AGRI-AMELIORATIVE INDICES OF LIQUID WASTES FROM PROCESING GRAPES, PRODUCING THE DIVINE AND ETHYL ALCOHOL

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Abstract

In the process of processing the grapes and the production of strong drinks, annually, at a national level, are formed and accumulated great quantities of liquid wastes (wine yeast, vinasse, cereal melasse and bagasse) which constitutes about 100 – 150 thousand meter^3. They are characterized by a reaction of strongly acid environment and a high content of water soluble salts. The pH-value varies from 3,4 to 3,8 units. Mineral residue constitutes: 1,9 g/dm^3 in vinasse, 12,0 g/dm^3 in vine yeast and 14,9 g/dm^3 in cereal bargasse. In the composition of cations predominate monovalent cautions of sodium and potassium, that, when reaching into the soil, can form toxic salts. With a high potential of salinity and sodium enrichment is characterized the bargasse. But the greatest danger of contamination of saline and alkaline soils can lead to the incorporation of their abusive and uncontrolled discharge. Along these wastes contain primary nutrients (NPK) that are very necessary for agricultural plant nutrition and soil fertility. Investigations have shown that the waste contains a significant amount of nutrients. NPK content in the waste summary accounts, kg/m3: vinasse - 1.8; cereals bargasse - 5.1, wine yeasts - 10.6. Solid (pressed) wine yeasts contain a higher organic matter and nutrients, in a ton of waste it is also contained summarily 48 kg NPK. Wine yeasts and cereals bargasse have a high content of organic matter, 34 and, respectively 51%. Because of the high content of organic matter and very acidic environment they have a toxic impact on the flora and fauna of surface waters and polluting the paedologic underground waters' action.

Keywords: Total Nitrogen, Bargasse, Wine Yeasts, Total Phosphorus, Vinasse.

Today at the wineries and the sections of divine and alcohol production on a large scale are accumulated as waste of about 40-80 thousand tons of wine lees, no less than 50 thousand cubic meters of vinasse and 50-60 thousand cubic meters of pulp grain and molasses (statistical Yearbook of the Republic of Moldova, 2012). The total volume of waste from the wine industry is tremendous and always increasing. Mineral residue makes up 2,0-2,7 g/dm^3 which characterize them as liquids with high mineralization, SAR index is greater than 6.0, and the coefficient Stebler 9-16 norm being 18 and more. Potentially higher salinity is characterized by grain marc, coefficient Stebler being 6-7. But the greatest danger of contamination of saline and alkaline soils can be caused by the abusive incorporation and uncontrolled diversification.

The respective wastes are containing also very basic elements needed for plant nutrition and soil fertility, which are strongly required to be recovered. In 100 m^3 of wine yeast is contained about 190 kg of nitrogen, as much phosphorous and potassium of a total of 550 kg. Less concentrated in nutrients, but not negligible is the grain marc and vinasse. These aren't used in any form in no way, there are no liquidation regulations. The purpose of this paper is to study the chemical composition of these wastes to assess the possible impact on pollutant and soil fertilizer.

MATERIAL AND METHOD

The research was conducted in 2010-2012 on fields of waste from grape processing industry and production of the divine and grain alcohol. Object of the study was: wine lees, vinasse and grain marc. Waste processing industry grapes and producing divine and grain alcohol were analyzed by five companies, in total being 21 samples.

For the analysis of wastes were used the following methods of determination: humidity STAS 26713-85, organic substance STAS 27980-88, pH – STAS 27979-88, ash – STAS 26714 -85, total nitrogen – STAS 26715-75, total phosphorus – STAS 26717 - 85, total potassium – STAS 26718- 85, $N–NO_3$ - after Grandval –Leaju, $N–NH_4$- STAS 26716-85, watery extract STAS 26428- 85. Stattistic processing of obtained results of the investigations was conducted by B. Dospehov (1990).

RESULTS AND DISCUTIONS

Wine yeasts in the wine industry are wastes that are created as a result of yeast fermentation of

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grape juice. Usually, it is formed as a result of fermentation juice of about 15% of wine yeasts, which are in a semi-solid state, with dry matter content of 12-13%. There were formed about 40 thousand cubic meters of yeast in an annual average according to estimated calculations of forming wine yeasts in the last three years.

At present, at the wine factories, from yeast, depending on the equipment available, is extracted the alcohol by distillation and/or concentrated on the filter press. After this treatment, the yeast will diverse in the environment. Are quite interesting the researches made (Gheorghe Duca, 2011) on the possibility of using them as nutritional additives in animal feed. Wine yeast is resulting from alcoholic fermentation of must, the highest weight is given at the first drawing transfuse or wine on the lees after fermentation. As a result, the physical and chemical composition of the yeast has a very heterogeneous group of substances to the influence of technology, such as wine, the conditions of fermentation, yeast species participating in the fermentation, the type of presses used to obtain the must, etc. The wine yeasts are, besides yeast biomass, such substances as: particle pulp, skins, clusters, seeds, sand, proteins, tannins and coloring substances (black grapes) and other colloidal substances, acid, precipitated during fermentation, some of them being absorbed with water, alcohol, and other soluble substances in wine.

Table 1

Chemical composition od liquid wine yeast from the wine factories of the Republic of Moldova. 5 samples taken and analyzed in 2010-2012 years

Component and measure unit	x	Min	max	S	V, %	Sx	Sx%	Δx(±)
pH	3,8	3,1	4,5	0,66	17,5	0,3	7,2	0,7
Total residue, g/dm^3	46,0	15	85	29	63,0	12,1	26,4	29
Mineral residue, g/dm^3	12,0	7	21	7,7	66,0	3,2	27,6	8
Organică substance, %	34,0	13	67	27,9	82,1	11,6	34,2	28
Total nitrogen, % N	0,21	0,08	0,58	0,2	100	0,08	40,0	0,2
N-NO_4, mg/dm^3	121	98	188	59	49	25	20,0	59
N-NH_3, mg/dm^3	13	4,02	21,0	8	63	3,3	26,0	8
Total phosphorus, % P_2O_5	0,1	0,03	0,21	0,07	66,3	0,03	27,5	0,07
Total potassium, % K_2O	0,75	0,07	0,77	0,61	82,0	0,25	34,0	0,60
Humidity, %	95,2	91,4	97,5	2,2	2,3	0,9	0,95	2,3
Ca^{+2}, mg/ dm^3	240	60	340	99	41	41	17	99
Mg^{+2}, mg/ dm^3	92	37	171	52	56	22	23	52
Na^+, mg/ dm^3	471	301	630	158	34	66	14	158
K^+, mg/ dm^3	4188	399	6427	2085	50	869	21	2085
Cl^-, mg/dm^3	131	83	138	28	22	12	9	28
SO_4^{--}, mg/ dm^3	340	118	451	117	34	49	14	117

Remarque: x – arithmetic average value; min – minimal value used; max – maximal value used; S – standard deviation of the average; v – variation coeficient; Sx – average precision in absolute sizes; Sx% - relative precision of average; Δx – seif interval of average at probalility 95%.

Liquid wine yeast is characterized by a high content of water, about 95.0%. Content of organic and mineral substances make up 3.4 and, respectively, 1.2%. Among the biofile elements predominates potassium, nitrogen and total phosphorus (Table 1). Total potassium content makes up an average of 0.75%, total nitrogen - 0.21% and total phosphorus - 0.1%. Of monovalent cations are of potassium and sodium. Their concentration is 4.2 and, respectively, 0.47 mg/dm^3. Of bivalent cations predominates calcium - 240 mg/dm^3 and magnesium - 92 mg/dm^3. In the composition of anion predominate the sulphates. Their concentration constitutes on average 0.34 g/dm^3, and 0.13 g/dm^3 of chlorine. Of mineral nitrogen form prevails N-NH4 - 121 mg/dm^3, N-NO3 is 13 mg/dm^3.

A cubic meter of yeast contains 10.3 kg NPK in a report to these elements of 1:0,5:3,6. Judged by the criteria for irrigation water, the liquid yeasts do not meet the requirements to be used as a source of water. Calculations have shown us that all indications irrigation are beyond the rules. Liquid wine yeast can be sold only as a source of nutrients. The solids yeasts are characterized by a content of 48% water, 46.8% organic matter and 5.3% minerals. Of biofile elements predominate potassium, nitrogen and total phosphorus. The content of these items constitutes 2.6%, 1.5% and, respectively, 0.7%. A ton of yeast also contains 48 kg NPK, with a ratio between these elements of 1:0,5:1,7, which corresponds approximately to nutritional needs of the main crop. The ratio of carbon:nitrogen is 16:1, being similar on the capacity after failing the nitrogen with manure (17:1).

Vinasse is formed as a result of waste distillation to obtain distillate wine. According to available data (Statistical Yearbook of the Republic of Moldova, 2012) it was shown that in recent years has been produced annually about 40-50000 cubic meters of vinasse. As it is observed from the data analyzed from year to year the production of distillated wine increases. Simultaneously increase the amount of

vinasse formed as a result of this activity, which requires no negative impact on the environment.

But to appreciate the value of secondary wine products originating as a result of their distillation by obtaining alcohol for cognacs and alcohol rectified, as well as resulted wastes from obtaining alcohol from melasses, at present there are no solutions. Vinasse that is resulting from the distillation of secondary wine products is primarily useful for obtaining tartaric acid compounds. Not being used for other purposes (such as obtaining food for animals) basically is discharged to the sewer system, preventing the development of aerobic biological processes, which are currently used in wastewater treatment and also damaging to the environment (Gh, Duca, 2011).

Table 2

Chemical composition of vinasse from wine factories of the Republic of Moldova. 5 samples collected and analysed in 2010-2012 years

Component and measure unit	x	min	max	S	V, %	Sx	Sx%	Δx(±)
pH	3,4	3,0	3,7	0,26	7,8	0,13	3,8	0,4
Total residue, g/dm^3	15,2	7,5	24,7	7,3	47,8	3,3	21,8	9,2
Mineral residue, g/ dm^3	1,9	1,2	2,9	1,2	65	0,5	28,7	1,3
Organic substance, %	1,3	0,63	2,17	1,07	82,3	0,53	40,2	0,91
Total nitrogen, % N	0,02	0,007	0,05	0,02	82,5	0,01	48	0,02
Total phosphorus, % P_2O_5	0,02	0,006	0,039	0,02	82,5	0,01	48	0,02
Total potassium, % K_2O	0,12	0,048	0,157	0,04	37	0,02	15	0,05
N-NO_4, mg/dm^3	67,4	0	86	25,4	37,7	12,7	18,8	35,6
N-NO_3, mg/dm^3	9,3	0,31	23,8	6,4	68,6	3,2	34,4	9,0
Ca^{+2}, mg/dm^3	106	72	120	20	19	9,0	8,0	23
Mg^{+2}, mg/dm^3	84	49	146	36	43	16	19	42
Na^{+}, mg/dm^3	172	125	210	44	25	20	12	51
K^{+}, mg/dm^3	579	335	1127	333	61	161	28	418
Cl^{-}, mg/dm^3	90	69	122	24	26	11	12	28
SO_4, mg/dm^3	155	79	280	75	48	34	22	88

Remarque: x – arithmetic aveerage value; min – minimum value used; max –maximum value used; S – average standard deviation; v – coeficient of variation; Sx – average precision in absolute size; Sx% - average relative precision; Δx – safe interval of average on probability 95%.

In general, the chemical composition of vinasse will be similar to the composition of wine, with the exception of alcohol content. Of course that, during the distillation, together with ethyl alcohol, methyl alcohol to be distilled as well as a part of superior alcohols, aldehydes, ethers and esters. If we look from the point of view of the effect of fertilizer, all of these compounds will play a role on this quality. More important is the content of organic matter, nitrogen, phosphorus and potassium. We have studied the composition and properties of the waste from the point of view of its influence on the soil chemical properties. We determined the indices that have an urgent task to change the status of soil quality, to put into value the vinasse, if possible, as a source of soil fertilization and reduced negative impact on the quality of natural waters as a result of direct discharges on water surfaces.

From this point of view, the vinasse is characterized by an acid medium in which the pH varies from 3.0 to 3.8 with the average value of 3.4 units. Dry residue varies from 6.0 to 24.4 g/dm^3 and constituted on average 15.2 g/dm^3. The content of organic substances constitutes an average of 13.3 dm^3, with a variation of from 0.6 up to 26 g/dm^3. The content of mineral compounds is ranging from 0.6 to 3.2 g/dm^3 with an average of 1.9 g/dm^3. From biofile elements in the composition of vinasse predominates the potassium content with the average of 0.12%. Total nitrogen and phosphorus content constitutes on average 0.02%. Ammoniac nitrogen makes up about 34% of the total nitrogen content (Table 2). Of the cations of vinasse are prevailing the monovalents of potassium - 579 and 172 mg/dm^3 of sodium. The concentration of divalent cations of calcium and magnesium is on the average 106 and 84 mg/dm^3, with a corresponding variation of up to 129-126 83-42 mg/dm^3. Among the anions predominates the content of sulphate, the concentration of which is on average 155 mg/dm^3. Chlorine content ranges from 62 to 118 mg/dm^3, constituting on average 90 mg/dm^3.

Calculations made on the quality of irrigation indices have shown us that all indices exceed applicable requirements. Vinasse can be incorporated into the soil to satisfy the water needs of plants, it can be incorporated into the soil just to exploit the nutrients contained therein, without adversely influencing the properties of the soil improvement.

Wastes from the manufacture of spirits from grain or melasses has always been a problem in terms of adverse consequences as these, but especially bargasse, is an extremely polluting the environment. Until land reform it has been a

natural and beneficial solution to this problem from all points of view, bargasse being fully used as animal feed, being turned into meat and milk. With the dismantling and destruction of livestock complexes this possibility disappeared, and ethanol producers are facing serious problems in complying with environmental legislation.

In recent years actively developing industry is producing ethyl alcohol from grain (wheat, barley, corn). Currently there are over 20 companies that produce alcohol from grain, but in the absence of outlets they operate in unstable rhythm. According to calculations based on data presented in the Statistical Yearbook of the Republic of Moldova (2012), in recent years the country has formed annually about 50 thousand cubic meters of bargasse from grain. Currently, some factories for the production of ethyl alcohol are installed dividers separating the solid fraction of grain mash, distributed feed. Otherwise, just some alcohol factories in cities that have wastewater treatment plants and have contracts with treatment plants discharging such waste in municipal sewers. However, most plants producing grain alcohol discharging the waste into the environment. Depending on technology of production of drinks, applied to corn as a raw material in the literature data and from the analysis carried out on bargasses the composition can vary within certain limits. The dry weight of the raw material (maize) in the literature reveals that about one-third goes foots. The dry matter content of bagasse varies between 4 and 8% and consists mainly of protein substances, hemicellulose, cellulose, starch, etc. pentose. (V. Nicolic, C. Petruşa, 2006). In the process of production of alcohol is fermented energy component of cereals - starch and other substances in dried protein content increases approximately 2.5 times the expense of nitrogenous substances from yeast, and total protein content in dry matter of the bargasse is 2-fold higher than in the original feedstock. Because the substances they contain grain bargasse is a valuable feed. He studied composition and properties of grain bargasse in terms of the influence of the degree of change agri-amelioration soil properties. We analyzed indications necessarily acting as change the state of the soil, grain bargasse to harness as a source of soil fertilization and reduced negative impact on the environment.

Cereal mash is characterized by a water content of 93.4% and 6.63% dry matter.

Table 3

Chemical composition of bargasse of production industry of ethylic alcohol. 6 colected and analysed samples in 2010-2012 years

Component and measure unit	x	min	max	S	V, %	Sx	Sx%	Δx(±)
pH	3,7	3,4	4,2	0,33	8,9	0,13	3,6	0,3
Total residue, g/dm^3	66,3	40,5	72,0	4,9	7,4	2,0	3,0	4,8
Mineral residue, g/dm^3	14,9	9,3	21,4	1,3	8,7	0,53	0,04	1,4
Organic substance, %	51,4	16,2	62,1	4,8	9,3	2,0	3,9	5,5
Humidity, %	93,4	92,1	97,0	1,3	1,4	0,53	0,57	1,6
Total nitrogen, % N	0,28	0,21	0,33	0,04	12,6	0,02	7,1	0,04
Total phosphorus, % P_2O_5	0,12	0,06	0,19	0,08	23,5	0,03	15,8	0,07
Total potassium, % K_2O	0,11	0,09	0,13	0,24	22,3	0,01	9,1	0,02
N-NO_4, mg/dm^3	143	71	224	63,1	44,2	25,7	18	62
N-NO_3, mg/dm^3	5,8	2,9	11,0	3,7	69,3	1,5	25,8	3,6
Ca^{+2}, mg/dm^3	97	60	100	26,6	27,5	11,1	11,5	27
Mg^{+2}, mg/dm^3	234	183	244	86,2	36,8	35,9	15,3	86
Na^+, mg/dm^3	450	185	550	19,4	43	80,7	18	194
K^+, mg/dm^3	783	649	850	166	21,2	69,2	8,8	166
Cl^-, mg/dm^3	299	138	321	98,4	32,9	41	13,7	98
SO_4, mg/dm^3	357	188	533	140	39,1	58,2	16,3	140

Remarque: x – arithmetic average value; min – minimum value used; max –maximum value used; S – average standard deviation; v – coeficient of variation; Sx – average precision in measure size; Sx% - average relative precision; Δx – seif interval of average at probability 95%.

The content of organic matter ranges from 45.9 to 56.9 g/dm^3 with an average value of 51.4 g/dm^3. Mineral residue makes up on average 14.9 g/dm^3 with a variation of 8.7%. Among the biofile items, in the composition of bargasse of grain prevails the nitrogen content - 0.28%, 0.12% phosphorus and potassium 0.11 (Table 3). The analysis of the aqueous extract has been found that the grain mash acid has a mean average pH of 3.7 units and range from 3.4 to 4.0 units. Of the monovalent cations are predominant cations of potassium and sodium - 783 and, respectively, 450 mg/dm^3. The concentration of calcium and magnesium cations constitutes an average of 97 and, respectively, 234 mg/dm^3. Of the predominant anion sulfates, their content accounted for an average of 357 mg/dm^3. The concentration of chloride ions ranges from 202 to 397 mg/dm^3 with an average of 299 mg/dm^3.

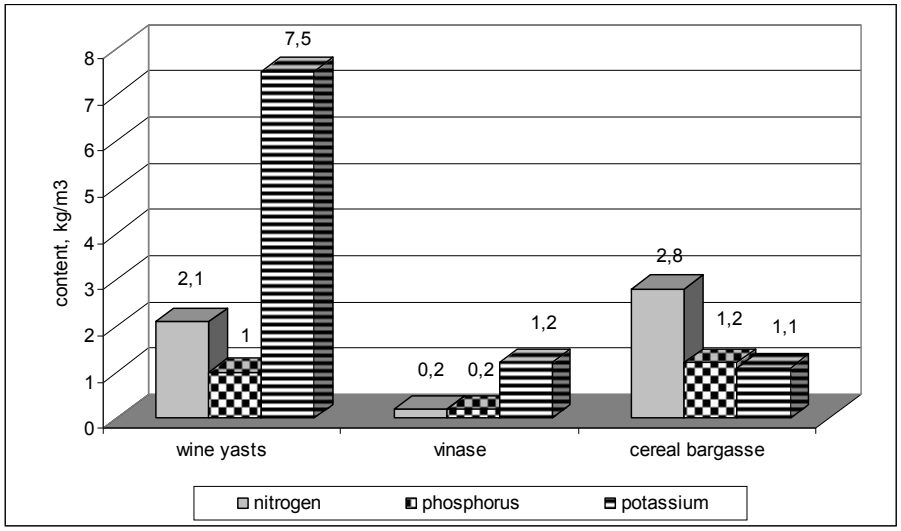

Figure 1. **Total content of nitrogen, phosphorus and potassium in liquid wastes of wine industry, kg/m^3**

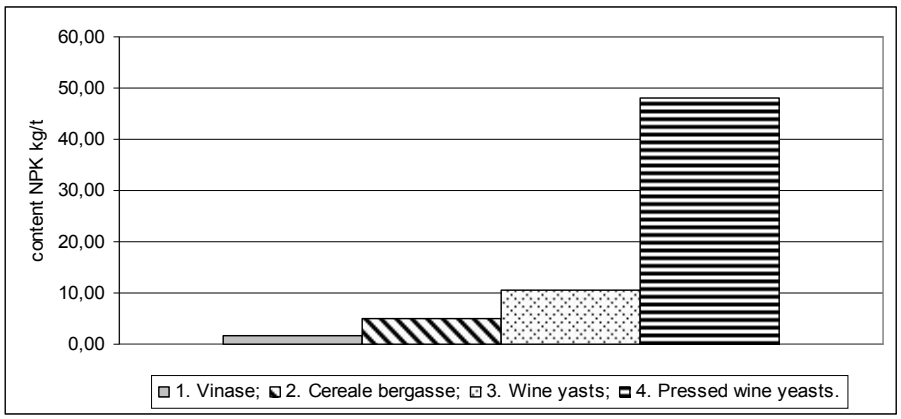

Figure 2. **Total quantity of biofile elements that are contained in 1 tonne of wastes**

The calculations performed in assessing the quality of irrigation, we have shown that grain bargasse does not meet the current requirements for use as a source of irrigation plant according to need in water. Grain bargasse can be used as a source of fertilizer, highlighting the biofile elements and organic matter it contains. According to organic matter content and total forms of biofile elements of waste studied on the first place is ranked pressed and liquid wine yeast, grain and bargasse followed by the vinasse. Total nutrient content of nitrogen, phosphorus and potassium in the waste studied are: the grain bargasse - 2.8, 1.2 and 0.2 kg/m^3 respectively in wine yeast - 2.1, 1.0, respectively 7.5 kg/m^3 and vinasse - 0.2, 0.2 and 1.2 kg/m^3 (fig. 1). The amount of primary nutrients in a cubic meter of waste varies from 1.8 kg to 5.1 to 10.6 kg the vinasse of grain and wine yeast (Fig. 2). C: N ratio is 8:1 and 9:1 in wine yeast and grain mash, which demonstrates that the decomposition of these waste plants will be supplied with nitrogen. When applying guilt because C: N ratio of 32:1 is manifestly higher than optimal (25:1), the action of plant nitrogen supply will do not immediately but gradually.

CONCLUSIONS

At the factories where the grapes are procesed annually are accumulated to about 40 thousand m^3 of wine yeast. As a result of the technological and filtering processes the wine yeasts are obtained in a liquid and solid form by being pressed. 1 m^3 of liquid wine yeasts contain total forms: 2,1 kg nitrogen, 1,0 kg phosphorus şi 7,5 kg potassium. On average the primary elements constitute 10,6 kg/m^3. One ton of wine pressed yeast contains 15,0 kg of nitrogen, 7,0 kg of phosphorus and 26,0 kg of potassium, which are total forms. Summarily the primary elements constitute 48 kg/t with a report between elements of 1,0:0,5:1,7.

The distillate obtained divine annually at the country accumulates an average of 50 thousand m^3 of vinasse, its volume is constantly increasing. 1 m^3 of vinasse contains 1.8 kg of primary cells. The resultant production of grain alcohol, obtained annual republican scale up to 53 000 m^3 of bargasse, which requires a user without a negative impact on the environment compo-

nents. One cubic meter of grain yeast contained on average: 2.8 kg nitrogen, 1.2 kg phosphorus and 1.1 kg potassium, total forms, summary they form 5.1 kg/m^3.

Waste from grapes, produce divine and rectified ethyl alcohol, is characterized by a highly acid and a high content of water-soluble salts. The pH value is ranging from 3.4 to 3.8 units. Mineral residue are: 1.9 g/dm^3 in vinasse, the lees of wine g/dm^3 12.0 and 14.9 g/dm^3 the grain mash. The cationic component predominates monovalent cations sodium and potassium, which enter the ground toxic salts may be formed to have an uncontrolled incorporation of abuse of such waste. Wine yeast and cereal bargasse with a high organic matter content of 34% and 51% respectively. Because of the high content of organic matter and very acidic environment they have a toxic impact on the flora and fauna of surface and pollutant impacts on paedofreatic water.

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