United States Patent Office 3,235,541 Patented Feb. 15, 1966

3,235,541 PROCESS FOR PREPARATION OF LEVOGLUCOSAN

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No Drawing. Filed July 26, 1963, Ser. No. 297,983
10 Claims. (Cl. 260—209)

This invention relates to a process for preparation of levoglucosan by pyrolyzing a glucose-yielding carbohydrate in the presence of an inert gas at atmospheric pressure.

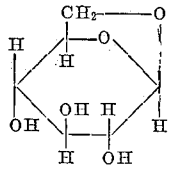
In the past, levoglucosan has been prepared by dry vacuum pyrolysis of starch, cellulose, or lactose. Levoglucosan has also been prepared by the pyrolysis of cellulose in the presence of superheated steam at reduced pressure. The common feature of these methods has been the use of reduced pressure to volatilize the decomposition products as they are formed by the heat. In these methods the main difficulty has been the maintenance of a vacuum during pyrolysis due to the presence of large amounts of non-condensable gases evolved. These methods are particularly difficult and costly when applied to the preparation of large scale commercial amounts of levoglucosan. Furthermore, the use of superheated steam under reduced pressure presents many problems in maintaining vacuum on a commercial scale. Namely, in order to maintain the vacuum, costly equipment is required making the process infeasible for commercial application. Also, such vacuum pyrolysis makes it difficult to attain rapidly a high temperature and maintain it uniform as required for pyrolysis of carbohydrate materials since these materials are poor conductors of heat. Lack of sufficient and uniform heat transfer is another disadvantage of such vacuum pyrolysis which results in a very low yield of levoglucosan on a commercial scale. Levoglucosan has also been formed during the pyrolysis in air of cotton fabric under the atmospheric pressure. In this latter method, oxygen in the air reacts instantaneously with the levoglucosan product as soon as it is formed thus degrading it completely or at best reducing its yield markedly.

Accordingly, an object of the present invention is to produce levoglucosan in high yield by prolysis of a glucose-yielding carbohydrate at atmosphereic pressure.

Another object is to provide a process for the preparation of levoglucosan on a large commercial scale, which process is simple and inexpensive.

Other objects and advantages of this invention will be apparent from the following description and appended claims.

According to the process of the present invention I have discovered that levoglucosan (1,6-anhydro-beta-D-glucopyranose) which is represented by the following formula:



can be produced in high yield by subjecting a glucose-yielding carbohydrate, such as cellulose, to pyrolysis by contacting the carbohydrate with heat and a stream of an inert gas at substantially atmospheric pressure for a time sufficient to produce a substantial amount of levoglucosan. The decomposition product which contains a substantial amount of levoglucosan is removed from the pyrolysis zone (reaction zone) by the inert gas and is

condensed by any common method of condensation. The non-condensable vapors are vented and the crude levoglucosan product is isolated from the pyrolysis condensate by evaporating the water and other relatively volatile materials. Levoglucosan product is then separated from the crude levoglucosan product by crystallization and filtration, sublimation, or other suitable methods. The heat for the pyrolysis may be supplied by employing a hot inert gas, by heating the carbohydrate while using a cold inert gas, and preferably by heating the gas and the carbohydrate.

Any glucose-yielding carbohydrate, preferably cellulose obtained from materials such as wood pulp and cotton, is suitable for the practice of this invention. Cellulose of varying purity, such as lignocellulose, can be used. However, the purer the cellulose the higher is the yield of levoglucosan product. A pure cellulose not only gives an increased yield of the crude levoglucosan product but also produces a higher percentage of levoglucosan therein thus simplifying its isolation. Exemplary of other glucose-yielding carbohydrates are polymers of glucose, such as lichenin, bacterial cellulose, dextran, glycogen, starch, and regenerated cellulose; disaccharides, such as cellobiose, lactose, maltose, and sucrose; and beta-glucose.

The term "inert gas" as employed herein denotes a gas or vapor which is substantially devoid of any substance, such as oxygen, which upon contact with the levoglucosan product may react therewith. Exemplary of such inert gas is steam, superheated steam, nitrogen, helium, neon, argon, carbon monoxide, carbon dioxide, or a mixture thereof. Thus, air is not suitable for the practice of this invention since it contains a substantial amount of oxygen which instantaneously reacts with the levoglucosan product as soon as it is formed and causes its degradation. Superheated steam has been found to be a preferred inert gas in the process of this invention since it is inexpensive, constitutes a good heat transfer medium, and gives a very high yield of levoglucosan product.

The flow rate of the inert gas in the pyrolysis zone may vary widely. For instance, for a 50-gram charge of cellulose, a flow rate of steam giving 30 to 60 ml. of condensate per minute is satisfactory. The flow rate of the inert gas determines the efficiency of the recovery of the crude levoglucosan product and the pyrolysis temperature since the rate and amount of the inert gas have a direct effect on the temperature in the reaction zone. The physical and chemical properties of the starting materials as well as the capability of the apparatus employed have a direct effect on the rate of the gas flow.

The pyrolysis proceeds, according to the present invention, in a temperature range of between about 250° C. and about 1000° C., preferably between about 350° C. and about 600° C. The upper practical limit of the pyrolysis temperature depends on the flow rate of the inert rate gas which in turn affects the pyrolysis time. The faster the flow rate of the gas the higher may be the operating temperature. The higher the temperature, the faster is the rate of pyrolysis. Better results are obtained by applying a high rate of gas flow which carries away the product more rapidly from the pyrolysis zone and causes faster and more efficient pyrolysis due to rapid and uniform heat transfer to the starting material. The pyrolysis time may vary widely. For instance, a pyrolysis time of less than 1 second is obtained when cellulose is heated in the neighborhood of 1000° C. using a stream of nitrogen, and a pyrolysis time of about 90 minutes is obtained when cellulose is heated at about 300° C. employing a stream of superheated steam.

The following examples illustrate but in no way limit the scope of this invention.

EXAMPLE 1

A conventional pyrolysis apparatus consisted of three major sections. The first section was a preheater for superheating inert gases, such as steam. The second section was a pyrolysis chamber containing a screen basket for pyrolysis of a charge therein. The third section was a suitable condenser to which an outlet from pyrolysis chamber was connected. Sulfite wood pulp containing 96% alpha-cellulose was treated with .04 N sulfuric acid for 2 hours at 105° C. and then with 7% sodium hydroxide aqueous solution for 10 hours at 80° C. After thorough washing and drying a 34.0 gram charge of this pretreated wood pulp was placed in the screen basket. The pyrolysis zone was preheated to 350° C. The system was closed, superheated steam was passed continuously through the pyrolysis zone at a rate of flow which gave 40 ml. of steam condensate per minute. The pyrolysis temperature was maintained between 350° C. and 400° C. through the reaction period. The pyrolysis was completed in about 34 minutes. The pyrolysis produced a solid residue and gaseous decomposition products which were condensed while the non-condensable vapors were vented. The pyrolysis condensate was collected and thereafter evaporated to about 500 ml. by removing a part of water therefrom. This volume was then extracted with chloroform to remove some colored impurities. The remaining aqueous solution was evaporated to remove the remaining portion of water and other relatively volatile materials. The residual syrup, i.e. the crude levoglucosan product, weighed 21.1 grams, corresponding to a yield of 62% based on the dry weight of the original pulp. The syrup contained 48% of pure levoglucosan by chromatographic analysis, corresponding to 29.8% by weight of the dry pulp. The syrup was dissolved in about 75 ml. acetone. On dilution with another 150 ml. acetone a small amount of impurities separated as a flocculent precipitate. This was removed by filtration, the filtrate was concentrated, and crystals of levoglucosan were separated therefrom and washed with acetone. The melting point of the crystals was 182°–184° C. Triacetate and tribenzoate derivatives of the crystals were prepared. The melting points of these two derivatives correspond to those given in the literature. Optical rotation and infrared specturm also confirmed that the crystals were levoglucosan.

EXAMPLE 2

The procedure of Example 1 was followed except that, in order to evaluate the effect of different pyrolysis temperatures on the yield of the crude levoglucosan product, the cellulose was first steamed at 250° C. and subsequently extracted with water. The following results indicate that the yield of crude levoglucosan product increases with an increase in the pyrolysis temperature.

Table 1

Pyrolysis temperature	Pyrolysis time, minutes	Percent Yield of Crude Levoglucosan
350° C.	67	45.3
400° C.	34	48.5
450° C.	28	49.5

EXAMPLE 3

The procedure of Example 1 again was followed, except that various starting materials were used and the wood pulp containing 96% alpha-cellulose was subjected to different purification treatments. The following results indicate that various starting materials and different purification methods therefor produce different yields of levoglucosan. The yields given hereinbelow are based on the weight of the dry starting material and were obtained by chromatographic analysis.

Table 2

Starting Material	Percent Yield of Crude Levoglucosan	Percent Yield of Pure Levoglucosan
Wood pulp heated in kerosene at reflux	58	26
Wood pulp partially hydrolyzed with Methanol-Hydrogen Chloride	55	23.1
Hydrocellulose (wood pulp treated with dilute sulfuric acid	61	27
Wood pulp extracted with sodium hydroxide	53	22
Wood pulp partially hydrolyzed and then caustic extracted (Example 1)	62	29.8
Cotton linters	60	27
Starch	55	23
Microcystalline cellulose	52	23

An advantage of the present invention is that levoglucosan may be produced simply, inexpensively and commercially on a large scale. Employing atmospheric pressure and an inert gas results in a high yield of levoglucosan which makes the process practical and commercially feasible. Another advantage of this invention is that a heat transfer medium, such as superheated steam, serves to heat the carbohydrate to be pyrolyzed rapidly and uniformly. The inert gas removes the products of the pyrolysis as soon as they are formed and provides a dilution effect, thus preventing polymerization or further breakdown of the molecules. A further advantage of this invention is that the process may be carried out batchwise as well as continuously, such as by fluidized or moving bed methods.

Levoglucosan is useful in the preparation of polymers, plasticizers, and as an intermediate for synthesis in the field of carbohydrate chemistry. The internal glucoside ring gives levoglucosan unique properties for the solution of synthesis problems.

Having thus described my invention in preferred embodiments, I claim:

1. A process for producing levoglucosan which comprises pyrolyzing a glucose-yielding carbohydrate in the presence of a stream of an inert gas at substantially atmospheric pressure for a time sufficient to produce a substantial amount of levoglucosan.

2. The process of claim 1 wherein said carbohydrate is a disaccharide.

3. The process of claim 1 wherein said carbohydrate is a polymer of glucose.

4. The process of claim 1 wherein said carbohydrate is cellulose.

5. The process of claim 1 wherein said gas is superheated steam.

6. The process of claim 1 wherein said carbohydrate is pyrolyzed at a temperature in the range of between about 250° C. and about 1000° C.

7. The process of claim 1 wherein said carbohydrate is pyrolyzed at a temperature between about 350° C. and about 600° C.

8. A process for producing levoglucosan which comprises the steps of

(a) contacting in a reaction zone a glucose-yielding carbohydrate with a stream of superheated steam at substantially atmospheric pressure and a temperature of between about 250° C. and about 1000° C. for a time sufficient to produce decomposition products containing a substantial amount of levoglucosan product,

(b) removing from the reaction zone said decomposition products by said stream of superheated steam,

(c) separating the levoglucosan product from the decomposition products.

9. The process of claim 8 wherein said temperature is between about 350° C. and about 600° C.

10. A process for producing levoglucosan which comprises pyrolyzing a glucose-yielding carbohydrate selected from the group consisting of microcrystalline cellulose,

cellulose, lichen, bacterial cellulose, dextran, glycogen, starch, regenerated cellulose, cellobiose, lactose, maltose, sucrose, and beta-glucose, in the presence of a stream of an inert gas at substantially atmospheric pressure for a time sufficient to produce a substantial amount of levoglucosan.

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