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K. M. Lakhanova[1], B. Sh. Kedelbaev[2], Zh. B. Makhatov[2], P. Lieberzeit[3], B. S. Begaliev[1], G. A. Rysbayeva[2], Zh. K. Ibraimova[2]

[1]Yassawi International Kazakh-Turkish University, Turkestan, Kazakhstan,
[2]M. Auezov South Kazakhstan state university, Shymkent, Kazakhstan,
[3]University of Vienna, Vienna, Austria.
E-mail: kedelbaev@yandex.ru, mjasik92@mail.ru

DEVELOPMENT OF TECHNOLOGY FOR PRODUCING SORBITOL FROM WHEAT STRAW CELLULOSE

Abstract. The aim of the work is to develop an enzymatic technology for processing wheat straw cellulose for the production of sorbitol by means of hydrolytic hydrogenation based on the use of a hybrid process.

Enzymatic hydrolytic hydrolysis and hydrogenation of wheat straw cellulose research have been carried out and optimal process parameters have been developed. As a result, a combined (hybrid) hydrolysis-hydrogenation process for production of sorbitol have been implemented. In this process, enzymes have been developed and tested for their activity. The influence of the process time, the temperature of the test and the pH on the conversion of cellulose and selectivity for sorbitol have been studied.

The developed technology will allow us to improve the traditional processes in terms of eliminating the numerous stages of purification and isolation of intermediate products. It enables the realization of a single-reactor combined (hybrid) process for the production of such a valuable chemical as sorbitol.

Key words: cellulose, wheat straw, hydrolysis, hydrogenation, polysaccharides, hydrolytic hydrogenation, glucose, sorbitol, enzyme.

Introduction. The growing interest in the use of carbohydrate-containing agricultural plant waste, rich in polysaccharides, determines the search for optimal methods for its processing [1, 2].The main criterion for processing these wastes is their cost, volume, availability and localization, as well as their chemical composition and technological properties. At the same time, the possibilities of using directly microorganisms, enzyme complexes, chemical hydrolyzing agents for effective conversion of non-food raw materials into digestible sugars [3].

The main factor restraining the processing of polysaccharides of wheat straw is the low profitability of these industries, due to shortcomings in the preparation of raw materials, highly energy inputs and low yield of the target product. This problem can be overcome when solving the problem of maximizing the use of raw materials.

At present, there are no such industries in the Republic of Kazakhstan, which makes it difficult to solve the problems of determining the prospects for introducing the scientific results obtained into production. Therefore, the development of an acceptable technology for the depolymerization of carbohydrate-containing plant raw materials is an extremely urgent task. Modern technologies for processing cellulose-containing raw materials are extremely diverse. They differ in the type of feedstock, processing processes, end products, and, therefore, are specific for use in different economic and regional conditions. Direct combustion is the most widely used method of processing biomass (wood and wood waste, urban solid waste, straw, etc.). It should be noted that even well-known technologies for the use of cellulosic raw materials are being improved. The authors of [7-20] investigated the process of joint hydrolysis and hydrogenation of cellulose.

According to the statistical data of the Ministry of Agriculture of the Republic of Kazakhstan, wheat is the leader among crops in terms of yield. Despite the fact that to date a number of measures developed and implemented for the processing and utilization of wheat straw, most of them are unclaimed. In most cases, it is used for feeding cattle and as litter to animals, the rest of it is plowed into the ground or burned in the fields. Thus, this waste is a large-capacity, affordable and promising secondary agricultural production resources in the Republic of Kazakhstan. The development of an integrated technology for the processing of wheat straw to produce sorbitol will not only improve the ecological situation, but also will provide raw materials and additional products for the industry.

Thus, the analysis of the literature showed that a significant increase in the number of scientific publications devoted to the one-stage processing of biomass components, especially polysaccharides over the last ten years, indicates the high relevance of the problem of its transformation into valuable chemical substances.

The goal of this work is to develop a technology for enzymatic hydrolytic hydrogenation of wheat straw pulp, in order to obtain sorbitol necessary for the food, pharmaceutical and chemical industries.

The development of such an efficient technology for processing wheat straw, with the possibility of obtaining sorbitol, is an extremely urgent task.

Materials and methods. In the present work, studied wheat straw, which formed as waste in the agricultural sector of the Republic of Kazakhstan. Previously investigated plant raw materials crushed and sorted. For chemical analyzes, raw materials were used,were fractionated through a sieve with a particle size of 2-3 mm.

The ash contents determined by burning the sample of raw materials followed by calcination in a muffle furnace at a temperature of 600°C, the content of easily and hardly hydrolysable polysaccharides determined by the method of Kiesel and Semiganovsky, lignin determined by the Koenig method in the Komarov modification using 72% sulfuric acid, pentosans - determined on the content of pentoses in hydrolysates of easily and hardly hydrolysable polysaccharides.

The analysis of the sugars carried out by the method of Bertrand and Maken-Shoorl, individual sugars were determined on a liquid chromatograph HPLC; ShimadzuLC10-ATVP, Differential Digital Detector TEST-900, Luna Column Investigation of the process of enzymatic hydrolytic hydrogenation of wheat straw in the presence of a complex enzyme preparations.

In this case, enzymatic hydrolytic hydrolysis and hydrogenation of each wheat straw cellulose sample carried out in an aqueous medium (the active acidity regulated with phosphoric acid and was within the range of 4.8-4.9 pH units).

The substrate concentration in all the experiments was 45.0 g/l. As catalysts, a composition of enzyme preparations used, introduced in an amount of 0.03 g of enzyme per gram of substrate at the start of fermentation. To carry out the hydrogenation-hydrolysis process, the amount of wheat straw, enzymes, phosphoric acid weighed accurately on the analytical scales and the necessary amount of water placed in the fermenter. After a specified period of time, the process was terminated and analyzes were carried out for the content of sugar alcohols and the degree of conversion of cellulose was determined by means of liquid chromatography.

Results and discussion. Studies of the processes of enzymatic hydrolytic hydrogenation of wheat straw cellulose in the presence of complex enzymes carried out. Dependences of the rate of enzymatic hydrolytic hydrolysis and hydrogenation of wheat straw cellulose on the process time showed in table 1.

Table 1 – Dependence of the rate of enzymatic hydrolytic hydrolysis and hydrogenation of wheat straw cellulose on the time of the process

#	τ, min	Conversion degree, %	Selectivity on sorbitol, %	Selectivity on mannitol, %	Total output, %	Selectivity on glucose
1	80	32.0	1.9	1.0	21.4	19.1
2	160	37.1	2.9	1.4	33.5	21.8
3	240	54.0	3.6	1.8	46.1	35.0
4	320	45.7	3.0	1.6	40.0	33.3
5	400	44.6	2.3	1.3	36.7	31.1

Table 1 shows the experimental data on the study of the regularities of the change in the rate of enzymatic hydrolytic hydrolysis and the hydrogenation of wheat straw from the time of the reaction. The reaction time varied from 80 to 400 minutes. The optimal time for the process of catalytic conversion of wheat straw in the conditions chosen by us is 240 minutes. Before this moment of reaction, the conversion of wheat straw gradually increases, and after this index its values are within the margin of error. The same pattern observed with the selectivity index for sorbitol. However, the selectivity for sorbitol and mannitol is much lower than in chemical hydrolytic hydrolysis and hydrogenation. This explained by the prevalence of the rate of the hydrolysis reaction over the rate of the hydrogenation reaction. This evidenced by the high values of the selectivity on glucose (from 19.1 to 35.0%).

When studying the effect of the temperature of the process of enzymatic hydrolytic hydrolysis and hydrogenation on the conversion of wheat straw cellulose and selectivity on sorbitol and mannitol, it showed that, with an increase in temperature from 30 to 50^{0}C, the conversion of wheat straw increased from 12.7 to 42.7% (table 2). Selectivity on sorbitol with increasing temperature (30-50^{0}C) increased from 7.7 to 17.8% and decreased to 7.0% with an increase in temperature to 70°C. The decrease in selectivity for sorbitol due to the fact that at temperatures above 70°C the process of inactivation of the enzymes in use takes place.

Table 2 – Experience temperature influence on enzymatic hydrolytic hydrolysis and hydrogenation process of wheat straw cellulose

#	T, ^{0}C	Conversion degree, %	Selectivity on sorbitol, %	Selectivity on mannitol, %	Total output, %
1	30	12.7	7.7	1.8	10.2
2	40	28.3	14.3	2.0	16.1
3	50	42.7	17.8	1.1	18.9
4	60	34.3	12.1	1.1	14.8
5	70	19.7	7.0	1.2	9.0

Table 2 shows the optimal temperature for experience is 50^{0}C, as soon as in this temperature we obtained maximum selectivity on sorbitol and mannitol.

During the study of the effect of pH (Table 3) on the process of enzymatic hydrolytic hydrolysis and hydrogenation of wheat straw cellulose on conversion and selectivity for polyols, it was established that the highest selectivity values for sorbitol-17.8% and conversion-42.7% were observed in when using a pH value of 5.0. The change in the pH of the medium leads to a change in the degree of ionization of the acidic and basic groups as the active center of the enzyme, and the substrate itself.

Table 3 – Effect of pH on the process of enzymatic hydrolytic hydrolysis and hydrogenation of wheat straw cellulose

#	T, ^{0}C	Conversion degree, %	Selectivity on sorbitol, %	Selectivity on mannitol, %	Total output, %
1	4.0	15.2	7.5	1.2	9.3
2	4.5	30.0	11.3	1.2	12.5
3	5.0	42.7	17.8	1.1	18.9
4	5.5	35.8	10.5	2.9	11.7
5	6.0	19.1	5.5	2.4	8.1

Consequently, a change in pH affects the affinity of the substrate to the active center of the enzyme and to the catalytic mechanism of the reaction. The dependence of the rate of the enzymatic reaction on the pH of the medium has the form of an extremum, since for each enzyme there is an optimum pH value at which the enzyme exhibits the greatest catalytic activity (the optimum pH of the enzyme). The pH value in the optimum corresponds to the best binding of the substrate by the enzyme and the highest catalysis rate. In our case, this value is 5.0.

Thus, we determined the optimal conditions for the enzymatic hydrolytic hydrolysis and hydrogenation of wheat straw pulp: pH 5.0, temperature 50°C, reaction time 3 hours.

Conclusion. Thus, we determined that the resource of wheat straw waste that we are interested in is quite sufficient for further implementation of the task. The effectiveness of a complex of enzymes for carrying out the process of enzymatic hydrolytic hydrogenation of cellulose of wheat straw substantiated and experimentally confirmed for the first time. The optimal conditions for the enzymatic hydrolytic hydrolysis and hydrogenation of wheat straw: pH 5.0, temperature 50°C, reaction time 3 hours are determined.

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К. М. Лаханова[1], Б. Ш. Кедельбаев[2], Ж. Б. Махатов[2], П. Либерцайт[3], Б. С. Бегалиев[1], Ғ. А. Рысбаева[2], Ж. К. Ибраимова[2]

[1]Х. А. Ясауи атындағы халықаралық қазақ-түрік университеті, Түркістан, Қазақстан,
[2]М. Әуезов атындағы Оңтүстік Қазақстан мемлекеттік университеті, Шымкент, Қазақстан,
[3]Вена университеті, Вена, Австрия

БИДАЙ САБАНЫ ЦЕЛЛЮЛОЗАСЫНАН СОРБИТТІ АЛУ ТЕХНОЛОГИЯСЫН ЖАСАУ

Аннотация. Жұмыстың мақсаты – үйлестірілген (гибридті) тәсіліне негізделген бидай сабаны целлюлозасынан сорбитті гидролитикалық гидрлеуді қолдана отырып ферментативті өңдеу арқылы алу технологиясын жасау. Ферментативті гидролитикалық гидрлеу және бидай сабаны целлюлозасын гидролитикалық гидрлеу үрдістері зерттелді, үрдістің тиімді параметрлері жасалып алынды. Нәтижесінде біз сорбитті алудың үйлестірілген (гибридті) гидролиз-гидрлеу әдісін іске асырдық. Осы үрдіс үшін ферменттер жасалды, олардың белсенділіктері анықталды. Үрдіске уақыттың әсері, температура және целлюлоза конверсиясына pH әсері, сорбит бойынша таңдама жасалынды. Біз жасап шығарған технология дәстүрлік үрдіс барысында, көптеген тазалаулар мен бөліп алуларда пайда болатын аралық өнімдерді болдырмайды. Ол біз үшін, бір реакторлы үйлестірілген (гибридті) үрдісті қолданып сорбит секілді құнды химиялық затты алуға мүмкіндік береді.

Түйін сөздер: бидай сабаны, гидролиз, целлюлоза, гидрлеу, полисахаридттер, ферментативті гидролитикалық гидрлеу, глюкоза, сорбит, ферменттер.

К. М. Лаханова[1], Б. Ш. Кедельбаев[2], Ж. Б. Махатов[2], П. Либерцайт[3], Б. С. Бегалиев[1], Г. А. Рысбаева[2], Ж. К. Ибраимова[2]

[1]Международный казахско-турецкий университет им. Х. А. Ясауи, Туркестан, Казахстан,
[2]Южно-Казахстанский государственный университет М. Ауезова, Шымкент, Казахстан,
[3]Венский университет, Вена, Австрия

РАЗРАБОТКА ТЕХНОЛОГИИ ПОЛУЧЕНИЯ СОРБИТА ИЗ ЦЕЛЛЮЛОЗЫ СОЛОМЫ ПШЕНИЦЫ

Аннотация. Цель работы – разработка ферментативной технологии переработки целлюлозы соломы пшеницы для получения сорбита посредством гидролитического гидрирования, основанного на использовании совмещенного (гибридного) процесса. Проведены исследования по изучению процесса ферменттивного гидролитического гидролиза и гидрирования целлюлозы соломы пшеницы, разработаны оптимальные параметры процесса. В результате чего нами реализован совмещенный (гибридный) гидролиз-гидрирование процесс получения сорбита. Разработаны ферменты для данного процесса, исследована их активность. Изучено влияние времени процесса, температуры опыта и pH на конверсию целлюлозы и селективность по сорбиту. Разработанная нами технология позволит усовершенствовать традиционные процессы в плане ликвидации многочисленных стадий очистки и выделения промежуточных продуктов. Она дает возможность реализации однореакторного совмещенного (гибридного) процесса получения такого ценного химического вещества, как сорбит.

Ключевые слова: солома пшеницы, гидролиз, целлюлоза, гидрирование, полисахариды, ферментативное гидролитическое гидрирование, глюкоза, сорбит, ферменты.

Information about authors:

Lakhanova Kulzada Mergenbaevna – doctor of agricultural sciences, professor, International Kazakh-Turkish University named after HA Yasaui; Department of Human Morphology and Physiology;

Kedelbayev Bakhytzhan Shilmirzaevich – Doctor of Technical Sciences, Professor, M.Auezov South-Kazakhstan State University, Higher School "Chemical Engineering and Biotechnology", Department of "Biotechnology", kedelbaev@yandex.kz;

Makhatov Zhaksylyk Baumanuly – doctoral candidate, M.Auezov South-Kazakhstan State University, Higher School "Chemical Engineering and Biotechnology", Department of "Biotechnology", makhatov_8008@mail.ru;

Peter Lieberzeit – PhD doctor, Professor, University of Vienna, mjasik92@mail.ru;

Rysbaeva Galiya Altynbekovna – Candidate of Biological Sciences, Associate Professor, M.Auezov South-Kazakhstan State University, Higher School "Chemical Engineering and Biotechnology", Head of the Department of "Biotechnology", galiya732014@mail.ru.

Ibraimova Zhylduz – PhD doctor, M.Auezov South-Kazakhstan State University, Higher School "Chemical Engineering and Biotechnology", Department of "Biotechnology".