GRAPE POMACE EXTRACTION EFFICIENCY INVESTIGATION IN SUBCRITICAL WATER ENVIRONMENT

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Abstract: The article presents the dry matter yield experimental studies results in the subcritical water grape pomace extraction of. Extraction was performed under a temperature range of T 100°C ÷ 160°C, pressure P = 12 MPa, exposure of 30 to 90 min and hydronic modules 1:5 and 1:10. High output common extractives were observed already at 100°C and 0.5 h (31.9 % at hydro module 1:5 and 39.4 % at hydronic module 1:10). The results showed that extraction with subcritical water of a dry extract yield at least 2 times greater than the sweet pomace by washing with hot water. Subcritical water extraction at 160°C for conversion of plant material is comparable to wood acid hydrolysis. However, compared with a catalytic hydrolysis sulfuric acid unnecessary neutralization of with the illiquid formation, hard recyclables departing - gypsum contaminated with organic compounds.

Key words: extraction, subcritical water, grape pomace.

Introduction

Grape pomace (GP) is an important and expensive raw material. According to their chemical composition, these secondary products are a grapes valuable source and produce a variety of valuable products: tartaric acid [8], tannins [1], ethanol [2], polyphenols [12], furfural [4] and other products.

Some researchers have reported high antioxidant activity of explosives extracts, suggesting their use as natural antioxidants [14].

Thus, the use of explosives is a potential alternative waste winemaking. However, it still remains the problem of recovering actual target components from the feedstock resulting from the grapes processing.

For the extraction of the target components in the vast majority of based used water- ethanol mixtures [3], methanol [11] and other organic solvents, sometimes with the use of additional physical extraction techniques. For example, a water- ethanol mixture with pulsed electric fields (PEF) [5], ethanol wave microwave [7], ultrasound [9], high-voltage electrical discharge (HVED) [3], and so forth.

The use of organic solvent is problematic due to the toxicity, high cost and problems with disposal. Thus extracts from the almost completely disappear glycolipids and phospholipids, acylglycerols, sterol esters, and other esters and ethers possessing biological activity. In addition, when exposure electro- physical methods used in product it is possible not only to changes in the molecule conformational structure, but its spatial orientation and properties, with deformation and molecular chains rupture into separate

fragments.

The solvents with a low boiling point used in the last decade suggested as extractants - Liquefied gases: carbon dioxide, propane, ammonia, methane, ethylene and some other compounds with low critical temperature [16].

However, it should be appreciated that carbon dioxide has a major greenhouse gases like methane, ozone, nitrogen oxides, the gases that contain fluorine. The presence of these gases in the atmosphere gives rise to a greenhouse effect. In addition, some fluid substance such as methane is toxic substances acting on the central nervous system. There is evidence that some of them, such as ethylene, propane and others have narcotic activity [6].

In recent years, for the extraction and chemical modification of biologically active compounds was requested subcritical water use (SCW - superheated water under pressure higher than the pressure of saturated steam at temperatures of from 100C to 374C, allowing the water to remain in the liquid state and having an interface with the vapor phase, with conditions for the existence of sufficient) [10, 13].

Even small variations in temperature and pressure changes in SWE are all physico - chemical characteristics of the water: dielectric constant, viscosity, specific heat and density of the diffusion coefficient. The water in these conditions behave like a polar organic solvent.

Properties of liquid water, which caused such important processes such as dissolution of various substances and transport of protons, are the molecules motion result in a constantly changing grid structure [15].

High compressibility, leading to significant changes in density with little change in pressure and a significant decrease of the dielectric constant under normal conditions up to supercritical (SC) conditions allows non-polar substances dissolve in water.

Water is non-toxic, non-combustible material and with low cost, has a lightweight division with the target products after completion of the process. Use of subcritical water instead of organic solvents increases the environmentally sound production and obtained products purity, given the toxic organic solvents sufficient traces lack and impurities contained therein. Water is also non-fire and non-explosive.

Replacement of toxic organic solvents, and clean liquefied greenhouse gases subcritical water will reduce the economic and environmental consequences of extraction processes.

Thus, studies in this area are relevant. The purpose of our work - to investigate dependence of the solids from dried grape pomace "Moldova", depending on the temperature, pressure, extraction time, hydronic module and definition of extraction process subcritical water rational parameters.

Materials and methods

Plant material

Grapes «Moldova» were acquired in late September in retail network of Donetsk (Ukraine) from the manufacturers - Republic of Moldova. «Moldova» - table grape. The average weight of bunches up to 350 grams. Berry large (2,5 x 1,9 cm), oval, dark purple, with a thick waxy coating. Peel thick, dense, durable. Pulp is fleshy, crunchy. Tastefully simple.

Preparation of raw materials

Berries spin with crests was carried out on a juicer to a moisture content of grape pomace industry - 55 %. Original drying was at 75 C ± 2 °C until constant weight was carried out in porcelain bowls placed in an oven TRTS02 TP- 1 with occasional stirring. The resulting agglomerates are crushed to a fraction passing through the sieve with an aperture of 3 mm. Samples in powder form packaged in paper bags to protect them from light and polythene bags to protect them from ambient moisture. Samples were stored at room temperature in a dark place in a laboratory.

Extraction by for sub-rcritical watter

The equipment used for extraction in subcritical water (SCW) has been designed and manufactured in a laboratory of fluid technology of DonNUET. Extraction was performed in a laboratory reactor under steady conditions. Usage ratio of raw material and extractant (water) is 1:5 and 1:10. The temperature was varied from 100 to 160 C in increments of 10C. The temperature was maintained by a controller with an accuracy of ± 1 0C. Exposure time was 30 min, 60 min and 90 min. Report time started after reaching the desired temperature. At each point three parallel experiments were performed. Level pressure P = 12 MPa.

Methodology to study the yield of dry matter in the extracts

The dry extract was determined by evaporating the extract exact volume (50 ml) at 75 C under vacuum on a rotary evaporator with 1M IR temperature controller ERA -M to constant weight. The weight of the extract refers to the weight of the dry original sample, i.e., determined the mass yield of dry extract of the original bone dry raw material). Processing of the results was performed in the Microsoft Excel 2003software package. Confidence probability was assumed to be 0.95. In the experiment, a uniform applied duplication experiments (triplicate in each experiment point).

Results and discussion

If accepted method of determining the output of dry extracts not all substances that have fallen to the solution remain in the dry residue. This is due to the volatility of many of the compounds produced in the extraction of superheated water under acidic conditions. These primarily include breakdown products of sugars - formic and acetic acid, hydroxymethylfurfural, furfural, as well as essential oils, terpenes, etc.

The yield of dry extract on the working masses at HR 1:5 describes the regression equation (1):

$$ВЭ = 14{,}649 + 0{,}103 \cdot t + 0{,}360 \cdot \tau - 0{,}0014 \cdot t \cdot \tau \quad (1)$$

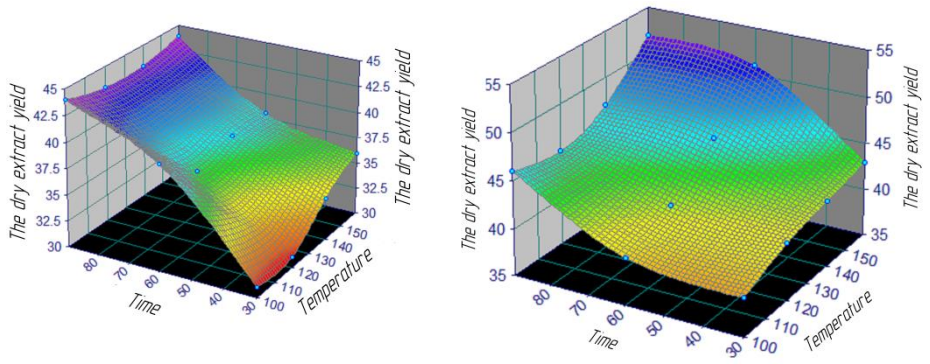
where t – extraction temperature, °C;

τ – curing time, min.

The yield of dry extract on the working masses at 1:10 HR describes the regression equation (2):

$$ВЭ = 28{,}971 + 0{,}0745 \cdot t + 0{,}0270 \cdot \tau + 0{,}0006 \cdot t \cdot \tau \quad (2)$$

Multiple correlation coefficient of the regression equation (1) R = 0,987, equation (2) - R = 0,950.



a) b)

Fig. 1. Response surface yield of dry extract on the working masses:
a) at hydro ratio 1:5, b at hydro ratio 1:10

Response surface yield of dry extract on the working masses of time, temperature and hydro ratio is shown in Figure 1.

High output common extractives were observed already at 100 ^{0}C and 0.5 h (31.9 % at 1:5 HR and 39.4 % at 1:10 HR) can be explained by the following factors:

- Residual grape marc sugar content;

- Partial hydrolysis of pectic substances, uronic acid and mucus. One would expect that this process will take place already active during drying. When drying the GP has been an exposed to relatively high temperature for a considerable period of time. Thanks to its own organic acids creates an acidic environment that can catalyze the hydrolysis process. However, the yield of dry extract and reducing substances from the source oil was only slightly less - 2-3% (absolute) than that of dried. This can be attributed to the high saturation of free water in the GP and solubles, primarily sugars. High concentration of solutes prevents hydrolysis of polysaccharides and the transition to the solution of other compounds.

During the extraction, at 1:5 HR, these factors result in a lower yield of dry extract than in 1:10 HR. This is especially noticeable when the holding time is 0.5 hours. When reducing concentration the extract is increased, which leads to acceleration of the thermal degradation at high temperatures?

It should be noted that 160 °C temperatures showed significant swelling of extractable mass. At this temperature, 1:5 HR, and the exposure time 1.5 hours in the mass, free water after extraction was not visually observed.

This testifies to the failure of 1:5 HR.

At high temperatures, the yield of dry extract determined by the ratio of two processes: development and the extract transition of water-soluble compounds and their decomposition under the action of temperature and acidity. The main contribution to increasing the yield of extract makes the process of polysaccharides hydrolysis with t

transfer into soluble compounds (oligosaccharides, dextrins, monosaccharides). Pectin cleavage followed by hydrolysis acetic acid.

With increasing exposure time and temperature 140 ^{0}C the extract yield increases. At 140 ^{0}C the hemicellulose decomposition and monosaccharides hydrolysis rate increases. Thus are formed strong organic acid - acetic, formic, and increase the concentration which leads to an acceleration of the decomposition and hydrolysis sugars. Breakdown of the sugars also leads to the formation of hydroxymethylfurfural, furfural, humic substances, etc.

We have decided to limit the upper temperature limit extraction 160 ^{0}C. At temperatures of 150-160 ^{0}C inpatient extraction and accepted slots excerpts begin dramatically accelerate the process of decomposition. As a result, 1:5 HR used to further increase the yield of the extract inhibited due to the formation of solid substances (humic substances) and products gaseous decomposition. At 1:10 HR, despite a significant increase in the yield of dry extract, extract quality is deteriorating and its further processing is required by laborious purification, so the target products yield falls.

Conclusion

When washing sweet marc by hot water yield of dry extract was up to 15% by weight of oven-dry bagasse. The bulk of the extract - the carbohydrates (mostly free monosaccharides) and acidic compounds. When subcritical water extraction extract yield at least 2 times greater. Image extract yield is due to the formation of water soluble polysaccharides, carbohydrates, also there is a significant amount of polyphenolic compounds.

Subcritical water extraction at 160 ^{0}C is used conversion of plant material to acid hydrolysis comparable timber. But the dissolution of the acid hydrolysis of plant components passes under more stringent conditions: temperature up to 180 ^{0}C, the presence of sulfuric acid. Therefore, in case of subcritical water with the formation of undesirable products (primarily due to the decomposition of carbohydrate) will be substantially less than if a similar flow diagram. The yield of the desired products is more above. Moreover, compared with a catalytic hydrolysis unnecessary neutralization of sulfuric acid with a low liquid form is recyclables difficult - gypsum contaminated with organic compounds.

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