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Original scientific paper

RETURNABLE BAKING WASTE — A NEW TYPE OF RAW MATERIALS FOR DISTILLATES PRODUCTION (PART I. BIOCHEMICAL COMPOSITION OF RAW MATERIALS)

Ludmila N. Krikunova, Elena V. Dubinina*, Valentina P. Osipova

All-Russian Scientific Research Institute of the Brewing, Non-Alcoholic and Wine Industry — Branch of the V.M. Gorbatov Federal Research Center for Food Systems of Russian Academy of Sciences, Moscow, Russia

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returnable bakery waste, biochemical composition

ABSTRACT

The paper gives an assessment of biochemical composition of various types of returnable baking waste, pre-grouped into five groups depending on recipe and bakery products production method, in comparison with traditional types of starch-containing raw materials — wheat and rye. It has been established that returnable baking waste has significant advantages over grain raw materials in terms of starch content and structural and mechanical properties, which will eliminate grinding cost. An analysis of carbohydrate complex of returnable baking waste showed that waste groups that include rye flour contain more glucose than groups derived from wheat flour, which can positively affect the fermentation process. The study of protein complex revealed that mass fraction of soluble protein was determined by type of raw material used to produce products. It is shown that the best raw materials for distillates production, from standpoint of protein complex evaluating, are samples of returnable baking waste products obtained from rye-wheat bread. The mineral composition (K^+, Na^+, Ca^{++}, Mg^{++}) of ash of various waste types was studied and it was found that products from wheat flour contain less potassium, calcium and magnesium than from rye-wheat, and no significant differences were found in sodium content. Identified distinctive features in biochemical composition of certain groups of returnable baking waste products are recommended to be taken into account when developing optimal technological regimes for their processing in distillates production.

1. Introduction

The trends observed in Russian alcohol market for shift in consumer demand towards alcoholic drinks with original taste and aroma characteristics, for example, whiskey, fruit vodka and others, lead to the need to search for new non-traditional types of raw materials. Due to increasing interest of domestic consumers in this group of strong alcoholic drinks, All-Russian Scientific Research Institute of Brewing, Non-Alcoholic and Wine Industry specialists developed a number of innovative technologies for distillates from starch-containing raw materials (different types of grain and malt), Jerusalem artichoke, and cultivated and wild fruit raw materials [1,2,3,4,5]. One of the new, promising types of raw materials for distillates production may be returnable waste from baking industry. Processing this type of raw material will not only expand raw material base of enterprises, but will also solve the problem of recycling baking industry waste.

Bakery waste is a marriage formed at bakery and products not sold in distribution network [6,7]. The appearance of bread defects (the reason for marriage), in most cases, is caused by mismatch of flour quality and technological process deviation at one of production stages, storage and transportation. The amount of defective products can reach more than 2% of the total output. In addition, in recent years there has been negative practice of returning unsold products to supplier by large chain trading companies. The share of returned products is about 10%, and in some periods it can reach 20%. The grain balance of the country from this annually loses about 3 million tons of wheat and rye. For bakery industry, this costs an average of 30 billion rubles a year. Thus, the use of baking production returnable waste is, of course, an urgent task.

The consumer properties of distillate-based alcoholic drinks are formed due to various groups of volatile components, and their composition and concentration are determined by biochemical composition characteristics of raw materials, including carbohydrate, protein complexes, organic acids, mineral and vitamin composition [8,9,10, 11]. The selected yeast race has significant effect on aromatizing substances formation during raw materials fermentation [12]. At distillation stage, the method and operating parameters of the process are decisive [13,14].

Returnable baking waste, as well as traditional grain raw materials intended for distillates production, are starch-containing. However, biochemical composition of this raw material type is significantly different due to the fact that flour components undergo profound changes in technological processes choir for bread production.

The research purpose was to assess prospects for use of returnable baking waste for distillate production.

2. Materials and methods

The objects of study in the work as starch-containing raw materials were used samples of wheat and rye (food and feed purposes) and returnable baking waste obtained from both wheat flour and a mixture of rye and wheat flour in different ratios, in addition to recipe for individual products included granulated sugar, vegetable oil, and complex additives. The used raw materials were products of Moscow industrial enterprises (bakery No. 24, «Peko» bakery, «Cheryomushki» bakery, Moscow bakery and confectionery «Kolomenskoye», «Nizhegorodsky khleb OOO» (Limited Liability Company), «Russky khleb OOO» (Limited Liability Company), «Cherkizovo OAO» (Open Joint-stock Company). Samples were obtained from products after their storage for 3 days by cutting into cubes, drying under mild conditions (up to 100 °C) and grinding to obtain grains of a certain particle size (similar to the process of obtaining breadcrumbs).

Biochemical composition assessment of returnable waste from bakery industry included determination of following indicators [15,6]: moisture mass fraction (drying method to constant weight); starch (Merkel modification chemical method); free sugars and amino acids mass concentration (HPLC method); mass protein concentration (Kjeldahl method); ash mass concentration (ashing method using accelerators); cations concentration in ash (capillary

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electrophoresis method); soluble proteins mass concentration (Lowry method); amine nitrogen mass concentration (copper method).

3. Results and discussion

3.1. Biochemical composition features of different types of starch-containing raw materials

Depending on recipe and method of bakery products production, samples of returnable waste from bakery production were divided into following groups:

- group I (hearth wheat bread, shaped wheat bread, white bread);
- group II (sliced loaves);
- group III (wheat-rye hearth bread);
- group IV (hearth rye-wheat bread, shaped rye-wheat bread);
- group V (rye-wheat custard bread).

The main indicators of biochemical composition of these returnable waste groups were evaluated in comparison with traditional types of starch-containing raw materials — wheat, rye grain (Table 1).

Table 1

Biochemical composition comparative characteristics of various types of starch-containing raw materials

Raw material type	Mass concentration,%			
	Moisture	Starch	Protein	Ash
Wheat	12.5–13.9	52.0–55.2	11.7–12.1	2.3–2.9
Rye	10.5–13.6	46.0–53.1	7.5–10.0	2.8–3.2
Returnable waste:				
— group I	4.7–6.4	61.2–66.3	12.4–12.7	1.9–2.3
— group II	5.0–5.5	62.5–64.6	11.1–12.2	1.9–2.1
— group III	4.0–4.6	58.0–60.4	11.5–11.9	2.4–2.6
— group IV	4.3–5.5	47.7–64.8	10.9–12.2	2.5–2.8
— group V	5.5–5.9	47.5–54.3	9.0–10.1	2.7–2.8

It was found that returnable waste moisture content, varying between 4.0–6.4%, is lower than grain moisture content, which is associated with change in structural and mechanical bread properties — its increased porosity. A significant difference between this new type of raw material is increased starch content — the main component that determines distillate yield from raw material unit. Revealed fact is due to the fact that during flour production, the external anatomical grain parts having reduced starch concentration are removed from production. Inverse relationship are ash indicators. The protein concentration in baking waste is determined not only by its content in flour, but also by yeast biomass protein.

When comparing biochemical composition of individual groups of returnable bakery waste, it was found that it depends on type of used raw materials. Such an important indicator for distillate yield as the starch content is determined primarily by percentage of wheat and rye flour used in bakery products production. Samples of groups I and II, obtained from wheat flour, are characterized by higher content of this indicator compared to other samples, production of which used rye flour. Those from standpoint of evaluating returnable waste to be used as raw material for distillate output, preference should be given to samples obtained from wheat bread. Moreover, it was noted that range of variation in starch mass concentration in these samples is in range from 61.2% to 66.3%. For group III samples obtained from wheat-rye bread, the starch content is reduced, but not significantly compared with samples of groups IV, V. It was also found that variation interval for last samples varies more significantly (within 47.5% — 64.8%) than for wheat bread samples. The revealed fact is associated with ability of product manufacturers to change, within certain limits, the percentage of rye flour use in recipe.

However, dependence of returnable waste type on such an indicator as total protein content was not detected. On contrary, ash mass concentration when receiving returnable waste using rye flour against samples obtained from wheat flour increases by 1.2–1.3 times.

3.2. Carbohydrate complex assessment of returnable baking waste

It is known that alcoholic yeast among carbohydrate components, which include starch, non-starch polysaccharides (fiber and hemicelluloses), dextrins and free sugars, can directly use only the latter. In this regard, composition and concentration of free sugars in feedstock can affect the process of wort obtaining and fermentation, especially in first stages.

In the work, free sugars determination in samples of returnable baking waste was carried out by their aqueous extraction followed by determination by HPLC (Table 2).

Table 2

Free sugar content in returnable bakery waste samples

Raw material group	Sugar content,%				
	Fructose	Glucose	Sucrose	Maltose	Maltotriosis
Group I	0.40–0.77	0.07–0.24	0.04–0.11	1.29–2.98	0.29–0.46
Group II	0.73–1.65	0.32–0.68	0.07–0.18	1.07–1.88	0.18–0.59
Group III	2.30–2.66	1.07–1.42	0.03–0.08	1.58–1.67	0.35–0.45
Group IV	0.64–1.05	1.09–1.44	0.05–0.11	0.60–1.03	0.23–0.30
Group V	0.55–0.81	0.99–1.31	0.01–0.03	0.65–0.83	0.30–0.41

It was found that within separate groups of returnable baking waste products, the amount of free sugars varied widely. For example, for samples of group II — from 2.38 to 4.40%. The maximum total content of free sugars (5.33–6.28%) was noted in samples of group III (wheat-rye bread), which may be due to use of baking improvers in formulation of these products. In general, the influence of returnable waste type on this indicator was not revealed.

In samples, which included rye flour (samples of groups III, IV, V), an increased concentration of glucose was revealed. Considering the sequence of consumption of various carbon sources (polyauxia) inherent in yeast cells, an increased concentration of glucose in raw materials is a positive factor, as it contributes to the intensification of the fermentation process, especially in initial stages.

3.3. Protein complex evaluation of returnable baking waste

When assessing bread and bakery products nutritional value from the point of view of protein complex study, total protein content and amino acid composition of proteins are determined. Protein content in bread varies depending on its type and flour type from 5.6 to 9.0 g per 100 g. Food products proteins consist of 8 essential amino acids, which include tryptophan, leucine, isoleucine, valine, threonine, lysine, methionine, phenylalanine, and 12 essential amino acids. Typically, essential amino acids total about 36% of total amino acids in human nutrition. The amino acid composition of bread is affected by chemical composition, type and grade of flour from which it was prepared, composition of other recipe components, etc.

An assessment of nutritional value of bread and bakery products adopted in baking industry doesn't provide for determination of protein and free amino acids soluble forms, information about content of which is necessary to predict processing of certain types of returnable baking waste in technology of distillates and alcoholic drinks based on them. The data on protein complex study formed in accordance with products types, variety, flour type, adopted technology for groups production are presented in Table 3.

Table 3

Protein complex of returnable baking waste

Raw material group	Mass fraction,%	
	Soluble protein	Amine nitrogen
Group I	0.53–0.73	0.22–0.26
Group II	0.65–0.85	0.24–0.29
Group III	0.75–1.13	0.22–0.34
Group IV	1.32–1.88	0.31–0.38
Group V	2.52–2.90	0.18–0.20

It was found that soluble protein mass fraction was determined by type of raw material used for raw material products. So, samples of groups I and II, in production of which only wheat flour was used, were characterized by lower value of this indicator compared to samples developed from rye and wheat flour mixture (2.5–3.5 times). The maximum content of soluble protein was characterized by samples of group V — rye-wheat custard bread «Borodinsky», production of which uses special technological methods.

In formulations for production of group III samples, developed, unlike other groups, according to technical conditions, the main component is wheat flour, but it is allowed to use complex food additives, which could cause an increased content of soluble protein in number of samples.

The content of amino nitrogen in first three groups, with exception of individual samples of group III, was at level of 0.22–0.29%. The increased value of this indicator for returnable baking waste (group IV) is noted. Samples of group V, in which rye flour component is installed, have minimum level of amino nitrogen. The probability of all, established fact is associated with more active reaction of melanoidin formation in production of «Borodinsky» bread.

It is known that enzymatic attackability of proteins is primarily determined by their solubility, therefore, higher content of soluble protein in feedstock will provide sugared wort with high nitrogen-digestible yeast content (low molecular weight peptides and amino acids). The amine nitrogen index also characterizes content of amino acids and, to a certain extent, mineral nitrogen compounds in feedstock.

Thus, obtained research results showed that the best raw materials for distillates production, from the point of view of protein complex evaluating, are samples of returnable baking waste from groups IV, V, that is, rye-wheat bread.

In production technology of distilled drinks, when assessing raw materials quality indicators, it is important to know qualitative composition and content of free amino acids. This is due to the fact that amino acids, firstly, are one of the sources of nitrogen nutrition for yeast and determine fermentation rate, and secondly, as a result of their deamination, higher and aromatic alcohols are formed, which form the basis of alcoholic drink aroma. Thus, threonine, valine, leucine, and phenylalanine are precursors of propyl, isobutyl, isoamyl, and phenylethyl alcohols formation, respectively [17].

Free amino acids composition and content of studied groups of samples are presented in Table 4. It has been established that the main amino acids of returnable bakery waste are aspartic and glutamic acids, serine and alanine, of which aspartic acid is highly absorbed, and glutamic acid and serine are poorly absorbed by yeast cell; alanine enhances yeast enzymatic activity [17,18]. When comparing amino acid composition of different groups of returnable waste, it was found that in comparison with other groups, samples of group IV contain an increased amount of easily assimilable aspartic acid and alanine with an approximately equal content of glutamic acid and serine. Thus, from standpoint of assessing raw materials amino acid composition, these samples (rye-wheat bread shaped and hearth) are the best.

In general, all studied samples were characterized by low total content of free amino acids, therefore, when using returnable baking wastes as raw materials for distillates production at the stage of wort preparation and fermentation, it is necessary to provide enzymatic hydrolysis of protein.

3.4.Assessment of returnable bakery waste mineral composition

Information on cationic composition of new type of raw material can be the basis for highly efficient technologies development for a number of reasons, including effect on enzymatic hydrolysis of raw materials polymers and yeast cells metabolism.

Table 4

Amino acid composition of returnable baking waste

Amino acid name	Content, mg%				
	Group I	Group II	Group III	Group IV	Group V
Aspartic acid	6.5–12.7	7.7–9.2	9.4–33.6	24.7–33.6	15.1–17.8
Glutamine acid	10.9–11.8	10.9–15.8	15.1–40.3	12.4–22.1	10.9–11.7
Asparagine	6.6–9.8	5.1–6.3	5.8–9.5	4.4–9.9	1.1–1.3
Histidine	2.5–8.4	3.1–4.4	2.5–4.1	7.6–11.4	0.9–1.1
Serine	22.7–25.0	18.9–20.3	23.2–75.6	22.9–50.2	19.8–21.4
Glutamine	3.3–7.3	5.0–6.5	5.2–17.1	4.2–4.8	3.8–4.4
Arginine	1.8–2.3	1.0–2.6	2.0–2.1	0.6–3.6	1.0–1.4
Glycine	1.0–3.1	2.6–4.0	5.1–13.2	0.9–6.3	1.5–1.8
Threonine	2.3–5.7	2.8–4.0	4.1–12.9	10.4–18.2	6.6–7.0
Alanine	14.9–15.4	9.5–12.6	12.0–16.9	15.5–35.7	7.5–9.8
Tyrosine	2.5–3.3	1.8–3.7	3.0–7.3	3.2–8.0	3.9–4.3
Valine	4.1–8.8	6.1–7.2	7.1–12.3	10.1–17.3	2.1–3.0
Methionine	2.2–3.7	2.6–5.0	3.5–4.7	2.0–3.6	0.9–1.1
Tryptophan	6.7–12.7	6.4–9.5	9.1–24.6	12.2–17.9	1.3–1.5
Isoleucine	3.9–6.6	3.0–4.4	4.0–8.4	3.5–9.7	3.0–4.0
Leucine	1.6–3.7	1.4–2.9	1.9–10.3	6.9–10.5	2.1–2.6
Phenylalanine	2.1–4.9	1.6–2.3	2.2–5.7	5.9–11.8	1.5–1.8
Lysine	1.1–1.8	1.0–1.4	1.3–6.5	2.2–6.2	0.6–1.0
TOTAL:	114.2–118.9	95.8–117.5	116.5–305.1	199.4–224.5	83.6–94.0

It is well known that Ca++ ion stimulates enzymes activity such as alpha-amylase, beta-amylase, and protease. In addition, it protects alpha-amylase from thermal inactivation, increases digestibility of protein by yeast, neutralizes toxins that reduce yeast cells growth and reproduction.

The Mg++ ion is necessary for yeast as contributing to formation of certain enzymes in starch-containing raw materials fermentation. However, it must be remembered, that excess magnesium, like calcium, can react with phosphates, while magnesium phosphates are more soluble than calcium, in addition, magnesium can give product bitter aftertaste.

The Na+ ion influences the processes of water and nutrients entering to yeast cell, however, its excess content can worsen the process of wort fermentation from returnable bakery waste. It was previously established that amount of table salt used in wheat bread production doesn't adversely affect alcohol yeast [19]. It was advisable to obtain data on sodium content in other products types of baking industry.

The K+ ion affects the process of raw materials polymers enzymatic hydrolysis, in certain quantities it increases activity of a number of enzymes, in increased ones it can reduce it.

In the work, ash samples obtained from certain types of returnable bakery waste were analyzed using atomic absorption spectrometry, which involves sample preparation using nitric acid, for sodium, potassium, calcium and magnesium content (Table 5).

Table 5

Mineral composition of various types of starch-containing raw materials

Raw material group	Metal content in ash, %			
	Na^{+}	K^{+}	Ca^{++}	Mg^{++}
Group I	24.2–37.7	4.9–7.1	0.6–0.8	0.9–1.4
Group II	27.2–30.8	6.6–7.7	0.7–0.8	1.0–1.3
Group III	27.5–28.6	5.0–6.2	0.5–0.9	0.9–1.3
Group IV	22.5–25.2	8.9–13.7	0.7–0.8	1.6–3.1
Group V	17.1–17.9	16.8–17.6	0.9–1.4	4.0–4.8

It was established that the main metal in samples is sodium, content of which, according to published data, in flour is insignificant; its amount in bread and loaves depends on amount of table salt introduced according to recipe. In general, the content of 4 analyzed metals in ash is 33.2–44.1% of ash mass fraction in samples.

Additionally, the content of metals in initial samples of returnable baking waste, calculated in table in mg%, was calculated. It was found that sodium content in samples ranges from 483.0–765.3 mg%, while there is no clear dependence on raw materials types. Rye and wheat varieties and varieties of wheat flour are included in established limit, which doesn't adversely affect the yeast development, and in samples from custard bread (Group V) this value is minimal.

Potassium content depends, as established, on used raw materials type. Wheat bread, wheat flour loaves and wheat-rye bread contain less potassium than rye-wheat bread. Moreover, the range of variation of this indicator in samples 8, 9, 10 and 11 is 228.7–380.9 mg%, i.e. varies significantly. Revealed fact can be associated with number of reasons. First, product manufacturers are allowed to vary the ratio of rye and wheat flour depending on raw materials biochemical composition. Secondly, metal content can be determined by varietal products characteristics. In the work were used samples of rye-wheat bread «Darnitsky», «Stolichny», «Ukrainsky novy».

Specific recommendations on potassium ions content in raw materials used for processing in fermentation plants are not given in literature. It is known that potassium content in wheat flour increases with decrease in grade and varies from 120 to 250 mg%, in rye flour it is on average: 350 for break flour, 400 mg for wholemeal flour [20]. In analyzed samples of returnable baking waste products, potassium content is near indicated values.

Analysis of calcium and magnesium content in samples of returnable bakery waste made it possible to establish that products from wheat flour contain less of these metals than from rye-wheat. It is also known that these metals can be presented in form of water-soluble and insoluble salts, which must be taken into account when receiving wort and issuing recommendations on mineral composition of water used in production.

4. Conclusion

Biochemical composition evaluation of new type of starch-containing raw materials — returnable baking waste, including starch determination, total protein, soluble protein, amine nitrogen, free amino acids and mineral compounds, showed the promise of their use for distillates production.

The results analysis showed that returnable bakery waste has significant advantages over grain raw materials in structural and mechanical properties (don't require grinding costs) and in content of main component responsible for distillate — starch output.

Distinctive features in biochemical composition of individual groups of returnable baking waste are identified, which must be taken into account when developing optimal technological regimes for their processing in distillates production.

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AUTHOR INFORMATION

Ludmila N. Krikunova — doctor of technical sciences, professor, leading researcher, Department of spirits, All-Russian Scientific Research Institute of Brewing, Beverage and Wine Industry — Branch of V.M. Gorbatov Federal Research Center for Food Systems of RAS, 119021, Moscow, Rossolimo str., 7. Tel.: +7–499–255–20–21, e-mail: cognac320@mail.ru

Elena V. Dubinina — candidate of technical sciences, Leading researcher, Department of spirits, All-Russian Scientific Research Institute of Brewing, Beverage and Wine Industry — Branch of V.M. Gorbatov Federal Research Center for Food Systems of RAS, 119021, Moscow, Rossolimo str., 7. Tel.: +7–903–577–53–62, e-mail: elena-vd@yandex.ru
*corresponding author

Valentina P. Osipova — candidate of technical sciences, head of the Laboratory, Laboratory of Instrumental Methods of Analysis, All-Russian Scientific Research Institute of Brewing, Beverage and Wine Industry — Branch of V. M. Gorbatov Federal Research Center for Food Systems of RAS, 119021, Moscow, Rossolimo str., 7. Tel.: +7 916–508–57–32, e-mail: cognac320@mail.ru

Authors are equally relevant to the writing of the manuscript, and equally responsible for plagiarism

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