

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PRODUCTION OF GLYCERINE

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It is already well known that glucose and other carbohydrates may be reduced by means of hydrogen under pressure with formation of different products as propylenglycol, methyl alcohol, ethyl alcohol and also according to some authors, with formation of small quantities of glycerine.

According to Zartmann and Adkins (J. Am. Chem. Soc. 55, 4559, 1933) there are obtained methanol, alcohol, water, propylenglycol and high boiling fractions containing 1-oxyethyl-3-oxyhydrofuran polyvalent glycols as the tetraoxyhexan and the trioxyhexan and according to the "I. G. Farbenindustrie A. G." also propan and propylalcohol (Italian Patent 291,568 of 23rd 8, 1930).

The quantity of glycerine to be obtained with the processes of hydrogenation till now known is always small and not such as to allow an industrial starting of the same processes for the production of glycerine.

On the other side the processes of fermentation show relatively low yields about the 30-35% of the glucose employed and cannot be increased practically since part of the glucose is destroyed in the formation of alcohol, carbonic anhydride, acetaldehyde and other secondary products.

The present invention allows on the contrary to obtain high yields of glycerine, much higher than that obtained through fermentation causing the hydrogenation of the glucose and other sugars and carbohydrates to take place in particular conditions and by means of particular catalysers without the formation of products of an high hydrogenation, as propylalcohol, ethyl alcohol, hydrocarbons and the like.

It was on the contrary possible by varying the conditions in which the hydrogenation is conducted to obtain different proportions between glycerine and propylenglycol, for instance to obtain more glycerine and less propylenglycol or to obtain nearly no glycerine and exclusively the product of subsequent hydrogenation that is the propylenglycol with practical quantitative yields without the formation of secondary products.

It results then possible to conduct the hydrogenation in such a way as to obtain prevalently one than another of the products wanted.

Such really important results have been obtained by causing the hydrogenation to take place at a temperature exactly determined and by subjecting the products to a determined working cycle.

The process according to the present invention consists in hydrogenising the glucose and other

carbohydrates to be easily transformed in glucose through hydrolise (cane sugar, starch, cellulose destrin and the like) or of hydrogenation products thereof (sorbite, mannite and the like) at temperature higher than 200°C, and preferably below 270°C in the presence of convenient catalysers. The product of hydrogenation is distilled in order to separate propylenglycol and glycerine formed, the residual being hydrogenised again. By this way the nearly totality of the starting product may be hydrogenised without any loss owing to secondary reactions.

The operation of hydrogenation has to be conducted in presence of solvents as water, methyl alcohol, ethyl alcohol or superior alcohols, preferably methyl alcohol or ethylalcohol.

The catalysers may be of different nature for instance with a basis of chromite of copper prepared by means of thermic decomposition at a low temperature, of double chromate of copper and ammonium or with a basis of copper and nickel.

Active catalysers of this last type may be obtained by reduction of solid solutions obtained by means of coprecipitation of hydroxides or basic carbonates, or oxalates or other organic salts of copper and nickel or of copper and cobalt. The solid solutions among the salts or isomorphous hydroxides may be introduced into the chamber of reaction even without a previous reduction.

According to the temperature and the duration of heating it is possible according to the invention to vary the quantity mentioned of propylenglycol and glycerine obtained, in the sense to increase the proportion of the former with respect to the latter by increasing the temperature and the duration of hydrogenation.

A high yield of glycerine for instance may be obtained by using a very active catalyser for instance one containing copper obtained by means of the Natta-Roberti process (Italian patent application n. 7330/38 of 6th August 1938) and causing the hydrogenation to take place at a temperature lower than 250° C and preferably about 220-240°C but always by effecting short durations of hydrogenation. These depend also on the quantity of the catalyser used.

The hydrogenation may be executed in a discontinuous way or preferably continuously.

In the first case the reaction is stopped after 1-5 hours of reaction according to the activity of the catalyser and the pressure, through cooling or discharging of the hydrogenised product from the apparatus of reaction. The catalyser eventually transported is separated for instance

by filtration or centrifugation, the glycol and glycerine are distilled and the residue is put again into the cycle eventually added to small quantities of fresh catalyser.

In the second case the alimentation may take place without interruption in a column resistant to a high pressure and heated from the outside at a constant temperature (for instance with condensing vapours). The discharge may also be continuous or intermittent, as also the introduction of hydrogen for replacing the quantity consumed may be equally continuous or intermittent.

In the case of a continuous functioning the catalyser may be a fixed one and constituted by solid solutions of nickel and copper precipitated on a siliceous or aluminous support and the contact between these solutions and the liquid is secured by the circulation of the liquid which is made to fall on the catalyser.

This system possesses advantages over the methods of agitation with an agitator inside the chamber of reaction and over those based on the shaking of the whole apparatus.

It is necessary in order to obtain a considerable yield of glycerine to extract the liquid before the hydrogenation is too much advanced. It is convenient to stop the hydrogenation before the quantity of glycerine decomposed by further hydrogenation surpasses the half of the quantity of glucose hydrogenated to glycerine or still further. It is possible to realize this more easily if the hydrogenation is executed in such a way that the product may be subjected to a fractionated distillation and rectification at a low pressure in order to separate the glycerine formed and the residue of the distillation may be introduced again into the cycle to be further hydrogenated under pressure. For instance by subjecting a solution of glucose in alcohol in the proportion 1:2 with the addition of the 2% of the catalyser, comprising chromite of copper obtained with the Natta-Roberti method above cited to a hydrogenation at 230°C with a duration of 3 hours in continuous stirring there were obtained 130 parts of glycerine for each 100 parts of propylenglycol formed at the same time, while the residue of hydrogenation resulted for the greater part constituted by sorbite which may be introduced again into the cycle and transformed into glycerine.

At higher temperatures of about 240°-250°C more propylenglycol is obtained. For instance with saccharose for subsequent hydrogenations, each time with separation of the products formed, a transformation of about 50% of saccharose into glycerine and of about 50% into glycol was ob-

tained through the recuperation of the residues. It should on the contrary be executed a complete hydrogenation in an only operation of 5 hours at 270°C there is obtained the 71% of glycol and barely the 6% of glycerine. The residue may be still hydrogenated into glycol and glycerine.

By reducing the duration of the hydrogenation greater total yields in glycerine and smaller in glycol may be obtained, but there will ensue greater expenses for the separation of the solvent and the residues which are present in a larger proportion.

The separation of the glycerine may be effected as already mentioned by distillation or better rectification at a low pressure: separating first all the most volatile solvent, then the propylenglycol and at last the glycerine. The residue of the hydrogenation may be subjected again to hydrogenation alone or mixed with carbohydrates to be hydrogenated.

The process may be continuous with great advantage for the thermic and economical yield by introducing the products to be hydrogenated continuously in a column or in a series of pressure resisting tubes, fed at one end (for instance from above), while at the other end (for instance from the bottom) there discharged also continuously the products of the hydrogenation, which may be subjected afterwards to a rectification also continuous.

The residue of the rectification in such a case may be introduced also continuously into the hydrogenation apparatuses.

The catalyser may be mixed in powdery form and kept in suspension in the liquid to be hydrogenated or and preferably in the case a diluted solution or a very pure product is employed, fixed catalysers may be used with the advantage of simplifying the process by avoiding the separation of the catalyser in suspension from the product of hydrogenation. In this case the fixed catalysers, contained inside the hydrogenating apparatus, are dipped into the solution to be hydrogenated eventually preheated.

It is also possible to hydrogenate not soluble carbohydrates for instance polyosis, cellulose starch, wood and the like.

In this case the catalyser has to be transported and kept in suspension together with the carbohydrate in an aqueous or hydroalcoholic liquid, kept in agitation. This case is similar to the pre-calling ones when the hydrolise of the polyosis precedes the hydrogenation, but there is the advantage of reducing the number of the operations.

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