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PROCESS FOR PREPARING POLYHYDRIC ALCOHOLS FROM HEXITES

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The present invention relates to a process for preparing polyhydric alcohols from hexites by hydrogenation cleavage in the presence of catalysts at elevated pressure and temperature.

It is known to apply hydrogenation cleavage to hexites, obtained by reduction of hexoses, whereby polyhydric alcohols having less than 6 carbon atoms are obtained. (See Swiss patent application, Ser. No. 32,061, of April 12, 1956.) Cleavage products obtained are e. g. ethylene glycol, 1,3- or 1,2-propylene glycol, glycerine, and erithrite. The percentages of the cleavage products obtained vary widely in the processes practiced up to now.

It has now been found that the hydrogenation cleavage of hexites in the presence of catalysts, performed at elevated pressure and temperature, may be carried out with controlled production of any one of the cleavage products or a plurality of the same. Depending on which one of the cleavage products is preferred, the hydrogenation cleavage is effected in the presence of catalysts which contain elements of the group of nickel, copper, cobalt, chromium or silver. The temperature during the cleavage is maintained above 180° C. and pressure amounts to more than 10 atmospheres.

According to the invention, the cleavage of the hexites is carried out in approximately neutral aqueous solution. When it is desired to produce preferentially 1,3-propylene glycol, the cleavage is carried out with hydrogen pressure of 100–200 atm., preferably 140–160 atm., and temperatures from 190–220° C., in the presence of catalysts containing nickel in combination with copper and/or cobalt. The copper content in this case is about 1–24%, the nickel content also 1–24%. When it is intended to use a catalyst containing cobalt in addition to copper, the composition may be as follows: Nickel 10–14%, cobalt 10–14%, copper 1–5%. The metals are precipitated as hydroxides, or, together with the carrier, e. g. magnesium hydroxide, as mixed hydroxides. The precipitate is shaped as desired, in a conventional manner, dried, and reduced. Instead of the above named mixed catalysts, copper chromite may be used, which is preferably activated with silver. The yield in 1,3-propylene glycol can be increased up to 70%.

When, however, the output in 1,2-propylene glycol is to be increased, catalysts are used which contain a carrier, e. g. magnesium oxide, and thereon about 2–5% copper and about 20–25% nickel. The pressure is about 10–50 atm., preferably 20–30 atm., the temperatures 180–210° C. The yield in 1,2-propylene glycol can be increased to about 30% by this modification of the process.

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For preferred formation of glycerine and ethylene glycol, catalysts are used, according to the invention, which contain, only cobalt and nickel in addition to a carrier, e. g. alkaline earth oxides, such as magnesium oxide.

The content in cobalt is 1–24%, and the content of nickel likewise 1–24%. The temperature is preferably maintained between 200 and 220° C., the hydrogen pressure between 100 and 200 atm., preferably from 140–160 atm. Catalysts of cobalt and nickel on magnesium oxide as carrier can be prepared in a simple manner by precipitating the metals as oxalates by means of oxalic acid from an aqueous solution containing salts of cobalt, nickel and magnesium; the precipitate is washed and dried and then reduced in a known manner, e. g. by means of hydrogen at a temperature of about 400° C.

The reaction products may be worked up in a known manner, for instance by fractional distillation. First, water is driven off at normal pressure, whereupon the separation of the cleavage products is carried out advantageously in vacuo.

The catalysts and unreacted hexites remain in the residue of the distillation. The residue may be returned to the hydrogenation vessel, together with fresh amounts of hexite solution; the process is thereby made continuous.

The process according to the invention will now be more fully described in a number of examples, but it should be understood that these are given by way of illustration and not of limitation and that many changes in the details can be made without departing from the spirit of the invention.

Example 1

To 500 cc. of a 10% aqueous sorbite solution, 25 grams of a catalyst are added which consists of 12.4% nickel, 12.4% copper, and 75% magnesium oxide; the mixture is placed in an autoclave provided with a stirrer and treated with hydrogen under a pressure of 150 atm. at a temperature of 210° C. for 10 hours. After expansion, the contents of the autoclave are subjected to distillation, water being first driven off at normal pressure. The alcohols are then obtained by fractional distillation. The residue contains 8% of the sorbite used initially, the conversion is therefore 92%. The fractions of the distillate consist of 53% 1,3-propylene glycol, 18% 1,2-propylene glycol, 25% glycerine and no glycol. The remaining 4% consist partly of erithrite. (The values are given percent by weight of the sorbite converted during the reaction in this and all the following examples.)

Examples 2

The same amount of 10% aqueous sorbite solution as used in Example 1, is hydrogenated under the following conditions: The catalyst used is 3% copper, 22% nickel, and 75% magnesium oxide. Reaction temperature 220° C., pressure 150 atm., reaction time 5 hours. The products are worked up as described above; 40% of the sorbite initially used are recovered without change so that conversion amounts to 60%. The distillates obtained are 40% 1,3-propylene glycol, 12% 1,2-propylene glycol, and 15% glycol, and 30% glycerine. The remainder i. e. 3%, contains some erithrite.

Example 3

500 cc. of a 10% aqueous sorbite solution are hydrogenated and subsequently worked up by distillation as

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described in Example 1. Reaction temperature 195° C., pressure 150 atm., reaction time 20 hours.

Catalyst: 12% nickel, 12% cobalt, 1% copper, and 75% magnesium oxide.

55% of unreacted sorbite are obtained. The conversion is therefore 45%.

The distillates contain: 44% 1,3-propylene glycol, 11% 1,2-propylene glycol, 39% glycerine, and no ethylene glycol. The residue of 6% still contains erithrite.

Example 4

In an autoclave provided with a stirrer, 25 grams of a copper chromite catalyst activated with silver, are added to 500 cc. of a 10% neutral aqueous sorbite solution: (pH=6-8). In the autoclave a hydrogen pressure of 150 atmospheres at a temperature of 200° C. is maintained for 20 hours.

After expansion and after the autoclave has cooled down, the content is fractionally distilled, water being first eliminated at normal pressure. The distillation is then continued at reduced pressure, whereby the polyhydric alcohols are obtained. In the residue, 34% of the used sorbite remain together with the catalyst. The conversion is therefore 66%. The distillates contain: 61% 1,3-propylene glycol, 10% 1,2-propylene glycol, 6% ethylene glycol, and 20% glycerine. The remainder consists partly of erithrite.

Example 5

The same amount of aqueous sorbite solution and the same catalyst are used as in Example 4, with the following conditions:

Temperature 200° C., pressure 150 atm., reaction time 10 hours. Work-up as in Example 4. 42% of the sorbite used are unreacted. The conversion is therefore 58%. The yields calculated on the conversion are 60% 1,3-propylene glycol, 8% 1,2-propylene glycol, 7% ethylene glycol, and 23% glycerine. The remaining 2% contain some erithrite.

Example 6

To 500 cc. of 10% sorbite solution (pH=7.5) in an autoclave with stirrer, are added 25 grams of a catalyst consisting of 2% copper, 23% nickel, and 75% magnesium oxide. Hydrogenation takes place at a temperature of 210° C. and a hydrogen pressure of 25 atm. during 10 hours.

After expansion and after the autoclave has cooled down, the contents are distilled for driving off water and are then fractionally distilled at reduced pressure. The distillation residue contains in addition to the catalyst 17% unreacted sorbite. The conversion is therefore 83%. The distillation fractions contain 32% 1,2-propylene glycol, 20% 1,3-propylene glycol, 10% glycol, and 19% glycerine. The remaining 19% contain still some erithrite.

Example 7

500 cc. of a 10% sorbite solution are hydrogenated as in Example 6. Reaction conditions: Temperature 220° C., pressure 25 atm., reaction time 5 hours, 25 grams catalyst of the same composition as in Example 6. The work-up of the reaction products results in 21% unreacted sorbite in the residue (conversion 79%) and 27% 1,2-propylene glycol, 30% 1,3-propylene glycol, 19% glycol and 18% glycerine in the distillates.

This example shows that upon raising the temperature to 220° C., the yield in 1,3-propylene glycol is considerably increased.

Example 8

500 cc. of a 10% sorbite solution are hydrogenated as described in Examples 6 and 7, with the following conditions: Temperature 210° C., pressure 25 atm., reaction time 10 hours, 25 grams of catalyst consisting of

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3% copper, 22% nickel, and 75% magnesium oxide. 16% of unreacted sorbite are obtained, the conversion is therefore 84%.

The fractional distillation yields 27% 1,2-propylene glycol, 21% 1,3-propylene glycol, 18% glycol, and 15% glycerine.

Example 9

In an autoclave provided with a stirrer, 500 cc. of a 10% sorbite solution are mixed with 25 grams of a catalyst consisting of 20% cobalt, 5% nickel, and 75% magnesium oxide. Hydrogenation is carried on for 10 hours at a temperature of 210° C. and a hydrogen pressure of 150 atm.

After expansion and after the autoclave has cooled down, the content is distilled, water being first driven off at normal pressure, and the mixture being then fractionally distilled at reduced pressure. The residue contains in addition to the catalyst 7% unreacted sorbite. The conversion is therefore 93%. The distillates contain 34% glycerine, 31% glycol, 11% 1,2- and 19% 1,3-propylene glycol. The remaining 5% still contain some erithrite.

Example 10

500 cc. of a 10% aqueous sorbite solution are hydrogenated as described in Example 9, but under the following conditions:

Temperature 210° C., pressure 150 atm., reaction time 10 hours, 25 grams catalyst consisting of 5% cobalt, 20% nickel, and 75% magnesium oxide. The work-up as in Example 9; the yield is: 4% unreacted sorbite (conversion 96%), 34% glycerine, 32% glycol, 15% 1,2- and 19% 1,3-propylene glycol.

Example 11

500 cc. of a 10% aqueous sorbite solution are hydrogenated as described in Example 9, but under the following conditions: Temperature 215° C., pressure 150 atm., reaction time 5 hours, 25 grams catalyst consisting of 12.5% cobalt, 12.5% nickel, and 75% magnesium oxide.

Work-up as in Example 9. 22% of unreacted sorbite are obtained. The conversion is therefore 78%. The reacted sorbite is converted into 36% glycerine, 30% glycol, 16% 1,2-propylene glycol, and 13% 1,3-propylene glycol.

What we claim is:

1. A process for preparing 1,3-propylene glycol and glycerol plus ethylene glycol by hydrogenation cleavage of hexitols in the presence of catalysts at elevated pressures and temperatures, which comprises effecting the hydrogenation cleavage in the presence of catalysts selected from the group consisting of mixtures of nickel, copper and cobalt; copper chromite and silver; copper and nickel; cobalt and nickel, at temperatures of 180-220° C. and at pressures of 100-200 atmospheres; the 1,3 propylene glycol being selectively produced at temperatures between 190-220° C. and at pressures of 100-200 atmospheres, the catalyst being selected from the group consisting of mixtures of nickel, copper and cobalt; copper chromite and silver; copper and nickel; the glycerol plus ethylene glycol being selectively produced at temperatures between 200 and 220° C., the catalyst being selected from the group consisting of mixtures of cobalt and nickel.

2. The process according to claim 1, wherein the catalyst used in the preparation of glycerol plus ethylene glycol consists of 1-24 percent each of nickel and cobalt, the remainder being magnesium oxide on which said nickel and cobalt are precipitated.

3. The process according to claim 1, wherein the catalyst used in the preparation of 1,3-propylene glycol consists of 1-24 percent each of nickel and copper, the re-

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mainder being magnesium oxide upon which said copper and nickel are precipitated.

4. The process according to claim 1, wherein the catalyst used in the preparation of 1,3-propylene glycol consists of 10-14 percent nickel, 10-14 percent cobalt and 1-5 percent copper, the remainder being magnesium oxide on which said copper, nickel and cobalt are precipitated.

5. The process according to claim 1, wherein the catalyst used for the preparation of 1,3-propylene glycol consists of copper chromite activated by silver.

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