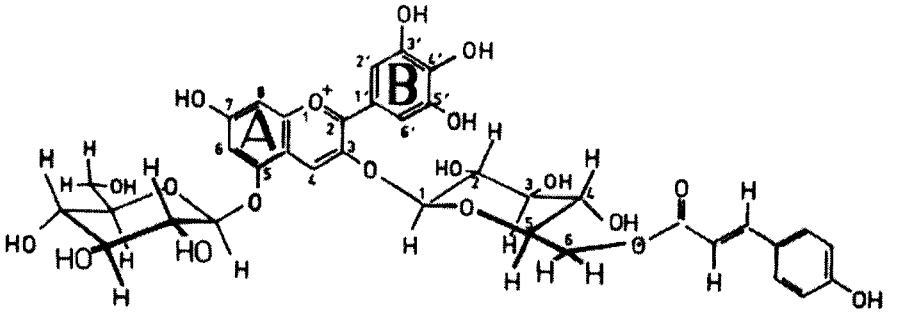

Fig. 1. – The basic structure of antocyanins (stereostructure of awobanine)

The production of raspberry juice can be achieved by a single-stage or two-stage enzymatic treatment, according to a brochure of leading company in the sphere of enzyme production (DSM, 2003).

Raspberry is a very delicate fruit, so usually it is not washed or is exposed to gentle washing only. The process of defrostation is necessary if fruit was frozen. Crushed raw material is subjected to thermal break at 90°C for better extraction of juice, inactivation of endogen polyphenoloxydase and partial reduction of initial number of microorganisms. Extracted juice is left to be cooled and exposed to enzymatic decomposition.

The basic difference between a single-stage and two-stage enzymatic treatment is in the quantity of enzyme added before extraction, and in temperature of enzymatic treatment and extraction. In a single-stage enzymatic processing enzyme is added before extraction, when maceration and complete depectinization has taken place. In two-stage enzymatic treatment the half amount of enzyme for maceration is added before extraction, and the other half is poured into the vessel for depectinization of juice. The temperature for enzymatic treatment and extraction is 50°C for single-stage processing and 20°C for two-stage processing. Lower temperature of processing in two-stage treatment provides minimal loss of aromatic compounds and greater stability of colored compounds. The main disadvantage of two-stage processing is in efficacy of extraction i.e. extraction is a bit harder, slower and the pomace is humid. To overcome this problem a stronger extractor (Bucher extractor) should be used. The characteristic of this processing is a high quality with a bit harder extraction. After the extraction, the pasteurization of juice is necessary to make possible denaturation of proteins and partial reduction of initial number of microorganisms. The pasteurization is performed at 90°C, for several minutes.

Figure 2 shows the technological scheme of production of concentrated raspberry juice. The chemical clarification of juice used in many factories in Serbia has much deficiency. According to literature data, the introduction of "cross-flow" micro and ultrafiltration has shown many advantages. However, not a single scientific work was published concerning clarification of raspberry juice by "cross-flow" micro and ultrafiltration. The aim of this work was to present the first data obtained for quality of clarified and concentrated raspberry juice, from a view of stability of colored compounds.

The application of membrane process for clarification of fruit juices has many advantages. The results attained by an industrial, half industrial and laboratory equipment demonstrated many advantages of "cross-flow" ultrafiltration, such as: the yield of juice is 99% compared with 93-94% by a chemical treatment; duration of technological process of production of concentrate juice is only 2^{h}; the process is continual with reduction in labor and energy; vessels and other utensils for clarification and filtration are not necessary;

there is no risk of insufficient or exaggerated clarification; the juice is microbiologically stable; further turbidity is not detected; there is no contamination of waste water with organic matters; the juice is of a high quality; the price of final product is satisfactory; the process is automatized with high level of control. The only disadvantage of a mentioned process is a relatively high level of investement costs and a phenomenon of concentration polarization and gel formation.

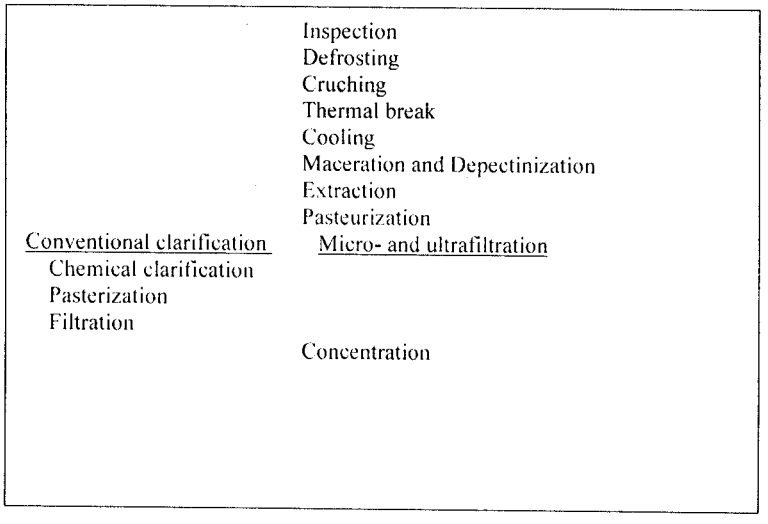

Fig. 2. – Technological scheme of production of concentrated raspberry juice by single stage processing

Material and Methods

In all experiments we used raspberry frozen for 60 days and defrosted spontaneously at room temperature. All juice samples were frozen prior to further analyses. By using brochures of a leading world company in the sphere of enzyme production (DSM, 2003), we carried out the experiments that can be grouped into two modes of extraction i.e. enzymatic maceration (table 1).

Fruit extraction from a red fruit (raspberry) is a very delicate process because natural juice color and aroma must be preserved. Hence, the choice of the right preparation to be used for maceration and depectinization is of great importance. Klerzyme®120 is a pectin preparation used for maceration and depectinization of "sour fruit" with pH below 3.2. It is an ideal enzyme preparation since it is active at low pH values and high concentrations of polyphenolic substances in raspberry.

No matter whether it is used for maceration or depectinization, it enables full decomposition of pectin substances as well as the release and stability of colored substances. Klerzyme®120 is a pectin preparation obtained from the moulds *Aspergillus niger*. Pectinases and hemicellulases stable at low pH values make its ingredients. It is active at the temperature range from 10 - 60 °C, its maximum activity being from 45 - 50 °C and at pH 2 - 6.

T a b. 1. - Two types of processing of raspberry juice

Assay I - single stage processing:	*Assay II - two stage processing:*
Enzymatic maceration and extraction: - Defrosting – 5 kg villamette – sample 1, - Crush – sample 2, - Thermal break - 90°C, 5 minutes, - Cooling at 50°C, - Enzymatic maceratiom and depectinization – 0.2 g/kg klerzyme® 120, 120 minutes, 50°C, - Extraction 50°C, with 1 shaking - sample 3, - Pasteurization 90°C, 2 minutes, - Cooling at 20°C - sample 4, Clarification: - Conventional clarification (3.6 g/hl gelatin, 100 g/hl bentonite) - sample 5a, - Conventional clarification (6.5 g/hl gelatin, 100 g/hl bentonite) - sample 5b, - Ultrafiltration, M9, 300 000 g/mol, (Δp = 1 bar, t = 20°C, Q_v = 1 l/min) - sample 5c, - Ultrafiltration, M8, 50 000 g/mol, (Δp = 1 bar, t = 20°C, Q_v = 1 l/min) - sample 5d, - Ultrafiltration, M7, 30 000 g/mol, (Δp = 1 bar, t = 20°C, Q_v = 1 l/min) - sample 5e, - Microfiltration, 0.2 µm, (Δp = 1 bar, t = 20°C, Q_v = 1 l/min) - sample 5f, - Ultrafiltration, polisulfone, 30000 g/mol, (Δp = 0.5 bar, t = 20°C, Q_v = 1 l/min) sample 5g, Concentration (P_v = 0.1 bar, T_{klj} = 50 °C, soluble solid at 60°B_x, cooling, dilution at 10°B_x) - Conc. and dilution 5a - sample 7a, - Conc. and dilution 5b - sample 7b, - Conc. and dilution 5c - sample 7c, - Conc. and dilution 5d - sample 7d, - Conc. and dilution 5e - sample 7e, - Conc. and dilution 5f - sample 7f, - Conc. and dilution 5g - sample 7g,	Enzymatic maceration and extraction: - Defrosting – 5 kg villamette – sample 1, - Crush – sample 2, - Thermal break - 90°C, 5 minutes, - Cooling at 20°C, - Enzymatic maceratiom – 0,1 g/kg klerzyme®120, 60 minutes, 20°C, - Extraction 20°C, with 1 shaking - sample 3, - Pasteurization 90°C, 2 minutes, - Cooling at 20°C - sample 4a, - Depectinization - 8 g/hl klerzyme®120, 120 minutes, 20°C, - sample 4b, Clarification: - Conventional clarification (3.6 g/hl gelatin, 100 g/hl bentonite) - sample 5a, - Conventional clarification (6.5 g/hl gelatin, 100 g/hl bentonite) - sample 5b, - Ultrafiltration, M9, 300000 g/mol, (Δp =1 bar,t=20°C,Q_v=1 l/min)- sample 5c, - Ultrafiltration, M8, 50000 g/mol, (Δp =1bar,t=20°C,Q_v=1 l/min)- sample 5d, - Ultrafiltration, M7, 30000 g/mol, (Δp =1bar,t= 20°C,Q_v =1l/min)- sample 5e, - Microfiltration, 0,2 µm, (Δp = 1 bar, t = 20°C, Q_v = 1 l/min) - sample 5f, - Ultrafiltration, polisulfone, 30000 g/mol, (Δp = 1 bar, t= 20°C, Q_v= 1 l/min) - sample 5g, Concentration P_v = 0.1 bar, T_{klj} = 50 °C, soluble solid at 60°B_x,cooling, dilution at10°B_x) - Conc. and dilution 5a -sample 7a, - Conc. and dilution 5b-sample 7b, - Conc. and dilution 5c- sample 7c, - Conc. and dilution 5d-sample 7d, - Conc. and dilution 5e- sample 7e, - Conc. and dilution 5f - sample 7f, - Conc. and dilution 5g-sample 7g,

The enzymes were added in the process of fruit crushing or they were pumped in a vessel for maceration. In a two-stage processing 0.1-0.2 g/kg of enzyme was added for maceration, and 4-8 g/hl for depectinization of raspberry juice. For single-stage it was used 0.2-0.4 g/kg of enzyme preparation. The maceration and depectinization were performed during 60-120 minutes at 20°C or 50°C, depending on quantity of enzyme added.

The clarification was carried out by a conventional chemical treatment as well as by a membrane separation process with 5 different membranes. For ultrafiltration, tubular inorganic membranes type Carbosep M9, M8 and M7 (Rhone-Poulenc group, Tech-Sep, Mirabel, France) were used. The technical characteristics of those membranes are as follows: inner diameter of 6mm, length 222mm. Carbosep membranes were composed of thin permselective layer from inner side, made of circonium-dioxyde and titan-dioxide. The membrane for microfiltration Kerasep (Tech-Sep, Mirabel, France) was inorganic ceramic membrane, with "cut-off" of 0.2μm. The membrane was 270 cm in length with 19 channels and 4mm diameter, set in plastic module. Membrane, in a shape of hallow fibers was made of polysulfone (AV1000S, Fenesius, Germany). It was composed of 10258 fibers, inner diameter of fiber was 220μm, and thickness of fiber wall was 35μm. It was set in module of polycarbonate with polyuretene sealing material. This membrane is ultrafiltration membrane with molecular cut-off of 30kg/mol. The technical characteristics of membranes are shown in table 2.

T a b. 2. – The characteristics of Carbosep M9, M8 i M7, Kerasep and polysulfone membranes

Characteristics	Carbosep M9	Carbosep M8	Carbosep M7	Kerasep	Polisulfone AV1000S
Selective layer	ZrO_2-TiO_2	ZrO_2-TiO_2	ZrO_2-TiO_2	Ceramic	Polysulfone
Support	Carbon	Carbon	Carbon	Ceramic	-
Type of membrane	tubular	tubular	tubular	tubular	Hollow fibers
Molecular weight cut-off or pore size	300 000 g/mol	50 000 g/mol	30 000 g/mol	0.2 μm	30 000 g/mol
Allowed pH	0 – 14	0 – 14	0 – 14	0 – 14	-
Maximum pressure	1.5 MPa	1.5 MPa	1.5 MPa	1.0 MPa	0.1 MPa
Inner diameter	6 mm	6 mm	6 mm	4 mm	220 μm
Length	0.225 m	0.223 m	0.225 m	0.27 m	0.254 m
Effective membrane area (m^2)	$4.24 \cdot 10^{-3}$	$4.20 \cdot 10^{-3}$	$4.24 \cdot 10^{-3}$	0.0644	1.8
Number of channels or fibers	1	1	1	19	10258
Thickness of wall	-	-	-	-	35 μm
Max. temperature	350°C	350°C	350°C	650°C	150°C

Experiments were carried out by a laboratory hydraulic extractor manufactured by "Ivo Lola Ribar" – Belgrade. Commercial operating conditions were emulated during extraction by using "Bucher" extractor, only shaking being done manually. Between each shaking raspberry pomace was subjected to the pressure of 180-200 bar for 10-15 min. The number of shakings represents the number needed for obtaining maximum yield at given working pressures of 180 bar. The concentration was performed by a laboratory vacuum-evaporator (Iskra, Slovenia).

The physico-chemical analyses of samples of raspberry juices were necessary for regular conduction of experiments. The samples of raspberry juice were frozen before analyses. The following analytical methods were used: soluble solid at 20°C, titric acidity, pH value – potentiometric method, qualitative determination of pectin substances by alcoholic test, and qualitative determination of β-glucane (DSM-2003, Law methods, 1983)

Change of color can be monitored by using various methods. The following analytical methods were applied in this work: 1- Determination of total anthocyanins by the method of Niketić-Hrazdina (1972); 2- Determination of total anthocyanins and some forms of anthocyanins by Somers-Evans method (1977); 3- Determination of raspberry juice clarity was measured by transmission at 625 nm (DSM, 2003).

Results and Discussion

Red raspberry (Rubus idaeus L.) commonly contains β-glucane. Its presence in this fruit can result in harder extraction, clarification and filtration during juice processing. β-glucane is present due to a contamination of raspberry fruits with some species of microorganism (*Botrytis* sp., *Leuconostoc* sp.). With qualitative analysis it was seen that β-glucane was present neither in raw material nor in produced juice. This was expected because raw fruit was a high quality raspberry (Rolend), without any sign of moldiness or other impurity.

Decomposition of pectin substances was necessary due to the problem they could cause during extraction. The qualitative analysis of pectin substances is used particularly if they are present in small amounts. In samples 1 and 2, crushed raspberry without enzymatic treatment, was extracted, so it was obvious that some level of pectin substances was present. In other samples, after enzymatic treatment with commercial pectin preparation (Klerzyme®120), the presence of pectin substances was not detected.

The investigation of soluble dry matter and pH value was being monitored because of the regularity of technological process.

Figure 3 shows that both methods of raspberry juice production had almost the same extraction yield. The yield in a single stage process was 88.2%

compared with a two stage process of 88.0%. However, there was some difference in efficacy of extraction. The easier and more efficient extraction was in a single stage process. In a single stage process yield without pressure and extraction yield without shaking showed higher values. It was indicated that the viscosity of juice was lower in single stage treatment because of higher level of pectin decomposition but also the higher temperature of extraction (50°C).

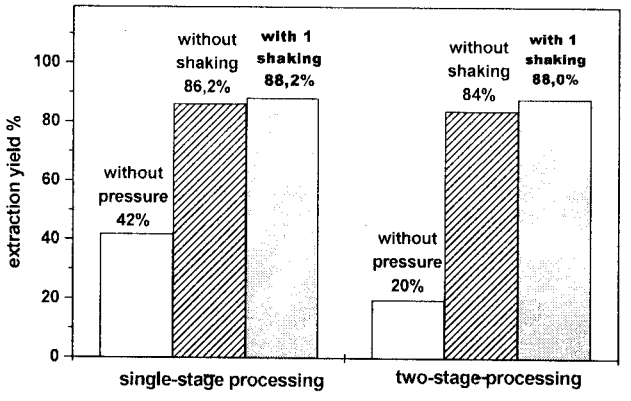

Fig. 3. – A yield obtained during extraction of raspberry in single-stage and two-stage enzymatic treatment (processing)

It was shown that there was no difference in anthocyanins content in samples 1 and 2, while in sample 3 the slight increase in anthocyanins content was the result of a positive effect of thermal break on extraction of colored compounds (figure 4). However, this effect was not noticed in a two-stage process. On the contrary, the small amount of decrease in colored compounds was detected. It was observed that thermal break in some cases could cause the increasement of anthocyanins content, and in some other cases their decreasement (Markakis, 1982).

The increase in colored compound was achieved due to the physical damage of cells vacuoles in which colored compounds were present, as well as due to the extraction at higher temperatures. The decrease in antocyanins content at higher temperature in sour environment was the result of anthocyanins decomposition at anthocyanidines and carbohydrates. The anthocyanidines are not colored. At the same time, the higher temperature stimulated the structural transformation of anthocyanins and loss of color. It is known that flavilium form of anthocyanins is colored, in sour environment, in contrast to carbinol and halcon forms. The increase or decrease of anthocyanins content depends on the fact which of these two effects is dominant. Each thermal treatment of raspberry during processing

should be carried out carefully. After thermal break, it was important to apply fast cooling. It was obvious that thermal break had positively affected anthocyanins content in extracted juice. In sample 3 (two-stage enzymatic treatment) a slight drop in anthocyanins content could be caused by slow cooling. The decrease of anthocyanins content in samples 4, 4a and 4b was the result of short pasteurization, where the negative effect of raised temperature was detected. This loss in colored compounds was below 8%, and this could not be treated as a high loss. The greater loss in color was determined during clarification and concentration of juices. During these processes the loss of almost 70% of initial content of anthocyanins could be reached.

Two questions should be borne in mind: a) if the enzymatic treatment with pectin preparation could cause hydrolysis of glucozide in molecule of anthocyanine, and the loss of color, and b) if oxidative enzymes, present in pectin preparation could cause oxidation of antocyanins to hynone, and loss of color. Comparing the sample 4a and 4b it was obvious that there was no difference in color i.e. enzymatic treatment has not affected anthocyanins decomposition.

By a conventional clarification with gelatin and bentonite (samples 5a and 5b) 50% of anthocyanins was removed. It was found out that there was a greater removal in color in sample 5b (greater content of gelatin added) compared with 5a (lower content of gelatin added). In sour environment gelatin is acting as a positively charged colloid. In contact with negatively charged molecules it can cause aglomerization and sedimentation. Although the anthocyanins are present especially in positively charged flavilium form, their higher removal could be caused by different colloidal interaction among molecules during chemical clarification. On the other hand, two-stage process with conventional clarification has shown greater loss of anthocyanins than a single-stage process.

During subsequent process of juice concentration the destruction of color compounds continued, so the total decreasement of anthocyanins by a conventional clarification was 70% (samples 7a and 7b).

Ultrafiltration of all tested inorganic anisotrophic membranes (Carbosep M9, M8, and M7) has shown a greater degree of colorless raspberry juice, compared with other procedure of clarification. Proportionally, as regards a pore size at selective layer (the greater molecule "cut-off" possessed membrane M9-300 kg/mol, afterwards membrane M8-50kg/mol and the lowest "cut-off" possessed membrane M7-30kg/mol) the highest content of anthocyanis was achieved by membrane M9 and the lowest one by membrane M7. By comparing all investigated procedures of clarification it was seen that a lower content of anthocyanins was performed by M7 membrane. The loss of colored compound during concentration reached 70%. The loss of color with membranes M7 and M8 should be treated as high for fruit with "relative low" content of anthocyanins, like raspberry. This is of great interest especially if some cultivars of raspberry,

with lower content of anthocyanins (cultivare Meeker) will be applied for juice processing (Mišić, 1998).

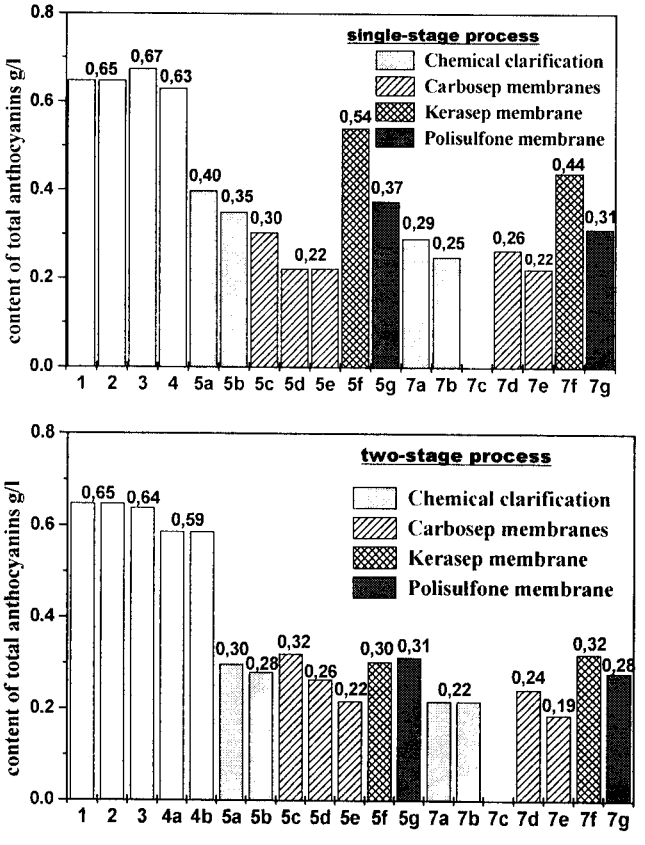

Fig. 4. – Change of content of total anthocyanins during single-stage and two-stage raspberry processing as determined by Niketić-Hrazdina method

Microfiltration with 0.2μm pores size has shown the best results from the aspect of preservation of total anthocyanins after clarification (5f) and after concentration (7f). Ultrafiltration with membranes of polysulfone, has also shown good results, but lower than those obtained by microfiltration (samples 5g and 7g).

The data obtained in these experiments did not give a complete insight into the quality of clarified raspberry juice. For that reason it was necessary to determine the clarity of juices tested (fig. 5). Visually the clarity of all examined

juices was good. It is known that the excellent clearness is 90% of transparency and satisfactory clearness more than 80% of transparency. Some differences among tested samples were performed for their clarity. Ultrafiltration with inorganic membranes with lowest pores size (Carbosep M8 and M7) demonstrated higher degree of clarity for both single-stage and two-stage processing.Carbosep M9 membranes with pores size of 300kg/mol showed almost identical degree of clarity as the microfiltration membrane Cerasep 0.2μm. Considering that the limit of separation of microfiltration and ultrafiltration is in the range of pores size of these two membranes, this result was expected. Conventional clarification i.e. chemical clarification has resulted in the lowest values of transparency. The best result for produced juice with high quality in color and clarity was obtained using Kerasep membrane for microfiltration.

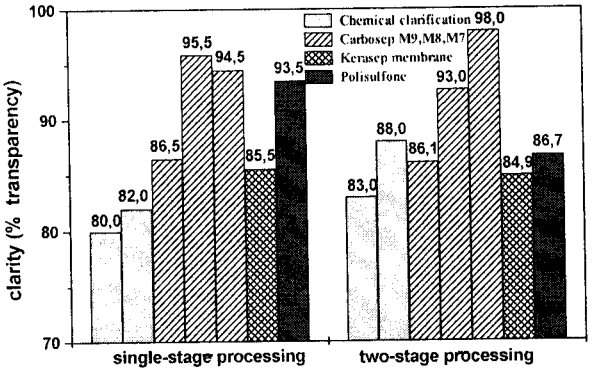

Fig. 5. – Clarity of raspberry juices during single-stage and two-stage processing

However, the content of total anthocyanins is not the right indicator for good color of juice. Total anthocyanins are determined as an aggregate of polymerized, non-colored and colored forms at raspberry juice pH value. The percentage of colored forms of anthocyanins at real acidity of juice was in the range of 15-25%, compared with non-colored form of 70-80% and polymer form about 5% (Vukosavljević et al., 2003). This means that ¾ of total anthocyanins were in the uncolored form at juice pH value. The data obtained for the share of polymer form in the color of fresh juice at pH value 1 reached 3%. A three year old raspberry juice contained expectedly much more polymer forms - 64%, and the same ratio of colored and uncolored forms, 18% each of them. This was the reason why "old" juices visually attained greater intensity of color. This was due not only because of the increasement of red color (apsorption at 513nm) but also because of increasement of yellow-brown pigments (apsorption at 420nm).

The selectivity of tested membranes on polymer forms was different (fig. 6). Carbosep M8 and M7 membranes completely detained the polymer forms of anthocyanins (samples 5d and 5e). Carbosep M9 membrane had 10 times greater molecular cut-off than M7 membrane (sample 5c). Polysulfone membrane for ultrafiltration was almost impermeable for these forms of anthocyanins ("cut-off" 30000 g/mol). Microfiltration membrane, as well as chemical clarification, has shown the lowest degree of detaining of polymer forms of anthocyanins.

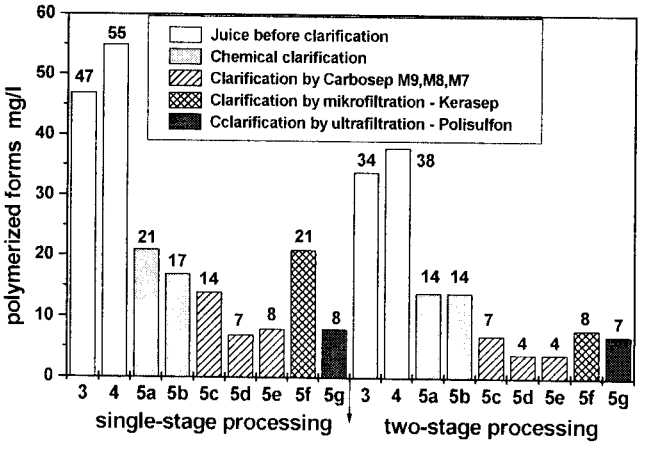

Fig. 6. – Change of polymerized forms anthocyanins during single-stage and two-stage processing (method Somers-Evans)

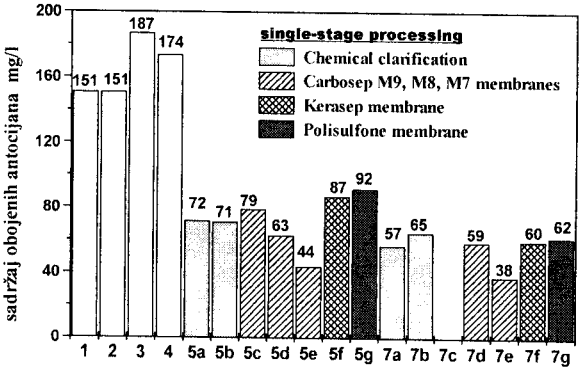

Fig. 7. – Change of colored forms of anthocyanins during single-stage and two-stage processing (method Somers-Evans)

Change of total anthocyanins (fig. 4) has not given an insight in the change of colored forms of anthocyanins (fig. 7). According to the method of Niketić-Hrazdina, trend in changing of color compounds was the same as the total amount of anthocyanins. However, as has already been pointed out, the ration of visible anthocyanins in total amount of anthocyanins is around 20%, resulting in their proportional decreasing during clarification and concentration. This decrease was visualized, particularly with Carbosep M7 and M8 membranes (with the smallest molecular weight cut-off - 30 and 50 kg/mol).

Comparing the samples 2 and 3 (fig.7) it was obvious that thermal break of raspberry had positively effected extraction of colored form of anthocyanins. At the same time, it was estimated, for samples 3 and 4, that pasteurization had demonstrated negative effect.

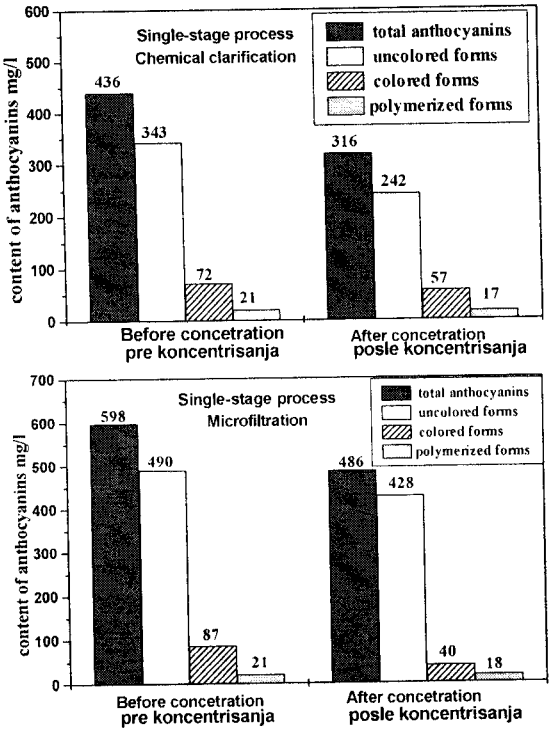

Fig. 8. – Change of anthocyanin forms during concentration by single-stage processing (method Somers-Evans)

The average loss of total content of anthocyanins during concentration was in the range of 10-30% (fig. 8). On the other hand, the loss of uncolored forms was

greater (up to 30%). This change in anthocyanins after concentration was expected, considering the fact that ¾ of total content of anthocyanins represent uncolored forms. Change of juice color derived from visual and changed polymer forms.

The intensity of juice color (optical density) presents the sums of absorptions of red and yellow colors. It had high value at fresh juices but also at "old" juice due to the rise of absorption at 420nm. This value in raspberry juices should be 8 units minimum, with desirable value over 10 units. In the fig. 9 it could be seen that raspberry presents a fruit with relatively low content of colored pigments. In the samples 1 to 4 the intensity of color before clarification was over 10 units.

In the process of clarification and concentration of raspberry juice, the irreversible loss of color compounds was over 70%, so the intensity of color of clarified samples was not over 8 absorption units (except for sample 5f-microfiltration). Regarding the fact that all tested juices were fresh with relatively low absorption values, it could be concluded that raspberry does not represent a fruit with high content of anthocyanins. Also, the clarification has extremely negatively affected the quantity of colored compounds. It was evident, even visually, that Carbosep M8 and M7 membranes (samples 5d and 5e) produced juices with low intensity of color. Microfiltrated juice, chemically clarified and ultrafiltrated juice through Carbosep M9 membrane (in single-stage processing) has shown visually as well as analytically the highest intensity of color. However, bearing in mind that juices were fresh it could be expected that during the aging of juice the intensity of color would increase. A three year old juice, chemically clarified, had intensity of color of 17.5 absorption units (Vukosavljević et al., 2003). The reason for increasement in color intensity in old juices is in connection with oxidation processes on phenol compounds (rise A_{420}).

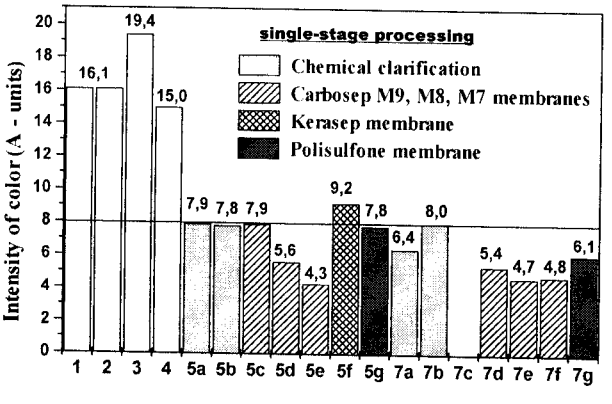

Fig. 9. - Intensity of raspberry juice color during single-stage and two-stage processing (method Somers-Evans)

Conclusion

Color is one of the most important parameters for fruit juice quality. Color is expected to be attractive and stable during both processing and storage. The presence of anthocyanins in juice is primarily the cultivar property but is largely dependent upon technological maturity and applied technological method of processing.

The decrease of total content of anthocyanins during raspberry juice processing was significant, being 70% of their initial amount. The thermal break positively affected the stability of juice color. The reason for that was better extraction of anthocyanins from vacuoles of fruit cells at higher temperatures, as well as because of inactivation of enzymes which could cause decomposition of fruit pigments. Each subsequent thermal treatment can have a significant effect on decreasement of anthocyanins content. The short pasteurization of juice has influenced the loss of 8% of total anthocyanins. The loss of color compounds during clarification and concentration of raspberry juices was significantly greater, over 50% of initial anthocyanins content.

Among all tested procedures of clarification, the microfiltration through membrane with 0.2μm pores size has shown the best result from the aspect of color preservation. Ultrafiltration with all investigated Carbosep membranes (M9, M8 and M7) has demonstrated a high degree of colorless raspberry juice what was in accordance with the molecular weight cut-off of these membranes. Considering the fact that excellent clarity means the transparency of over 80%, it could be concluded that with all tested membranes satisfactory results in clarity were recorded. The best clarity (over 95% of transparency) was performed with membranes Carbosep M8 and M7.

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ODREDJIVANJE PROMENE BOJE MALINE PRI PRERADI U SOK I KONCENTRAT

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Rezime

U radu je odredjivana promena sadržaja antocijana pri različitim uslovima enzimiranja maline, kao i bistrenja i koncentrisanja soka od maline. Za maceraciju i depektinizaciju korišćen je pektinski preparat Klerzyme®120, proizvodjača DSM – Francuska. Cedjenje i koncentrisanje su izvedeni na laboratorijskoj hidrauličnoj cednici i laboratorijskom vakuum uparivaču. Bistrenje je izvedeno klasičnim hemijskim bistrenjem i membranskim separacionim procesom sa pet različitih vrsta membrana. Ultrafiltracione neorganske membrane, Carbosep M9, M8 i M7, imaju granicu separacije ode 300, 50 i 30 kg/mol. Mikrofiltraciona membrana Kerasep je sa granicom separacije od 0,2 μm, dok membrana u obliku šupljih vlakana od polisulfona je sa granicom separacije od 30 kg/mol. I pored istog randmana cedjenja, znatno lakše i efikasnije cedjenje je primenom jednostepenog enzimiranja u odnosu na dvostepeno. Prednosti jednostepenog enzimiranja su i u pogledu očuvanja boje. Sadržaj ukupnih, kao i pojedinih formi antocijana, se pri cedjenju, bistrenju i koncentrisanju u većoj meri sačuvaju. Primećen je blagi porast sadržaja antocijana posle blanširanja. Klasičnim bistrenjem želatinom i bentonitom, uklanja se oko 50% početnog sadržaja antocijana. Još viši stepen je primećen kod ultrafiltracije sa sve tri neorganske anizotropne membrane, Carbosep M9, M8 i M7. One pokazuje najviši stepen obezbojavanja soka maline, u odnosu na ostale načine bistrenja i to shodno veličini pora na selektivnom sloju. Poredjenjem svih načina bistrenja, najviši stepen obezbojavanja je kod M7 membrane. Ukupni gubitak boje po koncentrisanju iznosi i do 70%. Mikrofiltracija sa veličinom pora 0,2 μm, pokazuje najbolje rezultate u pogledu očuvanja boje.

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