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**STUDY OF THE COMBINED HYDROLYSIS-HYDROGENATION
OF WHEAT STRAW CELLULOSE IN ORDER TO OBTAIN SORBITOL**

Abstract. The article presents the results of studying the implementation of a combined (hybrid) hydrolysis-hydrogenation process for the production of sorbitol. However, the selectivity for sorbitol has a maximum at a pressure of 6.0 MPa. That is, the proportion of the desired product-sorbitol with increasing hydrogen pressure above 6.0 MPa is reduced due to the formation of five-atom alcohols. This expressed in the growth of the total yield of the polyols. Thus, we chose 6.0 MPa as the optimum pressure. In the process of chemical hydrolytic hydrogenation of wheat straw cellulose into sorbitol, the influence of the temperature of the experiment studied in the range of 140-220 °C. The optimal time for the process of catalytic conversion of wheat straw cellulose under the conditions chosen by us is 60 minutes. Until the sixtieth minute, the cellulose conversion reaction is insignificant, and after 60 minutes its values are within the error margin. The same pattern observed with the selectivity index for sorbitol.

Analysis of the resulting polyols carried out by paper chromatography. The nickel catalyst prepared by impregnation, in addition, a ferroalloy (FS) was added in an amount of 5% by weight of nickel.

Thus, we have shown the possibility of obtaining sorbitol from wheat straw cellulose by hydrolytic hydrogenation in the presence of a supported nickel catalyst. The optimum process conditions were determined: the temperature of the experiment was 180°C, the hydrogen pressure was 6.0 MPa, and the reaction time was – 60 minutes.

Key words: wheat straw, sorbitol, cellulose, catalyst, chemical hydrolysis, biomass.

Introduction. The world's reserves of fossil organic raw materials are huge they represented by oil, natural gas and coal, but soon or late they will be exhausted. As an alternative to fossil fuels, renewable sources of energy and organic raw materials used. The most important of these is plant raw materials, which formed in the process of photosynthesis.

Biomass is a renewable resource and plays a role in preventing global warming by slowing down carbon dioxide emissions. In the production of chemical products from biomass, methods for converting biomass to sorbitol, ethanol, lactic acid and other useful chemical products by enzymatic or chemical methods [1-6].

At present, the main material used for biological processing is starch, obtained from corn. From the point of view of the resources of the main structural constituents of plant components can used, cellulose is present in much larger quantities than starch. However, methods for converting cellulose into chemically useful products by reducing its molecular weight (depolymerization) not developed, and this resource is currently not actually used. A large number of studies carried out in the field of cellulose decomposition by means of enzymes. However, there remain important problems associated with enzymatic methods, due to low reaction rates and the need significantly increase the activity of the enzyme and separate it from the product. The advantages of cellulose in its renewability or even the practical inexhaustibility of plant raw materials [7-12]. Of particular interest is the search for technologies of a one-stage, combined (hybrid) method of obtaining valuable substances from the cellulose that excludes the stages of isolation and purification of products. A one-step organisation makes it possible to obtain from a plant polysaccharide, by hydrolysis-hydrogenation, a compound such as sorbitol, which is one of the

promising sources of raw materials for industry [13-18]. Among the possible applications of sorbitol - alcohol sugar - there are three most important. The first area of application relates to a sweetener, which is widely distributed in the food industry. The second area is the use as intermediates in the synthesis of useful compounds such as isosorbide, propylene glycol, ethylene glycol, glycerol, 1,1-sorbitan and lactic acid. Isosorbide, in particular, also used in modern processes, such as copolymerization in the manufacture of polyethylene terephthalate (PET) for the production of polyethylene isosorbide terephoate (PEIT). Polymer PEIT has a higher glass transition temperature than PET, so it is expected to be used for transparent plastic containers that can withstand hot water. The third field of application is its use as an intermediate in the production of hydrogen and liquid hydrocarbons (containing mainly C5 and C6 alkanes) that can be reproduced from biomass. Hydrogen is used in fuel cells, and hydrocarbons are the starting material for petrochemicals [19, 20].

Methods of research. We have previously shown the possibility of obtaining cellulose from wheat straw by autohydrolysis. This cellulose was used for the realization of a combined (hybrid) hydrolysis-hydrogenation process for the production of sorbitol. The process of chemical hydrolytic hydrogenation of wheat straw pulp was carried out in a 100 cm³ steel reactor in an aqueous medium with vigorous stirring at a temperature range of 140-220 °C, a hydrogen pressure of 2.0-10.0 MPa, a reaction time of 2100 minutes. Analysis of the resulting polyols was carried out by paper chromatography. The nickel catalyst was prepared by impregnation, in addition, a ferroalloy (FS) was added in an amount of 5% by weight of the nickel.

Results of the study. In the process of chemical hydrolytic hydrogenation of wheat straw cellulose in sorbitol, the influence of the temperature of the experiment was studied in the range 140-120 °C. From table 1 it can be seen that the optimum temperature of the experiment is 180 °C, since at this temperature we obtained the maximum selectivity for sorbitol and the total yields of sorbitol and mannitol. At temperatures of 140 and 160 °C, cellulose conversion rates (22.6-24.6%), selectivity for sorbitol (12.5-16.1%) and total yield (16.4-17.7%) are much lower, than at 180°C. Despite the fact that at temperatures of 200-220 °C the conversion of wheat straw pulp significantly increases (81.8-83.8%), a decrease in sorbitol selectivity (10.0-10.8) and a total yield of 11.0-11.9%. This is explained by the appearance in the solution of other substances, for example, polyols with a number of atoms below five.

Table 1 – Effect of the temperature of the experiment on the process of chemical hydrolytic hydrogenation of wheat straw pulp. Experimental conditions: 0.5 g of 3% Ni/Al₂O₃ S, 60 minutes, P H₂ = 6.0 MPa

#	T, °C	Degree of conversion, %	Selectivity for sorbitol, %	Selectivity for mannitol, %	Total output, %
1	140	22.6	12.5	2.64	16.4
2	160	24.6	16.1	3.2	17.7
3	180	58.3	23.9	3.3	24.8
4	200	83.8	10.8	1.4	11.9
5	220	81.8	10.0	1.3	11.0

The effect of hydrogen pressure on the process of chemical hydrolytic hydrogenation of wheat straw pulp was studied in the range from 2.0 to 10.0 MPa. It can be seen from table 2 that with increasing hydrogen pressure, the degree of conversion of cellulose increases from 46.5 to 85.6%. The effect of hydrogen pressure on the process of chemical hydrolytic hydrogenation of wheat straw pulp was studied in the range from 2.0 to 10.0 MPa. It can be seen from table 2 that with increasing hydrogen pressure, the degree of conversion of cellulose increases from 46.5 to 85.6%.

Table 3 shows the experimental data on the study of the regularities of the change in the rate of chemical hydrolytic hydrogenation of cellulose in wheat straw from the time of the reaction. The reaction time varied from 20 to 100 minutes. The optimal time for the process of catalytic conversion of wheat straw pulp under the conditions chosen by us is 60 minutes. Until the sixtieth minute, the cellulose conversion reaction is insignificant, and after sixty its values are within the error margin. The same pattern is observed with the selectivity index for sorbitol.

Table 2 – Influence of hydrogen pressure on the process of chemical hydrolytic hydrogenation of wheat straw pulp.
Experimental conditions: 0.5 g 3% Ni/Al₂O₃ (S), 60 minutes, Top = 180 °C

#	P H ₂ , MPa	Degree of conversion, %	Selectivity for sorbitol, %	Selectivity for mannitol, %	Total output, %
1	2.0	46.5	14.3	1.8	14.8
2	4.0	56.7	14.8	2.0	15.6
3	6.0	58.3	24.0	3.3	24.9
4	8.0	84.3	20.8	3.0	34.4
5	10.0	85.6	18.2	2.9	36.08

Table 3 – Dependence of the rate of chemical hydrolytic hydrogenation of wheat straw pulp on the time of the process.
Experimental conditions: 0.5 g 3% Ni / Al₂O₃ (S), Top = 180 °C, Pn2 = 6.0 MPa

#	t, min	Degree of conversion, %	Selectivity for sorbitol, %	Selectivity for mannitol, %	Total output, %
1	20	42.0	16.6	3.3	20.8
2	40	48.9	19.5	3.4	23.4
3	60	58.3	23.9	3.3	24.8
4	80	59.8	22.3	2.4	26.0
5	100	60.5	22.1	2.3	26.3

Conclusions. However, the selectivity for sorbitol has a maximum at a pressure of 6.0 MPa. That is, the proportion of the desired product-sorbitol with increasing hydrogen pressure above 6.0 MPa reduced due to the formation of five-atom alcohols. This expressed in the growth of the total yield of the polyols. Thus, we chose 6.0 MPa as the optimum pressure. In the process of chemical hydrolytic hydrogenation of cellulose of wheat straw into sorbitol, the influence of the temperature of the experiment studied in the range of 140–220 °C.

Thus, we have shown the possibility of obtaining from wheat straw wheat sorbitol by hydrolytic hydrogenation in the presence of a deposited nickel catalyst. The optimal process conditions were determined: the temperature of the experiment was 180°C, the hydrogen pressure was – 6 MPa, and the reaction time was 60 minutes.

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СОРБИТ АЛУ МАҚСАТЫНДА БИДАЙ САБАНЫНЫҢ ЦЕЛЛЮЛОЗАСЫН БІРЛЕСКЕН ГИДРОЛИЗ-ГИДРЛЕУ ҮДЕРІСІН ЗЕРТТЕУ

Аннотация. Мақалада сорбит алу мақсатында бидай сабанының целлюлозасын бірлескен гидролиз-гидрлеу үдерісін жүзеге асыруды зерттеу бойынша нәтижелер келтірілген. Бірақ, сорбит бойынша селективтілігі 6,0 МПа қысым кезінде максималды болады. Онда бізге қажетті өнім сорбиттің үлесі сутегі қысымын 6,0 МПа арттыру кезінде бес атомды спирттердің түзілуінен төмендейді. Бұл полиолдардың шығымы қосындысының артуымен сипатталады. Осылайша, бізбен оптималды қысым ретінде 6,0 МПа таңдап алынды. Сорбит алу үшін бидай сабанының целлюлозасын химиялық гидролиз-гидрлеу үдерісін жүзеге асыру кезінде сынақ жүргізуде температураның әсерін 140–220 °С аралығында зерттедік. Біздің таңдап алынған жағдайларымызда бидай сабанының целлюлозасын каталитикалық конверсиясы үдерісінің оптималды жүру уақыты 60 минут. Алпыс минутқа дейін целлюлоза конверсиясының реакциясы баяу жүреді, ал алпыс минут өткенде оның мәндері ауытқу мәні аралығында болады. Осындай заңдылықтар сорбит бойынша селективтілік көрсеткіштерінде байқалады.

Түзілген полиолдарға талдау жасау қағазды хроматография әдісімен жүргізіледі. Никелді катализаторды қанықтыру әдісімен дайындайды, оған қосымша никел массасынан 5% мөлшерде ферроқұймалар (FS) қосады.

Осылайша, біздің тарапымыздан енгізілген никелді катализатордың қатысуымен гидролитикалық гидрлеу әдісімен бидай сабанының целлюлозасынан сорбит алу мүмкіндігі көрсетілген. Үдерістің оптималды жағдайлары анықталды: сынақ температурасы – 180 °С, сутегі қысымы – 6 МПа, реакция жүру ұзақтығы – 60 минут.

Түйін сөздер: бидай сабаны, сорбит, целлюлоза, катализатор, химиялық гидролиз, биомасса.

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ИССЛЕДОВАНИЕ ПРОЦЕССА СОВМЕЩЕННОГО ГИДРОЛИЗ-ГИДРИРОВАНИЕ ЦЕЛЛЮЛОЗЫ ПШЕНИЧНОЙ СОЛОМЫ С ЦЕЛЮЮ ПОЛУЧЕНИЯ СОРБИТА

Аннотация. В статье приведены результаты по изучению реализации совмещенного (гибридного) процесса гидролиз-гидрирование с целью получения сорбита. Однако селективность по сорбиту имеет максимум при давлении 6,0 МПа. То есть, доля нужного нами продукта- сорбита с увеличением давления водорода выше 6,0 МПа снижается за счет образования пятиатомных спиртов. Это выражается в росте суммарного выхода полиолов. Таким образом, нами в качестве оптимального давления выбрано 6,0 МПа. При осуществлении процесса химического гидролитического гидрирования целлюлозы пшеничной соломы в сорбит влияние температуры опыта изучали в пределах 140–220 °С. Оптимальным временем протекания процесса каталитической конверсии целлюлозы пшеничной соломы в выбранных нами условиях определено 60 минут. До шестидесятой минуты реакция конверсия целлюлозы незначительная, а после шестидесяти ее значения находятся в пределах погрешности. Такая же закономерность наблюдается и с показателем селективности по сорбиту.

Анализ образующихся полиолов осуществляли методом бумажной хроматографии. Никелевый катализатор готовили методом пропитки, в него дополнительно добавляли ферросплав (FS) в количестве 5% от массы никеля

Таким образом, нами показана возможность получения из целлюлозы пшеничной соломы сорбита методом гидролитического гидрирования в присутствии нанесенного никелевого катализатора. Определены оптимальные условия процесса: температура опыта – 180°C, давление водорода – 6 МПа, продолжительность реакции – 60 минут.

Ключевые слова: пшеничная солома, сорбит, целлюлоза, катализатор, химический гидролиз, биомасса.

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