

Potato Granule Processing Line by-Products as Feedstock for Ethanol Production

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Received: 11 October 2011

Accepted: 26 April 2012

Abstract

Our research assessed fermentation characteristics of mashes prepared from oversized waste granules containing potato peel and potato dust formed during dried potato granule production. Due to the high water binding capacity of materials, applied fermentation was carried out at low gravities of 10 and 15% w/w of raw materials dry matter. Mashing of materials resulted in total soluble sugar (glucose, maltose, and maltotriose) concentrations ranging between 95.10 and 66.33 g·L⁻¹. Fermentation dynamics evaluation showed that CO₂ secretion was nearly over after 24 h. In all the samples collected, yeast utilized the whole amount of sugars after the first day of the process. Ethanol production by yeast ended after 24 h of the process, resulting in of 36.86-39.89 g·L⁻¹ concentration for 10% and 54.44-61.66 g·L⁻¹ for samples at 15% concentration. In both variants of concentration higher ethanol yield was obtained in aspiration channel dust.

Keywords: potato granules, by-products, fermentation, ethanol

Introduction

Considering the growing demand for biofuels, we have investigated new raw materials for their production. Bioethanol is one of the most popular biofuels. According to EU directive (2003/30/EC), the content of biofuels in petrol or diesel until 2020 cannot be lower than 20%. Due to the high costs of traditional raw materials (corn, grain, potatoes), their share in the price of produced ethanol can reach even 70% [1]. Also, growing demand for cereals as a material for distilleries can lead to increases in prices of agricultural products destined for food production [2]. These facts are a reason to search for industrial and domestic wastes to be used in production of ethanol fuel [3].

The potato is known as an efficient material for ethanol production [4], although in recent years its importance as a raw material for ethanol production has been decreasing due to high price. While the designation of

potatoes for ethanol production has decreased, the production of their processed products like French fries, chips and dried products such as potato granules and flakes has been growing [5]. In Poland the food industry processes nearly 1.7 million tons of potatoes and ca. 600,000 tons in the starch industry [6]. In the course of potato processing for food products a significant amount of by-products that can be used in other industries is formed. The most important are potato peel waste [7] and potato pulp [8]. However, the mentioned products contain a considerable amount of water, so they have to be directly processed to avoid microbial contamination. Some authors have suggested the use of these materials in isolation of biologically active compounds [9, 10].

To other valuable potato by-products belong oversized granules and dust from aspiration channel, formed during potato granule production. Until now, they have been mostly utilized as animal feed. However, these by-products, rich in gelatinized starch and sugars, can become an efficient raw material for distilleries. They are also very convenient because of their low moisture.

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The aim of our study was to assess the suitability of wastes from potato granule production (oversized granules containing potato peel and dust from aspiration channel) as raw material in ethanol production.

Experimental Procedures

Raw Materials

Materials used in the present study were oversized granules containing potato peel (material A) from fractioning stage and dust from aspiration channel (material B), formed during industrial production of dried potato granules. The materials were obtained from SOLAN (Głowno, Poland). Materials moisture was measured with the use of a WPS 50P weighing dryer (Radwag, Poland). Starch content was determined by polarimetric technique according to standard method [11]. Materials used contained over 92% of dry matter. Concentration of starch was 66.33% (material A) and 70.47% (material B) in relation to total mass.

Enzymes and Yeast

Liquefaction enzyme Termamyl SC, containing thermostable α -amylase from *Bacillus licheniformis*, was provided by Novozymes (Denmark). Saccharification enzymes San Super (glucoamylase from *Aspergillus niger*) and Optimash BG (β -glucanase, xylanase from *Trichoderma reesei*) were provided by Novozymes (Denmark) and Genencor (USA), respectively.

Saccharomyces cerevisiae Ethanol Red industrial yeast strain was used in fermentation experiments. The culture was purchased from Fermentis (France) in a dried form.

Preparation of Fermentation Media

To prepare fermentation media, raw materials were mashed in an LB12 electronic mashing apparatus (Lochner Labor, Germany) using the energy-saving method of pressureless starch release. Mashing parameters were as follows: heating and cooling rate- $2^{\circ}\text{C}\cdot\text{min}^{-1}$, stirrer speed – 150 min^{-1} . The doses of enzymatic preparations and optimal conditions for their activity (temperature, pH) were set on the basis of producer recommendations [12]. Examined raw materials showed the ability to bind water at relatively low temperature. Therefore, to avoid problems with mixing efficiency during mashing we used low substrate concentrations. Preliminary liquefaction stage was applied in order to hydrolyze free starch formed by potato cells disrupted during potato granule processing [13]. Pre-liquefaction was carried out in the conditions of increasing temperature from 50 to 85°C . Mashings were prepared at concentrations of 10% (w/w) (samples A10 and B10) and 15% (w/w) (samples A15 and B15) of raw material dry matter. A detailed diagram of the mashing process is depicted in Fig. 1. Hydrolysis efficiency was calculated on the basis of stoichiometric values of starch conversion into glucose.

Inoculation and Batch Fermentation

Yeast was rehydrated prior to inoculation. To this end, 5 g of dried yeast (dry matter basis) was slurred in 100 mL of sterile water and mildly agitated for 30 min in a sealed 200 mL conical flask. Prepared mashes were inoculated with 5 mL of yeast slurry, which equal initial cell density of 1 g of yeast dry matter per 1 L of mash. Prior to inoculation, pH was adjusted to 5.0 with 1 M H_2SO_4 solution, inoculated and finally supplemented with distilled water to total mass of 250 g. Batch fermentation was conducted anaerobically for 48 h at 30°C in 250 mL conical flasks with 100 mL of fermenting mashes.

Analytical Methods

Fermentation dynamics was determined on the basis of the changes of fermenters mass, caused by CO_2 release. The samples containing 100 mL of fermenting mash were weighed every 3 h until mass changes amounted to less than 0.05 g. The percentage contribution of released CO_2 was compared after each day of fermentation. Alterations in concentrations of substrates (carbohydrates) and metabo-

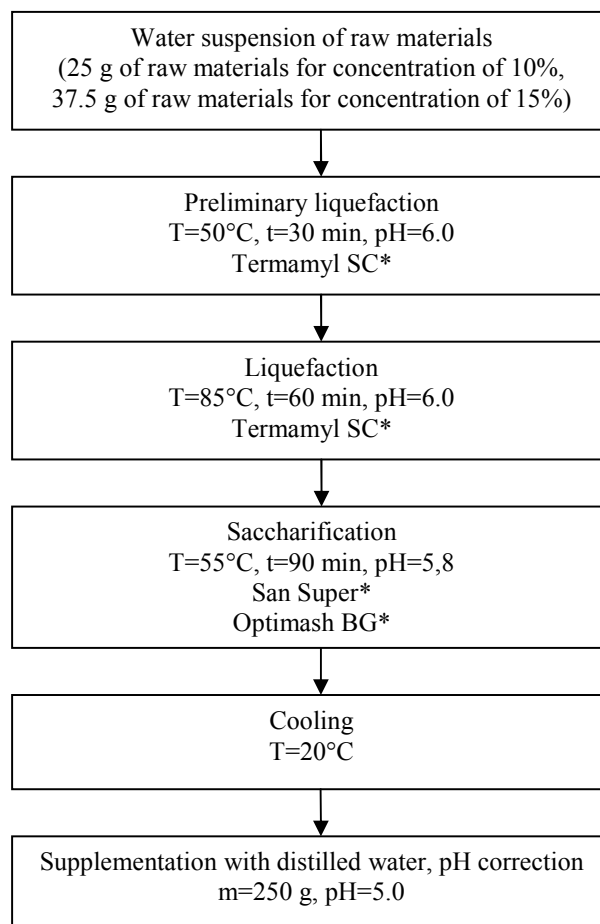


Fig. 1. Preparation of mashes from potato granule by-products. *doses of preparations: Termamyl SC and San Super – 0.1 mL for 10% mash concentration and 0.15 ml for 15%; Optimash BG – 0.12 mL for 10% mash conc. and 0.18 mL for 15% mash conc.

lites (ethanol, glycerol, organic acids) were determined every 24 h of fermentation using high-performance liquid chromatography on a D-7000 chromatograph (Merck, Germany) under the following measurement conditions: flow rate $0.6 \text{ mL}\cdot\text{min}^{-1}$, column temperature 80°C , ion exchange column Aminex HPX-87H (Bio-Rad, USA), refractive index detector at 40°C , eluent $0.005 \text{ M H}_2\text{SO}_4$. In order to prepare the samples for analysis, 10 mL of each sample was centrifuged at 3,000 rpm for 10 min. Supernatant was filtered through a $0.45 \mu\text{m}$ syringe filter (Agela Technologies Inc., USA) into an HPLC vial and analyzed.

Process Parameter Calculations

The assessment of kinetic parameters was performed by calculating sugar consumption rate (calculated over glucose) r_s [$\text{g}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$], rate of ethanol production r_p [$\text{g}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$], and degree of attenuation α [%]. Sugar consumption rates and ethanol production were computed after each day of the process in relation to the state from the previous day, and in the form of mean value according to initial and final quantities of sugars and ethanol.

Overall fermentation yield was estimated by grams of ethanol per 100 g of raw material dry matter – Y_{dm} [$\text{g EtOH}\cdot 100 \text{ g}^{-1}$ dry matter], grams of ethanol per 100 g of starch – Y_{st} [$\text{g EtOH}\cdot 100 \text{ g}^{-1}$ of starch], and by the calculation of practical ethanol yield – Y_p [%] on the basis of stoichiometric values of starch conversion into ethanol, wherein 100 g of starch is converted into 56.80 g of ethanol.

Results

Effect of Raw Material Type and Concentration on Fermentation Dynamics

On the basis of the amount of CO_2 , released by studied fermentation media we calculated dynamics of fermentation process (Fig. 2). After the first day of fermentation

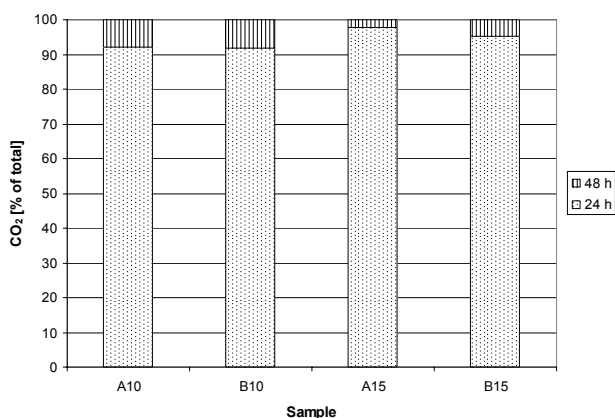


Fig. 2. Effect of raw material type and concentration on dynamics of CO_2 emissions from fermenting mash (A – oversized granules containing potato peel, B – dust from aspiration channel).

Table 1. Hydrolysis efficiency of by-products from potato granule processing line (samples A – oversized granules containing potato peel, B – dust from aspiration channel).

Sample	Mashing efficiency [%]
A10	89.34
B10	93.08
A15	81.75
B15	76.80

more carbon dioxide was released from the samples at concentrations of 15% (95.3% sample B15 and 97.8% sample A15). In both variants of raw material concentration in the mash we observed more advantageous fermentation dynamics regarding the samples prepared from raw material A (oversized granules). Fermentation of studied samples, regardless of the type of raw material and its concentration, was carried out for 48 h, but on the second day of the process the percentage of released carbon dioxide was insignificant, which suggests that fermentation time of studied samples could be shortened to 24 h.

Hydrolysis Efficiency and Dynamics of Carbohydrate Consumption in Fermenting Mash

Hydrolysis efficiency was more advantageous for the samples at lower concentration (Table 1). In this case more glucose was obtained from raw material B (potato dust). An increase in raw material concentration caused significant reduction in mashing effectiveness.

Initial glucose concentration in mash at concentrations of 15% was similar (ca. $90 \text{ g}\cdot\text{L}^{-1}$). In the samples at lower concentration it was $65.77 \text{ g}\cdot\text{L}^{-1}$ in sample A10 and $72.80 \text{ g}\cdot\text{L}^{-1}$ in sample B10 (Fig. 3a). After the first day of fermentation, traces of glucose were only in fermentation feed A15 (ca. $2.1 \text{ g}\cdot\text{L}^{-1}$). During the second day of fermentation yeast did consume all available glucose in investigated samples. The amount of glucose oligomers (maltose and maltotriose) was lower in mash of 10% concentration (Fig. 3b, 3c). After 24 h of fermentation their concentration decreased to below $0.1 \text{ g}\cdot\text{L}^{-1}$. In mash at concentration of 15% we found traces of maltotetraose, but they underwent hydrolysis after the first day of fermentation (data not shown).

Effect of Raw Material Type and Concentration on the Formation of Fermentation by-Products

We found typical by-products of fermentation (glycerol, organic acids) in fermenting mash prepared from studied materials. The amount of glycerol obtained from the mash at 10% concentration after the first day of the process was ca. $2.9 \text{ g}\cdot\text{L}^{-1}$ and did not significantly change until the end of the process (Fig. 4). In mash at higher concentrations the amount of glycerol formed by yeast was higher.

After the first day of the process glycerol concentration in sample A15 equaled $4.35 \text{ g}\cdot\text{L}^{-1}$ and in sample B15 it was $4.89 \text{ g}\cdot\text{L}^{-1}$ and did not actually differ at the end of the process.

We also found higher concentrations of organic acids (succinic, lactic, and acetic) in mashes at 15% concentration (Fig. 5). After 24 h of fermentation, concentrations of succinic acid in samples A10 and B10 were similar (ca. $0.24 \text{ g}\cdot\text{L}^{-1}$). It did not actually change until the end of the process in sample B10. The amount of succinic acid in samples at higher concentrations was similar and did not significantly change during fermentation. After the first day of the process concentrations of lactic acid were slightly higher in the samples prepared from dust from aspiration channel (material B). Its concentration grew in all samples till the end of the process. In the samples at higher concentration, the amount of lactic acid increased on the second day. The quantity of acetic acid in the samples of lower concentration of raw material was nearly constant during fermentation (average $0.15 \text{ g}\cdot\text{L}^{-1}$). The amount of acetic acid in fermentation media at 15% concentration showed elevated value at the end of fermentation (up to $0.43 \text{ g}\cdot\text{L}^{-1}$ in sample A15).

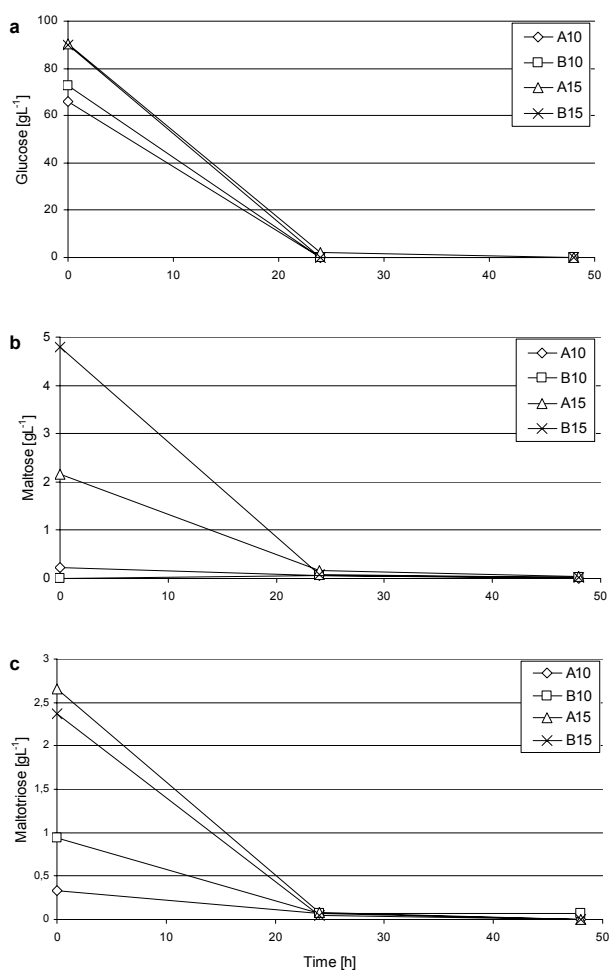


Fig. 3. Changes in glucose (a), maltose (b), and maltotriose (c) concentrations during fermentation of mashes prepared from potato granule production by-products (A – oversized granules containing potato peel, B – dust from aspiration channel).

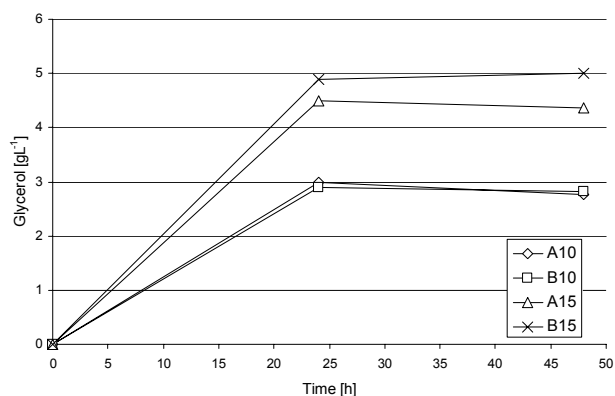


Fig. 4. Glycerol production during mash fermentation (A – oversized granules containing potato peel, B – dust from aspiration channel).

Dynamics of Ethanol Formation and Kinetic Parameters

After the first day of fermentation process, the amount of ethanol formed ranged from $34.24 \text{ g}\cdot\text{L}^{-1}$ to $37.60 \text{ g}\cdot\text{L}^{-1}$ in samples A10 and B10, respectively (Fig. 6). The concentration of ethanol did not significantly change during the second day of the process. A considerably higher quantity of alcohol was observed in media at 15% concentration of raw material. After 24 h ethanol concentration in those samples ranged from $54.44 \text{ g}\cdot\text{L}^{-1}$ (material A) to $61.66 \text{ g}\cdot\text{L}^{-1}$ (material B). As in fermenting media with a lower concentration of raw material, ethanol concentration did not significantly change during the second day of fermentation.

Rates of sugar consumption and ethanol production within the first 24 h of fermentation were higher for samples at 15% of raw material concentration (Table 2). After the second day the values of these parameters were about 0.00 due to substrate (sugars) exhaustion. The degree of attenuation was over 99% in all studied samples except A15 after the first day of fermentation. By the end of the process, nearly 100% of residual sugars was consumed by yeast in each studied sample. The fermentation process provided for high ethanol yield obtained from raw materials. Among the samples at concentration of 10% of raw material, higher ethanol yield was obtained from sample B10 (42.23 g ethanol per 100 g of dry matter and 49.08 g of ethanol per 100 g of starch). The increase of raw material concentration resulted in enhancement of ethanol yield by ca. 2.5 grams of ethanol per 100 g of raw material dry matter and per 100 g of starch. The obtained practical ethanol yield ranged between 83.61 and 94.48% of the theoretical value and, in both concentration variants, was higher for mashes prepared from potato dust (raw material B).

Discussion of Results

In recent years, studies on sustainability of industrial wastes have become particularly important due to the rising prices of traditional distillery raw materials. Potato industry

Table 2. Fermentation parameters for mashes prepared from potato granule by-products.

Sample	r_s [g·L ⁻¹ ·h ⁻¹]			r_p [g·L ⁻¹ ·h ⁻¹]			α [%]		Y_{dm} [gEtOH/100g dry matter]	Y_{st} [gEtOH/100 g of starch]	Y_p [%]
	0-24 h	24-48 h	Mean	0-24 h	24-48 h	Mean	0-24 h	24-48 h			
A10	2.78	0.01	1.40	1.43	0.02	0.73	99.53	100.00	36.66	47.49	83.61
B10	3.13	0.00	1.57	1.57	0.05	0.81	99.58	99.69	42.23	49.08	86.41
A15	4.22	0.12	2.17	2.25	0.00	1.14	97.08	99.91	39.47	50.34	88.62
B15	4.56	0.02	2.29	2.57	0.00	1.29	99.46	99.96	44.70	53.66	94.48

r_s – rate of sugar consumption, r_p – rate of ethanol production, α – degree of attenuation, Y_{dm} – ethanol yield per 100 g of raw material dry matter, Y_{st} – ethanol yield per 100 g of starch, Y_p – practical ethanol yield based on stoichiometric value of starch to ethanol conversion

wastes are especially valuable because of high starch content. Furthermore, with the development of the potato industry, the amount of waste generated is constantly increasing. In Poland, production of dried potato products processed ca. 115,000 tons, and nearly half of this amount is used in production of potato granules [14]. The percentage share of by-products in potato granule production can range up to 20% [13, 15] and, therefore, can generate up to 11,500 tons annually. This may be important in countries where large annual quantities of dried potato products are produced, for example the USA [16].

Another considerable advantage of the mentioned wastes is their low moisture content resulting from production technologies of potato granules. This fact allows us to store raw material for distilleries without the need of costly drying or immediate processing (to avoid microbial contamination), which is a problem in the case of wet waste. Moreover, low water content in the raw material can assure the repeatability of the process.

Despite low moisture and high starch content of the discussed wastes, their sustainability to ethanol may pose some technological problems resulting from changes in raw material during the production of potato granules. In the case of drying of cooked and mashed potatoes, starch solubility is reduced as a result of the retrogradation process [13, 17].

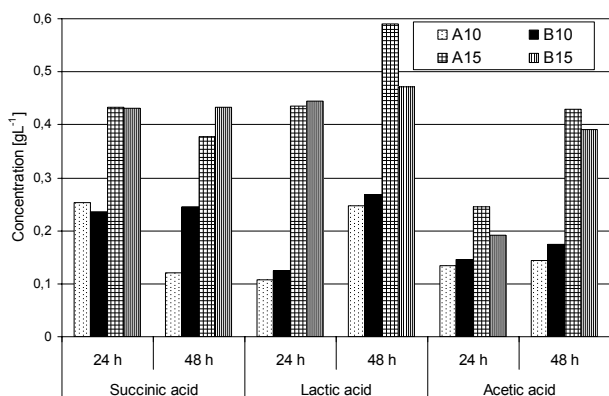


Fig. 5. The amount of organic acids (succinic, lactic and acetic) produced during mash fermentation (A – oversized granules containing potato peel, B – dust from aspiration channel).

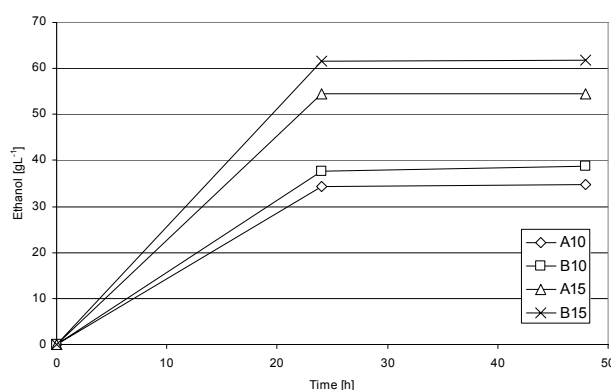


Fig. 6. Ethanol production in mashes prepared from potato granules by-products (A – oversized granules, B – dust from aspiration channel).

The products of this process are resistant to amylolysis, which can reduce the efficiency of starch hydrolysis during mashing [18, 19]. Furthermore, by-products from the processing line of potato granules feature high water-holding capacity at low temperatures [20]. This may reduce the efficiency of raw material mixing in a mash tank affecting efficiency of hydrolysis by amylolytic enzymes. The results of determination of carbohydrate profiles and hydrolysis efficiency confirm a significant impact of discussed problems on the usefulness of potato granule waste processing in ethanol production. Nevertheless, during the studied fermentation process residual oligosaccharides were hydrolyzed and eventually fermented by the used yeast strain. It was previously reported by Rattanachomsri and co-workers [21] that amylases retain their activity for a long period of time during fermentation, even if the temperature is below optimal. This was also observed in our previous studies [22, 23].

The results of fermentation tests proved high yield and productivity of ethanol from mashes prepared with tested materials. Our study was performed at low concentrations of raw material in mashes. Currently, in distillery technology most attention is paid to fermentation of mashes at above 30% of raw material using the method of very high gravity (VHG) fermentation [24]. The fermentation of concentrated mashes allows receiving high concentrations of ethanol,

which results in savings in energy expenditure for distillation and enables better use of the process apparatus in distilleries [25, 26]. In the case of raw materials used in this investigation, the application of high mash concentrations could cause difficulties at the enzymatic hydrolysis and fermentation stage due to the high water-binding capacity of the media. In order to eliminate this problem, additional treatment of raw material before fermentation should be introduced. It is known that additional enzymatic hydrolysis by proteases and enzymes degrading non-starch polysaccharides increases mashing and fermentation efficiency [27]. In the case of the materials used in the present study, it is necessary to analyze their chemical composition of raw material and the changes in its components occurring in the course of processing. As reported by Arapoglou et al. [7], additional enzymatic treatment improves fermentation efficiency of potato peel waste in comparison to acid hydrolysis. However, in the case of processed potato waste, acid treatment should be considered due to insoluble starch hydrolysis, which is not degraded during fermentation [28]. Moreover, wastes containing potato peel are rich in pectin, which also could increase mash viscosity [8, 9] and therefore the application of pectinases as a viscosity reduction agent could improve fermentation of dried potato waste.

Conclusions

Research results proved that by-products from a potato granule processing line are a highly efficient raw material for ethanol production. However, high water-binding capacity of raw materials and the presence of insoluble (retrograded) starch caused a reduction of hydrolysis efficiency in the samples at 15% of mash concentration, which reduces the utility of raw materials used for VHG fermentation. In order to decrease the impact of these factors on the fermentation process, additional raw material pretreatment should be introduced.

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