

NOT-WASTE TECHNOLOGY OF POST-SPIRITUOUS BARD RECYCLING

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The complex technology grain bards utilization which allows to receive clean water, dry residue, suitable for use as a feed additive for livestock, biogas, thermal energy obtained by the cooling output bard has been offered.

Keywords: bard, ethanol, processing, anaerobic decomposition, humidity, temperature, bioreactor.

Introduction. Currently, worldwide there is a dynamic development of ethanol production, which on one hand, is combined with the constant improvement of biotechnology of ethanol, and the other - with all growing needs for biofuels, which today is widely used as a more environmentally friendly motor fuel. Increased production of ethanol leads to some environmental stress related to waste management. Among the by-products of obtained ethanol 99.9% is accounted for post-spirituos bard (approximate yield is 13.4 m³/t of grain) because of its relevance of utilization due to increasing ethanol production is not in doubt. On the one hand, the bard is a waste, causing environmental pollution. So bard is forbidden to dump into waterways or drains without prior treatment. Most plants do not utilize bard and without purification together with sewage it is discharged into settling tanks where it rots, polluting groundwater and air. To the natural methane emissions distilleries add methane from fields of filtration, increasing the greenhouse effect on the planet. On the other hand, the bard, thanks to fiber, carbohydrates, protein and micronutrients, is secondary raw materials, it can serve as raw material for animal feed, fertilizer and other useful products [1-5].

Problem. Bard is the main waste of ethanol production. Currently, the majority of the world distilleries in some way process, bard mainly to feed. To transport the unprocessed bard is un-profitable, high content of liquid and relatively low - valuable substances makes transportation of waste unprofitable [1-5].

Analysis of recent research and publications. More recently, the technology provides processing of post-spirituos bards in the dry fodder yeast concentrate (DCC). DCC - a mixture of solids bards with grown from liquid phase fodder yeast. The introduction of yeast as a dietary supplement in the "cake" allows to get feed product. The proposed scheme can significantly save energy during processing of bard. Saving energy is conducted mainly by "mechanical" allocation of water from the liquid phase and the use for drying of rotary-tubular drying furnaces with energy 4-6 times lower than the spray dryer [5,6,9]. Biological sewage treatment plants with such figures can not accept, that is, it is required a previous deep cleansing liquid phase. Resolving this issue will allow companies to meet the requirements of the Federal Law on the full processing of post-spirituos bard. As a result, of the production of alcohol from molasses in Ukraine annually is

produced about 3,0-4,5 m³ concentrated wastewater or 200-300 ths. tons of pollutants. Most businesses do not utilize molasses bard and without treatment together with wastewater it is discharged to the field of filtration, which employs 1,500 hectares of fertile land. This leads to water pollution and even drinking water be runoff, and atmospheric compounds with unpleasant odors, which are formed during the decay of organic matter of wastewater. The most promising method of sewage treatment enterprises of alcohol industry, including bard is biological treatment, the essence of which is the use of microorganisms to release water from unwanted impurities. Since molasses post-spirituos bard belongs to waste with high concentrations of organic matter (biological oxygen is 50-90 thousand. Mg / dm³), it is necessary to apply the method of anaerobic treatment as a preliminary step before aerobic additional cleaning. In anaerobic conditions bacteria decompose organic substrates and biogas is an intermediate product of metabolism [5,6,7,9]. Anaerobic decomposition is divided into several stages, each involving different groups of bacteria. To achieve the high activity of all groups of organisms it is required to provide special conditions for their biological process, anaerobic conditions, humidity, temperature, duration of fermentation, pH, etc.

The purpose of research: task of developing of waste-free technology of recycling post-spirituos bard in connection with the increase of alcohol production is very important.

Results of researches. The proposed technology is virtually zero waste, can radically reduce the negative burden on nature and get:

- * Purified water, in the amount of liquid phase bard processed with the return of 80% for its production and technical needs of the company;
- * The dry residue suitable for use as a feed additive for pets;
- * Biogas containing methane to 70%, volume 0.5 m³ per 1 kg COD bard, with the possibility of its actual use instead of natural gas during combustion in the boilers of enterprises and technology needs;
- * Thermal energy obtained by the cooling output bards.

Integrated technology of utilization grain bard (in the original COD of 60-80 g / l) includes the following main stages:

1. Collection of output bard and preliminary acid fermentation of bard for 12-16 hours by acid bacteria. Simultaneous assertion of dense bards.
2. Filtering of dense bards on mesh drum filters with a mesh porosity of 1.5 mm with compartment pellet from the liquid phase bards (RSE)
3. RSE cooled to 40 ÷ 60 0C.
4. Collection and alkalization of cooled RSE to pH = 6.0 – izopotential point of bulk of the dissolved amino acids to maximize their transfer into insoluble colloids.
5. Dehydration of RSE in filter - presses with filtering membrane plates that provide a cake humidity 40 ÷ 50%, and deeply cleansed of suspended solids the filtrate RSE concentration of organic contaminants in HSK- to 15 ÷ 20 g / l.
6. Drying of dehydrated bard and filtered pellet to obtain feed staff on vacuum low-temperature ceramic infrared dryer platted or disc-type dryer SCM.

7. Methane fermentation of filtrate bard in anaerobic bioreactors using special enzymes that activate fermentation and reduce fermentation of dissolved organic compounds 18 ÷ 36 hours.
8. Clarification of treated wastewater in bioreactors at high speed shelf landfill with reuse of sludge settled in bioreactors.
9. Return of 50% clarified in sediment solution with a concentration of residual organic substances COD 1,5 ÷ 2,0 g / l in basic manufacturing, production of alcohol.
10. The refining of the second part of 50% clarified in sediment lagoons by galvanic coagulation and spinel ferritization followed by settling and sorption - mechanical filtration of the level of pollution by COD \approx 30 ÷ 50 mg / l.
11. Use 30% of water after refining for technical needs of the plant (feeding of cooling equipment, flushing of process equipment, etc.).
12. Discharge to the city sewer of 20% of treated water with the main pollution indicators corresponding MAC Gorvodocanal.

Major technological processes.

2.1 Previous filtration, cooling and neutralization. Output grain bard has an acid reaction, high temperature, and about 1% of the total weight of the bards suspended solids in the form of grains - the remnants of particles of grain and malt are corrosive - abrasive environment that when moving rapidly destroys pipelines and technological devices. To prevent this bard is to be collected (averaging) and allowed to settle for 12:00. Thus acid microorganisms at bard continue to process acidic digestion of carbohydrates and amino acids, making an initial hydrolysis of dissolved substrate to the low molecular organic acids and other small molecules. In settling of bard its thick part settles on the bottom of the collection - averagings and then is filtered by sparging mesh drum filters [5,6,7,9]. In the pooled liquid phase of bard there are suspended solids in the form of fine and colloidal suspensions of up to 1 ÷ 2 microns, and dissolved products of acid fermentation, amino acids, vegetable fat and nitrogen-free extractives (ERI) of up to 50% of the total weight of all organic substances contained in Bard, or 3,0 ÷ 4,0% a.s.v. of bards [5,6,7,9]. Amino acids are readily soluble in water, while in acidic solutions NH_2 - groups of amino acids protonate and amino acid becomes cation. In an alkaline environment carboxylic acid group is deprotonated and turns to acid anion. The pH at which the amino acid molecule is in solution in the form of bipolar ion (colloidal particles with a minimum solubility), called izopolar point. To translate truly dissolved amino acids in a balanced colloidal state the project provides preliminary alk of original bards to pH = 6 - izopotential point \approx 50% of dissolved amino acids. After preliminary acid fermentation, extraction of pellet and subsequent neutralization to pH = 6.0 bard liquid phase is cooled to a temperature regulated by processes of dehydration and treating leachate subsequent by methane fermentation.

2.2 Separation of phase and drying of dense phase bard.

For the separation of suspended and totally dissolved substances of liquid phase

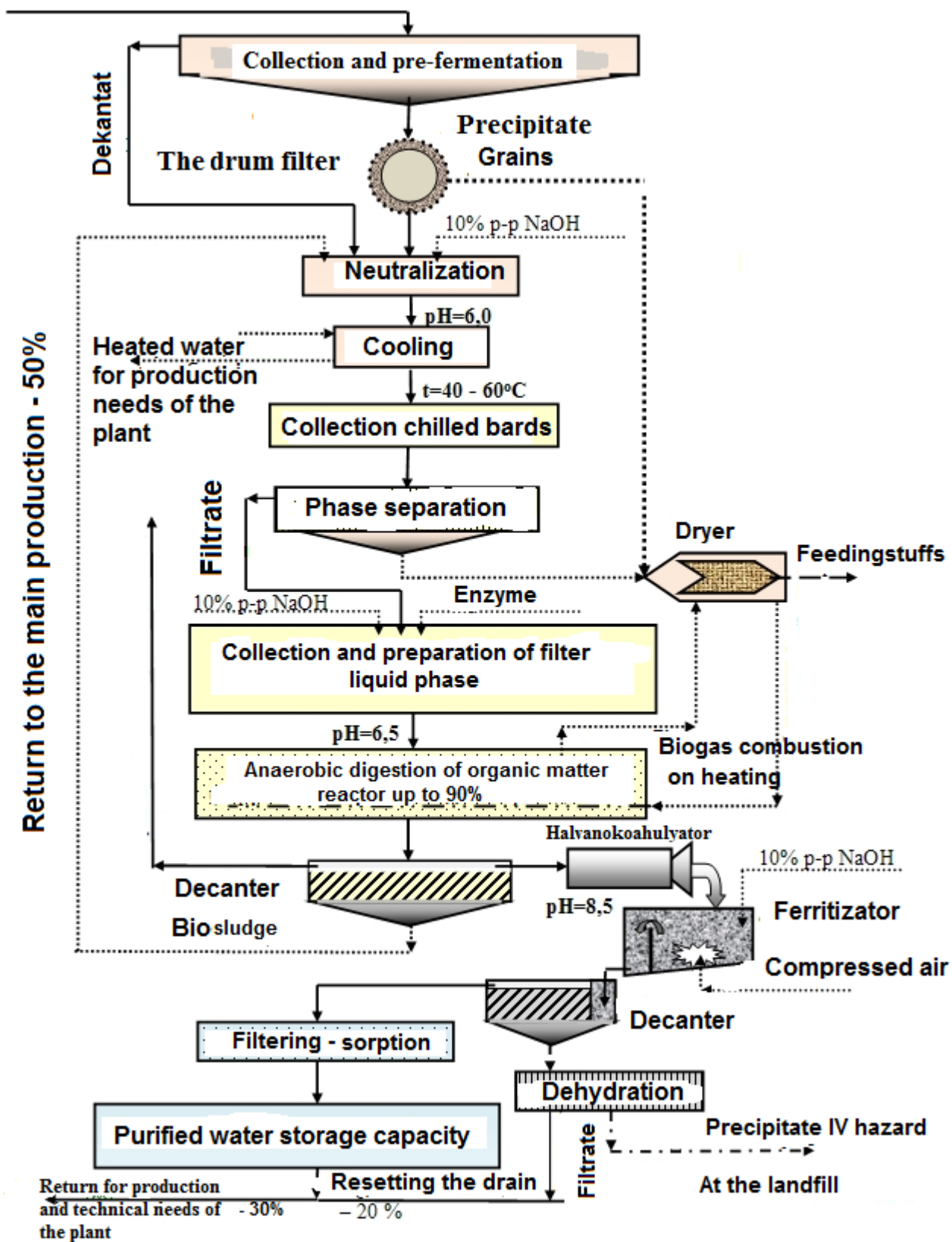


Fig.1. Flowchart of comprehensive full utilization of waste-free technology of grain bards.

bard the technology of utilization provides, as a rule, for mechanical separation and drying of dense phase and getting liquid phase (filtrate) - liquid phase of bard (ZHFB) or energy-intensive and highly costly evaporation of bard, getting at this

acidic condensate and difficult to utilize residual. Virtually all equipment that is now to separate dense and liquid phases of bard (separators, centrifuges, filter - press using a filter cloth, tape vacuum - filters, etc.) completely solve this problem. However, in the liquid phase or filtrate a large number of fine and colloidal pollution passes which reduces the effectiveness of further purification stages and generally the whole process of bard recycling. The real technology offers dehydration of bard on automated filter - presses with filtering membrane plates that allow to get not only cake with humidity $40 \div 50\%$, but deeply cleansed of suspended solids filtrate of liquid phase bard of the concentration of organic contaminants in HPK- $15 \div 20 \text{ g / l}$. Filter presses are equipped with a periodic regeneration (washing) of membrane platinum, which ensures high stability and usability of the equipment. Keck, with humidity $40 \div 50\%$ (according to passport data of filter presses) and then sent for drying. Given that proteins (amino acids) destructing at temperature $> 82 \text{ }^{\circ}\text{C}$, technology provides drying of dehydrated of bard and filtered grains on vacuum low-temperature ceramic infrared dryers.

2.3 Anaerobic purification of filtrate of bard liquid phase.

Purification of the concentrated organic contaminants of protein and carbohydrate nature (with COD of 20 to 80 g / l) cost-effective and technologically feasible only by anaerobic biological method. In anaerobic conversion of organic matter to methane under the influence of microorganisms (bacteria, anaerobic sludge) should be implemented consistently 4 stages of expansions. Separate groups of organic contaminants (carbohydrates, proteins, lipids / fats) in the first hydrolysis are converted to the appropriate monomers (sugars, amino acids, fatty acids). Then these monomers in the enzymatic decomposition (atsydohenez) become short-organic acids, alcohols and aldehydes, which are then oxidized into acetic acid, which is associated with hydrogen. Only then comes the turn to methane during methanogenesis creation. As a by-product along with methane also carbon dioxide (CO_2) is formed. All conversion processes are closely linked with each other and must occur in anaerobic capacity reactor in a strictly prescribed manner, as any violation of one of the intermediate stages leads to disruption of the process. Therefore it is require-a precise design of treatment facilities and their settings to the appropriate waste water. For the liquid phase bard in practice not all possible reactions of decomposition are made. In the so-called adaptive stage the choice of a particular way of decomposition of organic matter as a result of biological process of relevant microorganisms is made [5,6,7,9].

Depending on which class of organic compounds in the wastewater prevails, the composition of biogas and share of methane in it changes (see. Table 1). Carbohydrates in most cases decompose easily, but they provide a relatively smaller proportion of methane. During the decomposition of fat larger number of biogas with high methane content in it is formed, however, they decompose very slowly. In addition, fatty acids that are formed as by-products of the decomposition

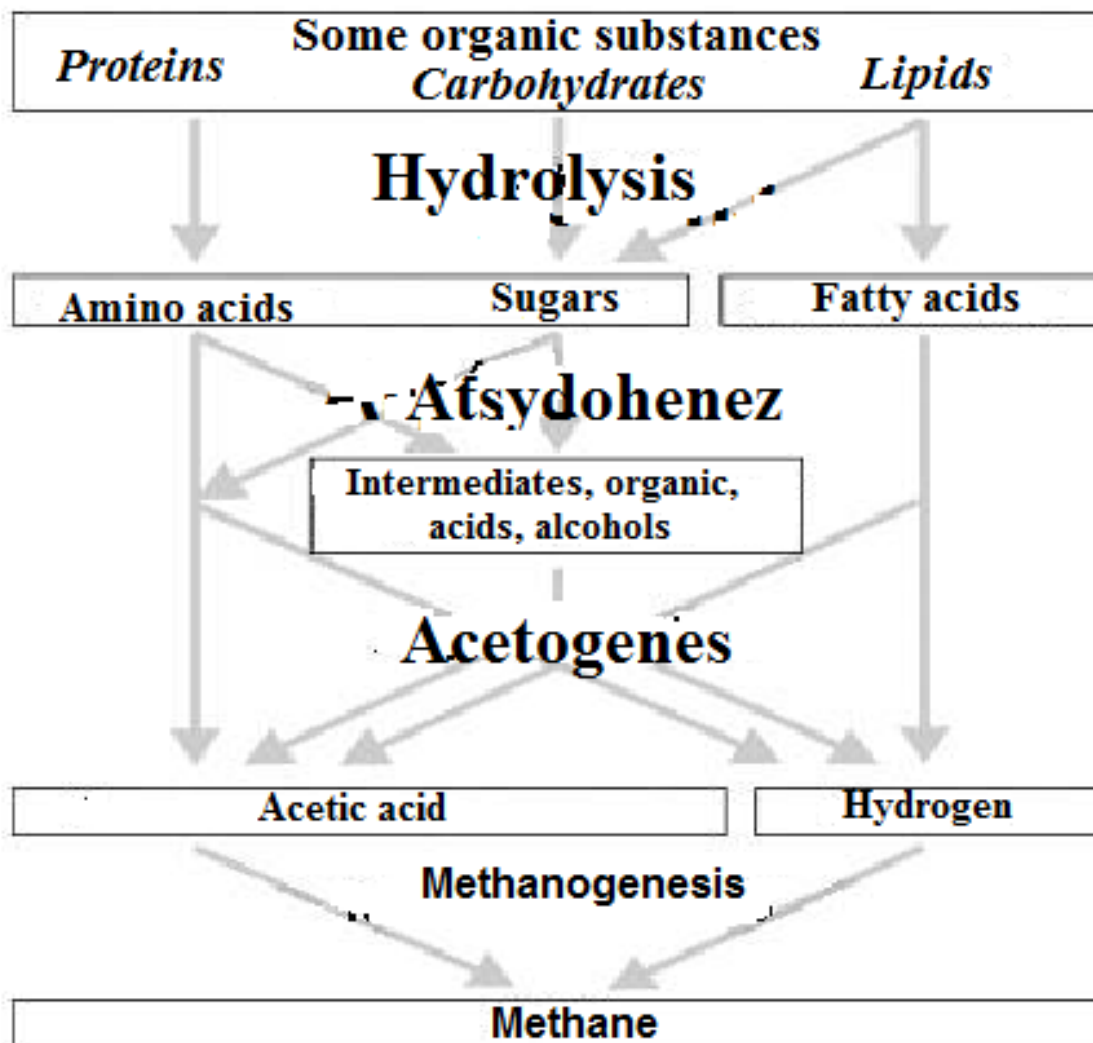


Fig.2. The stages of decomposition of anaerobic transformation.

of fats can interfere with the whole process of decomposition. Table 2.11 shows that for grain bard, consisting AS in which about 40% protein, 37.3% carbohydrate and just 5.6% of vegetable fat, anaerobic digestion technology is most preferred. However, it should be borne in mind that for each type of bard (from wheat, corn, potatoes and molasses raw) technology and the technical specifications for the full utilization should be developed on the basis of research work in the process of which it is determined the optimal conditions of decomposition of organic contaminants, are in the liquid phase of bard [5,6,7,9].

Table 1. Biogas yield and methane fraction of it, depending on substance

Class of substances	Biogas yield [Nl / g substrate]	The proportion of methane [%]
Carbohydrates	0,83	50
Protein	0,72	71
Fats / Oils	1,43	70

In our technology 2 ÷ 4 stages of biochemical processes fermentation is carried out in mesophilic (or termofyl) mode in anaerobic bioreactors with rising fluid flow through a layer of anaerobic sludge (Upflow Anaerobic Sludge Blanket reactor, UASB) with special enzyme accelerators [5,6,7, 9]. Regulated hydrodynamic regime and the bacterial composition of the sludge and enzymes provide high performance of reactor. Specific power of anaerobic digestion of reactor (without enzymes - accelerators of fermentation processes) is more than 10 kg COD / m³ a day with duration of the fermentation of dissolved organic contaminants within 18-36 hours. This technological process allows to remove about 90% of the mass of organic pollution in the concentration of COD at the outlet of the bioreactor within 1,5 ÷ 3,0 g / l. To extract the solutions imposed after methane fermentation of sludge technology provides clarification of waste at speed shelf landfill 50% of maximum purified water gets back into the main hall for cooking grains part of silt is settled back in head of methane fermentation. As a result of the anaerobic purification organic compounds decompose to carbon dioxide and methane (biogas). The averaged output of methane by biochemical reactions on real dirt grain bards is 0.35 m³ methane per 1 kg COD. The composition of biogas: CO₂ - 35 ÷ 30%, and CH₄ - 65 ÷ 70%, which allows you to safely burn it in the platted dryer in the boiler plant or the flare [5,6,7,9]. The formation of excess biomass during the anaerobic process is 3.0% of the fermented mass of organic matter, which rushes up to the head of recycling process for dewatering and drying.

3.4 Deep purification of RSE.

Deep refining of purified in bioreactors concentrated solutions of organic contamination with residual concentration COD ≈ 3,0 ÷ 1,5 g / l should be cleared with the requirements of enterprises (300 ÷ 350 mg / l or less). This post-treatment can be performed by aerobic method using 2 ÷ 3 degrees aerotanks, biofilters, other special equipment. The processes take place with a lot of excess sludge, with energy-intensive aeration system, using large areas. In our technology deep purification of waste water is carried by electrochemical method using galvanic coagulation and spinel fertilization. The most promising of these are Al (E_{0n} = -1.662 V), Fe (E_{0n} = - 0.44 V), Cu (E_{0n} = + 0.337 V) and carbon C (E_{0n} E = 0.36 V). The processes are carried out in "galvanic coagulators" - flow rotating drums, in which as electrodes of galvanic steam iron scrap mixture of crushed coke is loaded without introducing chemicals. The mechanism of cathodic reduction of organic compounds greatly depends on the capacity of the cathode (in case galvanic coagulation - iron or aluminum), whose influence on the course of the electrode process was offered by several theories. Anod oxidation in many ways is very similar to the action of strong oxidizing agent. However, the existing in practice mechanism of oxidative process compared with cathode recovery process is more complex, and as yet not fully established. It is assumed that in an aqueous solution hydroxyl ions discharge at low potential galvanic steam to form hydroxyl radicals, which, when combined, give hydrogen peroxide. Hydrogen peroxide then reacts with the organic compound, causing oxidation, or decompose to form oxygen and water:

Oxidation



The reaction takes place or with hydroxyl radicals, which are intermediate products, or as a strong oxidizing agent of oxygen. Further purification of organic substances is carried out in ferritizator, by sorption of activity glandular pulp of halvanic coagulation, followed by settling and filtering on the combined filtration-sorption filter. Purified water in amount of 30% returns for production and technical needs of the plant, and 20% to maintain a stable salt of recycled water is discharged into the city sewer. The sludge of this cleaning rate is non-toxic product, with a class of hazard - IV, which after dewatering can be disposed of or exported to the landfill and used as a waterproofing layer [5,6,7,9].

Conclusions. Proposed complex technology of utilization grain bards in terms of alcohol production growth is almost zero waste and allows you to get: purified water, in the volume of the liquid phase bards processed with its return of 80% for production and technical needs of the company; dry residue, suitable for use as a feed additive for livestock, biogas containing 70% methane with volume 0.5 m³ per 1 kg COD bard, with the possibility of its actual use instead of natural gas during combustion in boilers and technological needs of enterprises; thermal energy obtained by the cooling of output bard.

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БЕЗОТХОДНАЯ ТЕХНОЛОГИЯ УТИЛИЗАЦИИ ПОСЛЕСПИРТОВОЙ БАРДЫ

Уминский С.М., Макаrchук В.И.

Ключевые слова: барда, этанол, переработка, анаэробное разложение, влажность, температура, биореактор.

Резюме

Предложена комплексная технология утилизации зерновой барды, которая позволяет получить очищенную воду, сухой остаток, пригодный для использования в качестве кормовой добавки для домашних животных, биогаз, тепловую энергию, получаемую в результате охлаждения выходной барды.

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Summary

The complex technology utilization grain bards which can get clean water, dry residue, suitable for use as a feed additive for livestock, biogas, thermal energy obtained by the cooling output bard has been offered.