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STUDY OF THE COMPOSITION OF PRODUCTS OF ACID HYDROLYSIS OF SUCROSE BY CHROMATOGRAPHY

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Abstract:
The reaction of catalytic hydrolysis of sucrose with the use of carbon material sibunite modified with concentrated sulfuric acid, as well as a solution of sulfuric acid, was studied. The influence of operating parameters on the conversion of sucrose and the final yield of monosaccharides - glucose and fructose - was determined.

Keywords: Sucrose / hydrolysis / acid catalyst / glucose / fructose / sucrose / hydrolysis / acid catalysis / glucose / fructose

In recent years, the developed countries of the world, in order to reduce oil consumption and reduce greenhouse gas emissions, have been implementing a strategy of expanded use of plant biomass to obtain demanded chemical products and components of liquid fuels.

Obtaining monosaccharides, in particular glucose, used as a basis for the synthesis of various chemical products and motor fuels, is traditionally carried out by hydrolysis of polysaccharides (cellulose, starch) and disaccharides (sucrose, maltose, cellobiose). Sucrose is widely represented in the plant world and, along with glucose, is the main raw carbohydrate, suitable for the synthesis of ethanol, butanol, glycerol, citric and levulinic acids, dextran, and medicinal substances. As a result of hydrolysis, sucrose is converted into invert sugars - glucose and fructose, which are also widely used in the pharmaceutical and food industries.

At present, the scale of biomass processing is limited by the imperfection of traditional technologies for its processing, to increase the efficiency of which are increasingly used the catalysts are changing. For many years, corrosive and environmentally hazardous mineral acids, mainly HC1, I2804, as well as enzymes have been used in the processes of catalytic hydrolysis. The technological problems of their use are associated with the problem of catalyst regeneration and the difficulties in separating the target products and catalyst from the reaction medium. The use of solid acid catalysts instead of solutions of acids and enzymes allows solving the problem of separating products and catalyst, as well as ensuring the environmental safety of the process.

To date, there is information about the use of ion-exchange resins, sulfonated silicon dioxide, zeolites, transition metal oxides No. 205, A1203, U205 / A1203 carbon materials treated sulfuric acid to create ^ 03H groups on their surface.

The aim of this work was to study the kinetics of sucrose hydrolysis using Sibunite carbon material modified with concentrated H2804, as well as a H2804 solution, as catalysts.

Product analysis

The products of sucrose hydrolysis were analyzed by gas chromatography on a VARIAN-450 GC instrument with a flame ionization detector according to the method described in. A mixture of trimethylchlorosilane and hexamethyldisilazane in pyridine was used as a silylating reagent, and sorbitol was used as an internal standard. A VF-624ms capillary column with a length of 30 m and an inner diameter of 0.32 mm was used. Chromatographic conditions: carrier gas - helium; injector temperature 250 ° C; the initial temperature of the column is 50 ° C, the temperature rises to 180 ° C at a rate of 10 ° C / min, exposure at 180 ° C. Detector temperature 280 ° C. The duration of the chromatographic separation is 55 min.

Peaks were identified using the retention times of monosaccharides previously established for these chromatographic conditions. The ratio of the areas of each peak of the monosaccharide to the peak area of the internal standard was calculated. These ratios were used to find the mass fraction of each monosaccharide in the hydrolyzate sample using the calibration graph.

Characterization of catalysts.

Information about the structure and size of the modified carbon catalyst particles was obtained using a scanning electron microscope "TM-1000 HITACHI".

The specific surface area of the solid catalyst was determined by the adsorption of N2 at the temperature of liquid nitrogen on a SORBTOMETR-M device using the BET method.

The characteristics of the used carbon material are presented in table. 1. The specific surface area (SYS) of the carbon support as a result of modification decreases approximately 3.5 times, and the pore volume (V ^) - 5 times.

The determination of the total content of carboxyl and phenolic hydroxyl acid groups in the original and modified carbon materials was carried out by the barite method. Carboxyl groups were determined by the Ca-acetate method, and phenolic hydroxyl groups were determined by difference [12]. The S content in sibunites was determined according to GOST 2059-75.

Results and discussion

It is noted in the literature [13-15] that the temperature maximum of the sucrose hydrolysis process should not exceed 80 ° C in order to exclude the subsequent reactions of monosaccharides and the formation of such products as HMP (5-hydroxymethyl-furfural), D-fructose dianhydrides, humic substances, which deactivate the catalysts and "contaminate" the resulting solutions of monosaccharides, thereby complicating their fermentation.

It was determined that at a temperature of 30 ° C, the hydrolysis reaction of sucrose with a catalyst of 5% wt. H2804 proceeds very slowly, and after 4–9 min, the conversion of sucrose does not exceed 25% (Fig. 1). Therefore, further studies of sucrose hydrolysis in the presence of a senonic acid catalyst were also performed at temperatures of 40, 50, and 60 ° C. At a temperature of 60 ° C, in the course of the first 7 min, about 70% of the initial sucrose is converted, and almost complete conversion of sucrose (96%) at this temperature occurs within 50 minutes.

Hydrolysis of sachrrose using modified sulfuric acid sibunite was carried out at a temperature (60-80 ° C) and a total process duration of 2200 min. Available literature data [2, 9, 15, 21] indicate a slow course (200-500 minutes) of heterogeneous catalytic hydrolysis of sucrose. At the same time, not all catalysts contribute to the production of 10 0% conversion of the synharnza.

Linear dependences in the coordinates lnCd (Fig. 3) confirm the course of the reaction according to the first-order equation. Based on the data obtained, the rate constants of the sucrose hydrolysis reaction were determined at temperatures of 30-60 ° C and 5% wt. I2804 and at 50-80 ° C with the catalyst m sibunate, modified with I2a04. The results are presented in table. 2. For a sulfuric acid catalyst, the rate constant of the sucrose hydrolysis reaction depends significantly on temperature. With an increase in the reaction temperature by 2 times, the constant increases at 9 para. For a solid catalyst, an increase in the reaction temperature by 1.3 times leads to an increase in the reaction rate constant and by 5.6 times.

In the literature [19] it is reported that at a concentration of H2804 from 7 to 25% wt. in solution and temperatures of 17-40 ° C, the rate constants of sucrose hydrolysis vary from 0.53-10-4 to 59.73-10-4 s-1 and the activation energy is about 100 kJ / mol.

There is information [20] about the effect of dissolved and solid catalysts on the rate of the sucrose hydrolysis reaction. When using CH3COOH and PichShe C 106 EP as catalysts, the authors found that at a hydrolysis temperature of 50 ° C, the rate constant in a heterogeneous system (k = 4.90-10-5 s-1) is 18 times higher than in a homogeneous system (k = 2.69-10-6 s-1).

According to the data available in the literature [21], the rate constants of the sucrose hydrolysis reaction carried out under conditions similar to ours, but with a solid SiO2 catalyst modified with 12-phosphotungstic acid, for temperatures of 60-85 ° C are in the range 1.49-11, 10T0-6 s-1. The activation energy calculated for these values is about 80 kJ / mol. In the hydrolysis of sucrose using sibunite modified with H2SO4, the reaction rate constant is 2 orders of magnitude higher, and the activation energy is 1.4 times lower compared to SiO2 modified with 12-phosphotungstic acid.

In [9], the catalytic activity of V2O5 / y-Al2O3 (16% wt.) In the hydrolysis of sucrose under the same conditions as indicated in [21] and studied by us was studied. It was found that the rate constants for temperatures of 50-80 ° C are in the range of 2.20-12.2840-6 s-1, and the activation energy of such a reaction is about 54 kJ / mol.

When using the industrial catalyst Amberlite IR-120B (ion-exchange granules with -SO3H groups) [22] in the temperature range 55-70 ° C, the activation energy of sucrose hydrolysis is 59 kJ / mol.

Styrene divinylbenzene copolymers Amberlite IR-120H (20%) and Amberlite IR-200 (8%) showed high catalytic activity in the hydrolysis of sucrose in the temperature range 50-80 ° C, since the reaction rate constants were 7.0-56.3- 10-4-s-1 and 5.3-105.8-10-4-s-1, and the activation energy is 65 and 91 kJ / mol, respectively [15].

It is known [23-25] that modification of the mesoporous graphite-like carbon material of sibunite with NaClO and HNO3 leads to a decrease in the specific surface area and the formation of a large number of surface oxidized groups, mainly carboxyl. When sibunite is modified with sulfuric acid, a 3.5-fold decrease in the specific surface area of the carbon support is observed, and an increase to 1.69 mg-eq / g of the total content of acid groups (carboxyl and phenolic hydroxyl), while in the original sibunite the content of carboxyl and phenolic hydroxyl groups were found to be 0.009 and 0.139 mg-eq / g, respectively. Probably, the increase in the concentration of acid groups on the surface and in the pores of the carbon material after modification is the reason for its increased catalytic activity, comparable to or exceeding the activity of some ion-exchange and oxide catalysts.

CONCLUSION

A kinetic study of the reaction of acid hydrolysis of sucrose with dissolved (H_2SO_4) and solid carbon (sibunite) catalysts in the temperature range 30-80 ° C was carried out. The rate constants and the activation energy of the sucrose hydrolysis reaction have been determined. The activation energy of heterogeneous catalytic hydrolysis of sucrose is 54 kJ / mol and this value is comparable with the literature data for the catalysts V_2O_5 / y-Al_2O_3 [9], Amberlite IR-120B [22], and Amberlite IR-120H [15].

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