

ASPECTS ON THE VARIATION OF CERTAIN PHYSICAL-CHEMICAL INDICES DURING MUST ALCOHOLIC FERMENTATION

G. ODĂGERIU^{1*}, I. NEACȘU¹, B. GĂINĂ², M. NICULAU¹,
C. ZAMFIR¹, G. STOICA³

¹ Research Centre for Oenology – Iași Branch of the Romanian Academy

² Academy of Sciences from Moldova, Republic of Moldova

³ Research and Development Station for Vine Growing of Iași

Received April 12, 2007

ABSTRACT – The paper presented data concerning the variation of physical-chemical indices during must alcoholic fermentation: DM – soluble dry matter, pH – real acidity, ITP – index of total polyphenols, χ – conductivity, TDS – total dissolved substances, E_h – redox potential, rH – index of E_h quantification. In relation to the values of these indices, we have investigated the evolution of main composition characteristics, respectively reducing sugars, alcohol, total acidity, volatile acidity and total phenolic compounds. The experiments have been conducted on two musts obtained from white varieties (Muscat Ottonel and Sauvignon) from the Vine Growing Centre of Copou-Iași and on marc obtained from two red varieties (Fetească neagră and Băbească neagră), from the Vine Growing Centre of Uricani, Iași vineyard, vintage of year 2006. White musts were obtained by grape crushing, removal of berries from cluster and by pressing the marc resulted at primary grape processing. Marc obtained from black varieties has been submitted to maceration-fermentation for 120 h, then the must-wine mixture continued its fermentation until sugar finishing. Determinations have pointed out a variation in time of the values of studied indices, according to the oenological potential of each variety and the used technology. According to these variations of the values of studied indices, one may find that after a certain period of time (72 hours), a change took place in the equilibrium condition of the compounds formed during the fermentation process, especially of those involved in the insolubilization of tartaric salts; this aspect was also supported by the evolution of the values of conductivity, of redox potential and TDS, especially in white wines.

Key Words: must, alcoholic fermentation, physic-chemical indices

REZUMAT – Aspecte privind variația unor indici fizico-chimici în timpul fermentației alcoolice a mustului. În lucrare se prezintă date referitoare la variația unor indici fizico-chimici în timpul

* E-mail: odageriu@yahoo.com

fermentației alcoolice a mustului: S.u.-substanța uscată solubilă, pH-aciditatea reală, IPT-indicele de polifenoli totali, χ -conductivitate, TGS-substanțe dizolvate totale, E_h - potential redox, rH-indicele de cuantificare a E_h . Comparativ cu valorile acestor indici, s-a urmărit evoluția principalelor caracteristici de compoziție, respectiv zaharuri reducătoare, alcool, aciditate totală, aciditate volatilă și compuși fenolici totali. Experimentările au fost efectuate pe două musturi provenite din soiuri albe (Muscat Ottonel și Sauvignon) din centrul viticol Copou-Iași și pe mustuiala obținută din două soiuri roșii (Fetească neagră și Băbească neagră), provenite din centrul viticol Uricani podgoria Iași, recolta anului 2006. Musturile albe s-au obținut prin zdrobirea-desciorchinarea strugurilor și prin presarea mustuielii rezultate la prelucrarea primară a acestora. Mustuiala obținută din soiurile negre a fost supusă macerării-fermentării, un timp prestabilit (120 ore), după care amestecul must-vin a continuat fermentarea până la epuizarea zaharurilor. Determinările au evidențiat o variație în timp a valorilor indicilor studiați, dependentă de potențialul oenologic al fiecărui soi în parte și tehnologia folosită. Pe baza acestor variații a valorilor indicilor studiați se poate constata că, după o anumită perioadă de timp (72 de ore), are loc o modificare a stării de echilibru a compușilor formați în procesul de fermentație, în special a celor implicați în insolubilizarea sărurilor tartrice, acest aspect fiind susținut și de evoluția valorilor conductivității, a potențialului redox și a TDS, în special la soiurile albe.

Cuvinte cheie: must, fermentație alcoolică, indici fizico-chimici

INTRODUCTION

In the technology of grape transformation into wine, alcoholic fermentation, marc maceration and malolactic fermentation are very important. The way of stimulating or breaking these processes influences the wine quality (Cotea, 1985).

The knowledge of variation in certain physical-chemical indices during alcoholic fermentation allows the theoretical understanding of some phenomena which take place during maceration-fermentation. These phenomena concern multiplication of yeasts, dynamics of sugar metabolization by yeasts, evolution of compounds responsible of red colour in wines, ionization of main acids from must, total content of dissolved substances, conductivity, equilibrium of oxidation-reduction processes and insolubilization of tartaric compounds.

Taking into account the importance of these aspects, the main aim of our study was getting data on the dynamics of values in some physical-chemical indices during the fermentation processes and the correlation between them, useful for a rigorous control of maceration-fermentation stages in must obtained from different grape varieties.

The paper presents data concerning the variation of some physical-chemical indices during must alcoholic fermentation: DM – soluble dry matter, pH – real acidity, ITP – index of total polyphenols, χ -conductivity, TDS – total dissolved substances, E_h -redox potential, rH- index of E_h quantification. In relation to the values of these indices, we have investigated the evolution of main composition

THE VARIATION OF CERTAIN PHYSICAL-CHEMICAL INDICES DURING MUST ALCOHOLIC FERMENTATION

characteristics, respectively reducing sugars, alcohol, total acidity, volatile acidity and total phenolic compounds.

MATERIALS AND METHODS

Investigations were carried out in October 2006, within the Research Centre for Oenology, Iași Branch of the Romanian Academy. The experiments were conducted on two musts obtained from white varieties (Muscat Ottonel and Sauvignon) from the Vine Growing Centre of Copou-Iași and on marc obtained from two red varieties (Fetească neagră and Băbească neagră), from the Vine Growing Centre of Uricani, Iași vineyard, vintage of 2006.

White musts were obtained by grape crushing, removal of berries from cluster and by pressing the marc resulted at primary grape processing. Therefore, must obtained from different varieties (20 l) has been treated with selected yeasts and introduced for fermentation into two glass vessels of 25 litres, having fermentation funnel, in a room with temperature of $20 \pm 2^\circ\text{C}$ for finishing the alcoholic fermentation. Fermentation lasted 144 hours in case of both varieties. At the initial moment (0) and at time intervals of 24, 48, 72, 96, 120 and 144 hours, we took samples P_{M0} , P_{M1} , P_{M2} , P_{M3} , P_{M4} , P_{M5} and P_{M6} for Muscat Ottonel variety. For Sauvignon variety, at the initial moment and at the same time intervals of 0, 24, 48, 72, 96, 120 and 144 hours, samples P_{S0} , P_{S1} , P_{S2} , P_{S3} , P_{S4} , P_{S5} and P_{S6} were taken.

100 l of marc obtained by red grape crushing and removal of berries from clusters of each variety, after the treatment with pectolitic enzymes and selected yeasts, were introduced for maceration-fermentation into PVC vessels of 120 l, in a room at temperature of $20 \pm 2^\circ\text{C}$. In case of both varieties, maceration-fermentation lasted 120 hours; afterwards, musts obtained by pressing were bottled into vessels of 50 l, for finishing the alcoholic fermentation. For Fetească neagră variety, at the initial moment (0) and at time interval of 24, 48, 72, 96, 120, 144, 168 and 240 hours, we took samples P_{F0} , P_{F1} , P_{F2} , P_{F3} , P_{F4} , P_{F5} , P_{F6} , P_{F7} and P_{F8} . For Băbească neagră variety, at the same time intervals, we took samples P_{B0} , P_{B1} , P_{B2} , P_{B3} , P_{B4} , P_{B5} , P_{B6} , P_{B7} and P_{B8} .

The analyses concerning the main composition characteristics (reducing sugars, alcohol, total and volatile acidity, pH, total phenolic compounds and index of total polyphenols – ITP at 280 nm) were carried out according to in force standards (** 1997; *** 2005).

Soluble dry matter was determined refractometrically, conductivity (χ) and total of soluble substances were obtained with pX-meter Inolab 740–WTW.

The redox potential (volts) has been determined by the potentiometrical method with platinum electrode and reference electrode from saturated subchloride of mercury (Ingold, 1982; Luca et al., 1983; Zănoagă, 1988). The rH parameter was calculated according to Clark relation, the values being reported to normal hydrogen electrode, through factor f:

$$rH = (E_h + 0.058 \times pH + f) / 0.029 \quad (\text{volts})$$

RESULTS AND DISCUSSION

Data concerning the variation of main composition characteristics in must and wine samples obtained from white varieties (Muscat Ottonel and Sauvignon) and analysed during alcoholic fermentation are shown in *Tables 1 and 3*. The variation of main physical-chemical indices during the alcoholic fermentation in the same varieties is shown in *Tables 2 and 4*.

Table 1

Variation of main composition characteristics during must alcoholic fermentation in Muscat Ottonel variety

Sample	Time (hours)	Reducing sugars (g/L)	Alcohol (% vol.)	Total acidity (g/L C ₄ H ₆ O ₆)	Volatile acidity (g/L C ₂ H ₄ O ₂)	Total phenolic compounds (g/L)
P _{M0}	0	195.2	0.00	5.72	0.07	0.33
P _{M1}	24	168.2	1.59	6.15	0.13	0.30
P _{M2}	48	122.1	4.30	6.82	0.22	0.29
P _{M3}	72	44.6	8.86	7.35	0.31	0.28
P _{M4}	96	38.3	9.23	7.41	0.46	0.27
P _{M5}	120	23.2	10.12	7.50	0.54	0.27
P _{M6}	144	3.1	11.30	7.57	0.60	0.27

Table 2

Variation of main physical-chemical indices during must alcoholic fermentation in Muscat Ottonel variety

Sample	Time (hours)	DM (%)	pH	ITP D ₂₈₀	Conductivity $\chi \times 10^3$ (μ S/cm)	TDS $\times 10^3$ (mg/L)	Redox potential E _h (V)	rH (V)
P _{M0}	0	19.7	3.255	7.40	2.17	4.96	0.3743	27.1836
P _{M1}	24	19.0	3.213	6.37	2.10	5.31	0.4444	30.4501
P _{M2}	48	12.4	3.210	6.34	2.14	5.38	0.4430	29.4624
P _{M3}	72	6.2	3.215	6.30	2.19	5.43	0.4415	30.3580
P _{M4}	96	6.0	3.219	6.28	2.12	5.32	0.4021	28.0701
P _{M5}	120	5.8	3.222	6.26	2.08	5.18	0.3841	27.4554
P _{M6}	144	6.4	3.228	6.25	2.02	5.06	0.3682	26.8136

For red varieties (Fetească neagră and Băbească neagră), data concerning the variation of main composition characteristics of must and wine samples, analysed during maceration-fermentation, are shown in *Tables 5 and 7*, and the variation of main physic-chemical variation is shown in *Tables 6 and 8*.

THE VARIATION OF CERTAIN PHYSICAL-CHEMICAL INDICES DURING MUST ALCOHOLIC FERMENTATION

Table 3
Variation of main composition characteristics during must alcoholic fermentation in Sauvignon variety

Sample	Time (hours)	Reducing sugars (g/L)	Alcohol (% vol.)	Total acidity (g/L C ₄ H ₆ O ₆)	Volatile acidity (g/L C ₂ H ₄ O ₂)	Total phenolic compounds (g/L)
P _{S0}	0	198.2	0.00	5.25	0.06	0.28
P _{S1}	24	165.9	1.90	5.88	0.12	0.26
P _{S2}	48	100.5	5.75	6.61	0.20	0.25
P _{S3}	72	45.1	9.01	7.21	0.28	0.24
P _{S4}	96	29.9	9.90	7.11	0.42	0.23
P _{S5}	120	11.2	11.00	7.04	0.49	0.23
P _{S6}	144	2.7	11.50	6.94	0.54	0.23

Table 4
Variation of main physical-chemical indices during must alcoholic fermentation in Sauvignon variety

Sample	Time (hours)	DM (%)	pH	ITP D ₂₈₀	Conductivity X × 10 ³ (μS/cm)	TDS × 10 ³ (mg/L)	Redox potential E _h (V)	rH (V)
P _{S0}	0	20.1	3.500	6.25	2.58	5.81	0.4313	25.6214
P _{S1}	24	19.0	3.425	5.84	2.42	5.54	0.4524	31.4300
P _{S2}	48	12.8	3.418	5.59	2.44	5.40	0.4434	29.8922
P _{S3}	72	6.7	3.427	5.23	2.45	5.32	0.4374	30.7115
P _{S4}	96	6.6	3.434	5.19	2.41	5.24	0.4045	28.5828
P _{S5}	120	6.5	3.440	5.15	2.37	5.17	0.3834	27.8672
P _{S6}	144	6.4	3.454	5.10	2.31	5.09	0.3699	27.5284

Table 5
Variation of main composition characteristics during must alcoholic fermentation in Fetească neagră variety

Sample	Time (hours)	Reducing sugars (g/L)	Alcohol (% vol.)	Total acidity (g/L C ₄ H ₆ O ₆)	Volatile acidity (g/L C ₂ H ₄ O ₂)	Total phenolic compounds (g/L)
P _{F0}	0	229.7	0.00	6.43	0.07	0.45
P _{F1}	24	207.9	1.28	6.31	0.13	0.78
P _{F2}	48	176.2	3.15	6.51	0.22	1.16
P _{F3}	72	149.8	4.70	7.16	0.31	1.53
P _{F4}	96	118.4	6.55	7.29	0.46	1.83
P _{F5}	120	89.7	8.24	7.68	0.54	2.05
P _{F6}	144	75.0	9.10	7.76	0.60	2.04
P _{F7}	168	67.4	9.55	7.84	0.67	2.03
P _{F8}	240	3.7	13.30	8.27	0.74	2.02

Table 6

Variation of main physico-chemical indices during must alcoholic fermentation in Fetească neagră variety

Sample	Time (hours)	DM (%)	pH	ITP D ₂₈₀	Conductivity $\chi \times 10^3$ ($\mu\text{S/cm}$)	TDS $\times 10^3$ (mg/L)	Redox potential E _h (V)	rH (V)
P _{F0}	0	24.0	3.357	9.89	2.47	6.75	0.3515	24.4807
P _{F1}	24	23.7	3.588	17.33	3.10	6.98	0.3606	27.4547
P _{F2}	48	22.7	3.421	25.79	2.60	7.12	0.3680	27.2478
P _{F3}	72	19.3	3.411	33.98	2.62	6.72	0.3706	27.4418
P _{F4}	96	15.5	3.421	40.56	2.62	6.50	0.3619	27.0498
P _{F5}	120	14.2	3.429	45.44	2.60	6.37	0.3811	27.9991
P _{F6}	144	11.2	3.425	45.30	2.58	6.22	0.3634	27.1334
P _{F7}	168	10.4	3.422	45.15	2.55	6.13	0.3446	26.2174
P _{F8}	240	9.3	3.427	44.80	2.50	6.01	0.3095	24.5370

Table 7

Variation of main composition characteristics during must alcoholic fermentation in Băbească neagră variety

Sample	Time (hours)	Reducing sugars (g/L)	Alcohol (% vol.)	Total acidity (g/L C ₄ H ₆ O ₆)	Volatile acidity (g/L C ₂ H ₄ O ₂)	Total phenolic compounds (g/L)
P _{B0}	0	232.9	0.00	6.90	0.08	0.49
P _{B1}	24	206.4	1.56	6.46	0.14	0.76
P _{B2}	48	156.4	4.50	6.98	0.24	0.80
P _{B3}	72	100.3	7.80	7.68	0.34	1.06
P _{B4}	96	60.0	10.17	7.53	0.51	1.38
P _{B5}	120	33.4	11.73	7.43	0.59	1.44
P _{B6}	144	17.8	12.65	7.33	0.66	1.43
P _{B7}	168	6.8	13.30	7.29	0.74	1.43
P _{B8}	240	3.4	13.50	7.33	0.81	1.42

Determinations have found a variation in time of the values of studied indices, depending on the oenological potential of each variety and the used technology. We noticed that the values of certain indices (DM, pH, χ , TDS) were higher in samples of black varieties than of white ones, probably because of their different composition.

Generally, we found that once with the metabolization of sugars, which concentration diminished after 48-72 hours (according to variety), a corresponding increase in the alcoholic concentration took place, which was accompanied by a diminution in total acidity during the first 48 hours. Afterwards, it has slowly increased until the end of alcoholic fermentation,

THE VARIATION OF CERTAIN PHYSICAL-CHEMICAL INDICES DURING MUST ALCOHOLIC FERMENTATION

because of the formation of by-products, respectively, volatile, lactic and succinic acids, but pH change was not high.

Simultaneously with the diminution in the values of the acidity, we found out that TDS and conductivity had reverse values; in the first 48 hours, their values increased then decreased slowly, excepting Sauvignon variety, in which their diminution took place since the beginning. At the same time, the values of redox potential, expressed by rH parameter, had a slightly different evolution, showing an increase tendency, especially after 72 hours, pointing out a prevalence of the oxidative processes in this fermentation stage.

Table 8

Variation of main physical-chemical indices during must alcoholic fermentation in Băbească neagră variety

Sample	Time (hours)	DM (%)	pH	ITP D ₂₈₀	Conductivity $\chi \times 10^3$ ($\mu\text{S/cm}$)	TDS $\times 10^3$ (mg/L)	Redox potential E _h (V)	rH (V)
P _{B0}	0	23.4	3.157	10.78	2.96	7.68	0.4293	25.1174
P _{B1}	24	23.4	3.585	16.99	3.04	6.97	0.3453	26.7076
P _{B2}	48	22.4	3.538	17.84	3.00	7.15	0.3461	26.6147
P _{B3}	72	17.4	3.478	23.57	2.82	6.76	0.3759	27.8805
P _{B4}	96	11.6	3.502	30.56	2.63	5.98	0.3755	27.9332
P _{B5}	120	9.2	3.537	31.93	2.60	5.85	0.3896	28.7119
P _{B6}	144	7.8	3.542	31.80	2.58	5.64	0.3580	27.2000
P _{B7}	168	6.0	3.553	31.68	2.57	5.38	0.3376	26.2463
P _{B8}	240	7.6	3.578	31.52	2.53	5.44	0.3347	26.2149

In Sauvignon variety, we have also found in case of the rH parameter a specific dynamics of values, because, after an initial increase in the first 48 hours, a slow diminution of values took place. In this variety, the fermentation processes have generated, in the first stage, compounds which required an increase in rH values; afterwards, the resulted compounds determined the prevalence of some reducing forms with the diminution of rH values, knowing that rH had values between 0–42.4 V, with the neutral value of 28.3 V, the acid field between 0–28.3 V and the oxidant one, between 28.3–42.4 V (Ingold, 1982; Zănoagă et al., 2006).

We conclude that, according to these variations of the values of studied indices, one may find out that, after a period of time (72 hours), a modification takes place in the equilibrium state of the compounds formed during fermentation, especially of those involved in the insolubilization of tartaric salts. This aspect is also supported by the evolution of the values of conductivity, of redox potential and TDS, especially in white varieties.

REFERENCES

- Cotea D.V., 1985** - *Treatise of Oenology*, vol. I. Ceres, Bucharest
- Cotea D.V., Sauciuc J., 1988** - *Treatise of Oenology*, vol. 2, Ceres, Bucharest
- Dragomirescu E., Rusu F., Contrea A., Bozac R., 1979** – *Elements of biophysics*, Didactică și Pedagogică Publishing House, Bucharest
- Cotea V.V., Zănoagă C. V., Odăgeriu G., 2006** – *Comparative redox aspects between yeast alcoholic fermentation and carbonic maceration*. Scientific works, series Horticulture, University of Agricultural Sciences and Veterinary Medicine vol. 49, Iași, CD, p. 615-618
- Delfini C., 1995** - *Scienza e tecnica di microbiologia enologica*, Edizioni “IL LIEVITO” , Asti, Italia
- Ingold W., 1982** - *Redox Measurements, Principles and Problems*, INGOLD, Urdorf, Switzerland
- Luca C., Duca Al., Crișan I.Al., 1983** – *Analytical chemistry and instrumental analysis*, Publishing House, Bucharest
- Odăgeriu G., Cotea V.V., Crețu Cl., Stoica G., Zănoagă C., 2005** – *pH variation during must alcoholic fermentation*. Cercet. agron. în Moldova, vol. 1-4 (123), vol. 1-4 (124) Iași, p. 97-106
- Nenițescu C.D., 1958** – *Elementary treatise of organic chemistry*, vol. II, Didactică și Pedagogică Publishing House, Bucharest, p. 252-257
- Renouil Y., Féret C., 1988** - *Dictionnaire du vin*. Éditions Sésame. Boulogne – sur – Seine, France
- Țârdea C., Sîrbu G., Țârdea Angela, 2000** – *Treatise of wine making*, “Ion Ionescu de la Brad” Publishing House, Iași
- Zănoagă C.V., Neacșu I., Zănoagă Mădălina, 1988** – *Observations on the technique of rH determination in some biological samples*, St. cerc. biochim., 31 (1), p. 53-58
- Zănoagă C.V., Cotea V.V., Niculaua M., Odăgeriu G., 2006** – *Aspects of the redox behaviour of alcohols from wine*. Scientific works, series Horticulture, University of Agricultural Sciences and Veterinary Medicine, CD, p. 611-614
- Würdig, G., Woller, R., 1989** - *Chemie des wines*. Germany, Ed. Ulmer
- *** **1997** - *Collection of standards for wine and alcoholic beverage industry*, Ministry of Food Industry, Bucharest
- *** **2005** - *Recueil des méthodes internationales d'analyse des vins et de moûts*. Office International de la Vigne et du Vin, Édition Officielle, juin, Paris