Antioxidant Protection During Processing And Grapes Improvement Of Antioxidant Protection Of White And Red Wines.

Irgasheva.G.R

PhD, assistant professor
of Tashkent Institute of Chemical Technology
(gulmirairgasheva656@gmail.com)

ABSTRACT

The enzymes included in the oxidative protection system of the technological cycle of processing white and red grape varieties have been studied. It has been established that some technological operations predetermine an increase in oxidative stress. When processing red grapes, bound forms of SO2 increase, which reduces its antioxidant properties. Sulfation of red wort in the amount specified in the technological instructions is clearly not enough to provide antioxidant protection

Keywords: Enzymes, antioxidant protection, catalase, superoxide dismutase, peroxidase, oxidation, dismutation, sulfitation, oxygen.

In the technological chain of wine preparation, oxidative processes begin immediately after the grape harvest, which, in accordance with recommendations [1], must be protected with sulfur dioxide (SO2).

Studying the state of the antioxidant protection system during grape processing and when obtaining wine materials is of particular interest and will make it possible to regulate the degree of protection of the must and wine materials from oxidative stress, which is especially important when processing grapes into low-oxidized table wines.

A variety mixture of both white and red wine grape varieties, sulfated to 150 mg/dm3, was subjected to analysis. Starting from the moment of acceptance of the grapes, right up to the receipt of wine material, before and after each technological operation, the concentration of oxygen and the activity of the enzymes superoxide dismutase (SOD), peroxidase and catalase, which are part of the antioxidant defense system (AOD), were determined. [2].

SOD activities were determined by a method based on its ability to inhibit the reduction reaction of nitrotetrazolium blue; Catalase activity was determined by the reaction with ammonium molybdate and by a method based on the oxidation of pyrogallol in the presence of hydrogen peroxide [3]. to purpurogallin, peroxidase activity was determined. Results of analyzes during the processing of white grape varieties.

Table 1

Indicators	splitting up		drainer		press		infusion		fermentation	
	Before	after	before	After	before	after	before	after	before	After
T0	1 2.7	1 3.7	15.2	14.3	14.0	14.12	17.8	18.2	15.5	14.4
0_2 mg/dm ^{3}	10.1	16	9.0	19	22.0	15	thirty	35	21	14
SOD standard unit	0.14	0.69	1.27	1.11	0.41	1.00	0.14	0.62	0.53	0.45
Catalase	0.87	0.69	1.91	1.71	3.51	1.20	1.22	0.80	0.62	1.64

m kmol/min/l										
Gluthione peroxidase m kmol/min/l	60.2	65.6	51.5	55.8	53.4	48.9	49.1	58.3	70.2	52.8

Results of analyzes during the processing of red grape varieties.
table 2

Indicators	splitting up		drainer		press		infusion		Fermentation	
	before	after	before	After	before	after	before	after	before	After
T0	24.3	24.4	24.3	25.2	24.4	24.6	26.3	25.5	25.6	25.3
0_2 mg/dm ^{3}	14	14	12	20	5	3	10.3	24	20	33
SOD standard unit	2.93	4.60	4.84	2.98	2.81	5.74	4.76	1.90	1.95	1.78
Catalase M kmol/min/l	3.929	4.35	4.44	4.11	3.95	4.77	4.28	4.08	4.13	6.15
Gluthione peroxidase M kmol/min/l	40.6	22.3	21.1	25.0	41.8	19.3	22.4	25.0	24.2	13.3

The ionic forms and mainly SO^-_3 bind oxygen most easily. Sulfuric acid [4]. inhibits the actions of oxidative enzymes and prevents the oxidation of polyphenols and other substances. SO_2 reacts directly with oxygen and protects polyphenols and other components from oxidation and the main function of SO_2 is to remove hydrogen peroxide formed during the oxidation of polyphenols. [5].

In samples where oxygen saturation is noted, the reaction of the active form of sulfurous acid with oxygen can be represented by reaction 2, where 2 moles of bisulfite react directly with one mole of oxygen, forming two moles of sulfate:

$$2\ HSO_3^- + O_2 \rightarrow 2\ H^+ + 2\ SO_4^{2-}\ (1)$$

During fermentation and dripping onto the VSSSH, the activity of SOD is negative, that is, these particular technological methods do not enhance oxidation.

Crushing and pressing gives SOD activity, hence dismutation occurs . An increase in SOD activity is determined by the presence of oxygen superoxide radical, which [6] intensifies the oxidation process and SOD protects against excessive oxidation.

Catalase is absent in both white and red worts during the draining and infusion; it is present during the fermentation of both worts, but the draining and infusion determined the activity [7]. catalase, only in red wort.

Peroxidase is significantly inactivated during fermentation and pressing. Draining and infusion activates peroxidase in both wines. This is probably due to the presence of hard parts of the grapes, in particular, the skin with enzymes deposited on its surface. A slight dismutation is present in the infusion of white wines; this fact is explained by Academician Oparin by the presence of an enzymatic process that takes place during the settling of the wort.

Only crushing makes a difference in the activity of peroxidase, so in the case of white grape varieties it appears, and in the case of red grapes it decreases intensively (see Table 1). Dripping and infusion are equally characterized by peroxidase and catalase activities, which have related effects. Peroxidases are peroxide oxidizers and catalyze according to the scheme:

$$AOOH + KH_2 \rightarrow K + AOH + H_2O.\ (2)$$

Catalase is also a peroxidase, oxidizing one molecule of hydrogen peroxide with another molecule of hydrogen peroxide to form two molecules of water and an oxygen molecule:

$$H_2O_2 + H_2O_2 \rightarrow 2H_2O + O_2\ (3)$$

If we judge the oxidation of the must by the number of active enzymes included in the AOD system, then during the processing of both white and red grapes, during the crushing process, the must is most susceptible to oxidation, and only the white must during infusion. What needs to be taken into account when choosing a technological scheme in the production of various types of wines.

And if we assume that SOD activity is the first sign of the presence of reactive oxygen species, then the most dangerous technological methods when processing white wines are pressing and infusion. In general, when processing white grapes, sources [8]. The following technological methods can serve as "oxygen stress": crushing, where the increase in SOD activity was 0.55 standard units ; pressing - 0.59 standard units , settling 0.48 standard units . When processing white grapes, catalase activity appears only during fermentation and its activity is 1.02 m kmol/min/l . Peroxidase oxidation is active during the infusion of white wort, when the increase in activity was 9.2 m kmol/min/l , then, during crushing, 5.4 m kmol/min/l , slightly during draining and is completely absent during pressing and fermentation.

The behavior of enzymes of the AOD system during the processing of red grape varieties is somewhat different in that the SOD activity is maximum during draining 2.93 a.u. , then during fermentation 2.02 a.u. , crushing 1.67 a.u. and 0.82 a.u. during pressing and is absent only during infusion of red wort. That is, all operations during grape processing, except for the infusion of the must, tend to oxidize the red must. [9].

If in white must catalase activity was noted only during the fermentation of white grape must, then the processing of red grapes activated it during fermentation to a maximum of 2.02 m kmol/min/l , then pressing 0.82 m kmol/min/l and during crushing 0.421 m kmol /min/l . Catalase activity, both in quantitative terms and in the technological methods in which its activity is manifested, predominates in the processing of red grapes. That is, when processing red grapes, the danger of oxidation of one molecule of hydrogen peroxide by another molecule of hydrogen peroxide with the formation of two molecules of water and an oxygen molecule is more significant than in white must.

But peroxidase activity during the processing of red grapes appeared only in two cases: with drainage 3.9 m kmol/min/l and with infusion 2.6 m kmol/min/l . It can be done [10]. conclusion that when processing red grapes, the must is less susceptible to peroxidation.

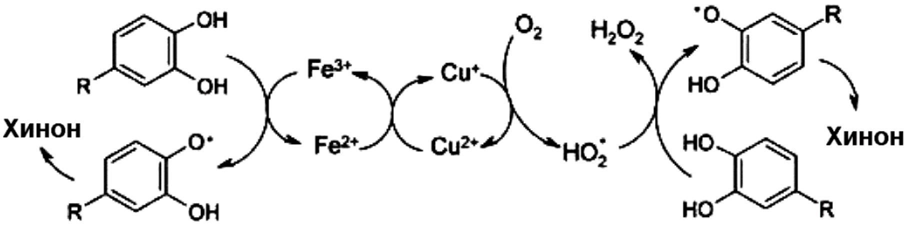
SO_2 performs its antioxidant function mainly in reaction with hydrogen peroxide. The main antioxidant effect of sulfur dioxide in wine comes from the bisulfite ion, which reacts with H_2O_2 to produce sulfuric acid, thereby limiting further oxidation of phenolic molecules or ethanol. Undissociated sulfurous acid H_2SO_3 ionic ($HSO^1{}_3$ and $SO^2{}_3$) and related forms have such properties to a small extent. In an aqueous system, SO2 forms sulfurous acid, which dissociates so that the bisulfite form (HSO3-) predominates in the wine as shown in the reaction:

$$H_2O + SO_2 HSO_3^- + H^+ \leftarrow\rightarrow SO_3^{2-} + 2H^+ \quad (4)$$

The antiseptic effect of SO_2 in red wort is much less frequent than in white wort, since most of the SO_2 is spent on binding with coloring substances. Dose increase SO_2 reduces color stability by up to 50%. To protect dyes from oxidation, it is necessary to introduce free SO_2 at a level of 20-30 mg/l. [eleven].

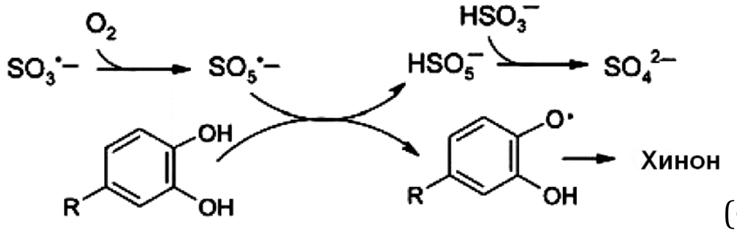
According to the analysis results (Table 2), it follows that red wines are not sufficiently protected from oxidative stress, which can be explained by the binding of SO_3 , reducing its antimicrobial effect. Part of the oxygen dissolved in wine is spent on its oxidation into sulfuric acid and is catalyzed. Ne, which are always present in wine in the form of iron ions. Sulfurous acid inhibits the actions of oxidases.

SO_2 into red wine in smaller quantities (as much) since tannins and catechins contained in sufficient quantities have natural antimicrobial properties and, secondly, SO_2 reacts with anthocyanides in wine and discolors them. It seems that for this reason in wine, especially red wine, the interaction of SO_2 with oxygen is effectively blocked by polyphenols. At the same time, wine aldehydes (acetic, etc.), reacting with anthocyanins, prevent excessive oxidation. Oxidation of catechins by Fe (III) catalysis to produce hydroperoxyl radicals and quinone is shown in Scheme 5.



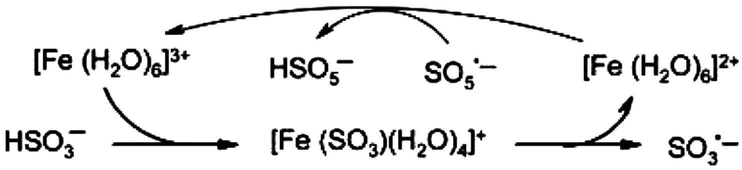
(5)

Removal of catechins using peroxmonosulfate radicals leads to suppression of SO_2 autoxidation according to scheme 6.



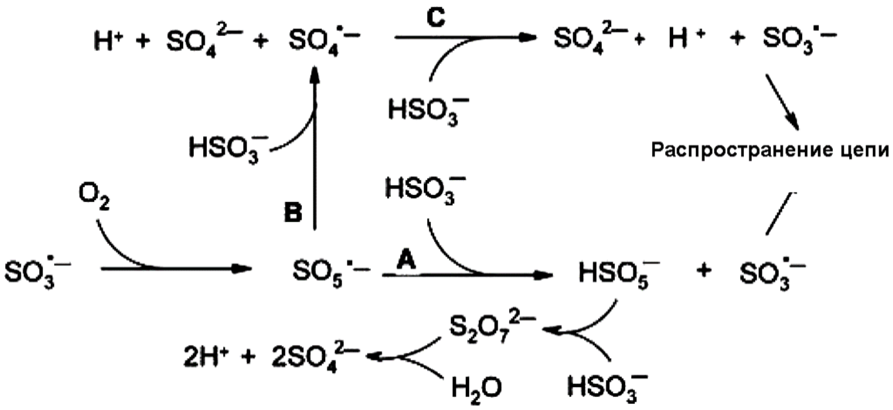
(6)

Under acidic conditions of grape must, bisulfite forms metal-sulfite complexes, according to scheme 7



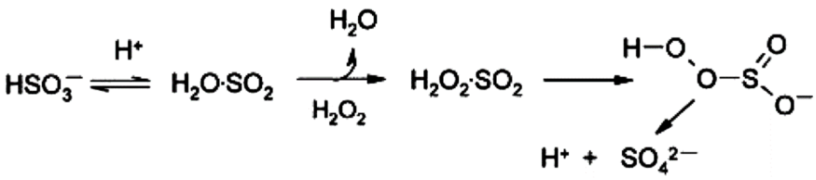
(7)

The sulfite radical quickly reacts with oxygen according to scheme 8, forming a peroxmonosulfate radical ($SO_5^{\bullet -}$) [12].



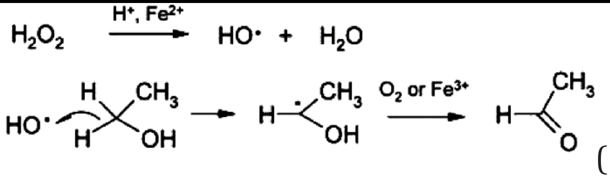
(8)

The reaction of hydrogen peroxide with SO_2 is represented as a nucleophilic displacement of water from the bisulfite ion Scheme (9) in a possible mechanism reactions of hydrogenated SO_2 with hydrogen peroxide:



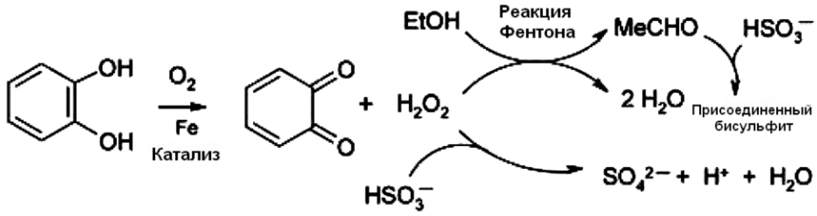
(9)

Oxygen is converted to hydrogen peroxide, which in the presence of iron forms a hydroxyl radical via the Fenton reaction, scheme 10).



(10)

It is obvious that SO_2 removes hydrogen peroxide, thus preventing its destructive action, as shown in diagram 11



(11)

However, the oxidation product of the sulfite radical ($SO_3^{\bullet-}$), the peroxmonosulfate radical ($SO_5^{\bullet-}$), is very [13]. strong oxidizing agent. In the presence of oxygen, SO_2 also promotes oxidation, which is prevented by the action of polyphenols, which scavenge radicals.

Therefore, processing of red grapes appears to increase the bound forms of SO_2, thereby reducing its antioxidant effects.

- SO_2 removes hydrogen peroxide, and polyphenols block its interaction with oxygen, and only then the antioxidant effect is realized.

-Sulfation of red wort in the amount specified in the technological instructions is clearly not enough to provide antioxidant protection.

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