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(54) Process and Apparatus for Modifying Carbohydrates

(57) A process and apparatus are described for producing a modified carbohydrate material, preferably starch, in fluid form. In the process a starch slurry is continuously moved through a confined tubular preheat zone where heat is very rapidly transferred to the slurry, whereby the slurry passes through a gelation stage and forms into a hot free flowing liquid. The heat transfer is from superatmospheric steam surrounding at least part of the tubular heating zone, the temperature of the steam and the cross-sectional area of each tubular preheat zone being selected to rapidly transfer heat from the steam throughout the slurry and minimize the magnitude of the zone of high viscosity gel formed during the gelation stage. The hot liquid formed is immediately forced through a restrictive opening and into a confined tubular reaction zone accompanied by a sudden decrease in pressure whereby the starch is made highly reactive. The reactive starch liquid, together with a reactive adjunct such as acid, is then continuously moved through a tubular reaction zone to produce a modified starch product in fluid form. A steam heated reactor for the above process is also described.

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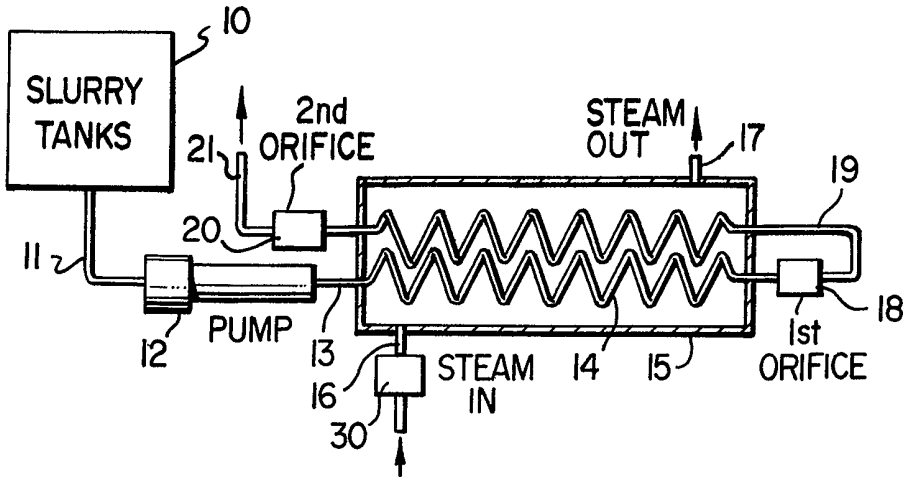

FIG. 1.

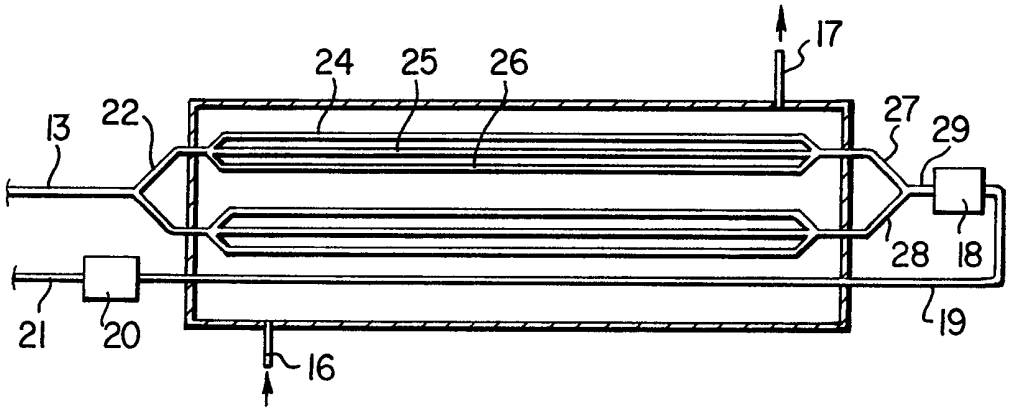

FIG. 2

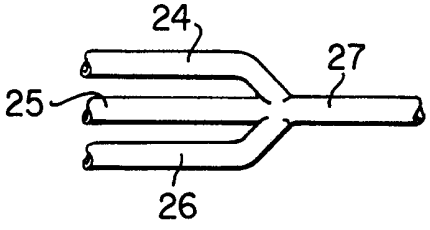

FIG. 3

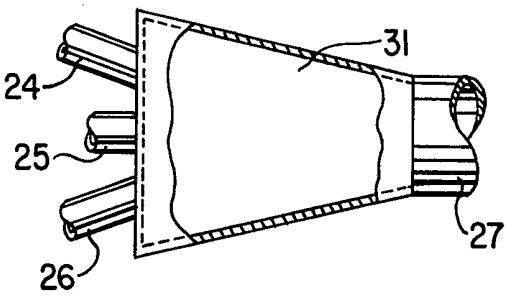

FIG. 3a

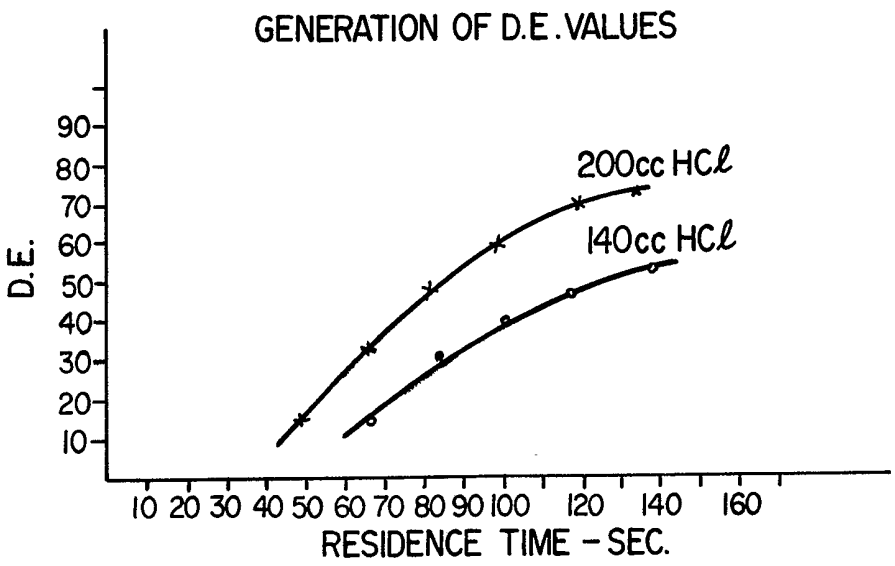
GENERATION OF D.E. VALUES
D.E.
90
80
70
60
50
40
30
20
10
200cc HCℓ
140cc HCℓ
10 20 30 40 50 60 70 80 90 100 120 140 160
RESIDENCE TIME - SEC.

FIG. 4

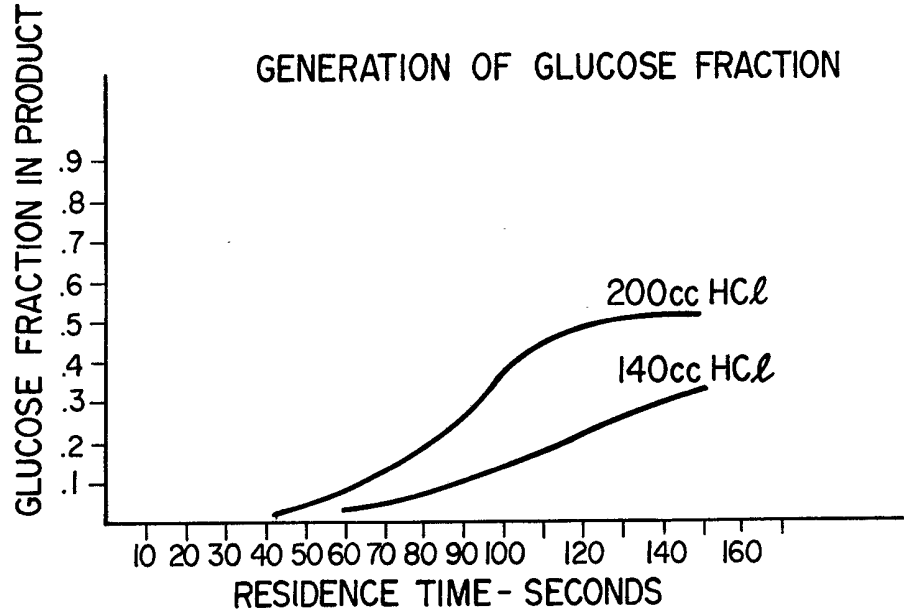
GENERATION OF GLUCOSE FRACTION
GLUCOSE FRACTION IN PRODUCT
.9
.8
.7
.6
.5
.4
.3
.2
.1
200cc HCℓ
140cc HCℓ
10 20 30 40 50 60 70 80 90 100 120 140 160
RESIDENCE TIME - SECONDS

FIG. 5

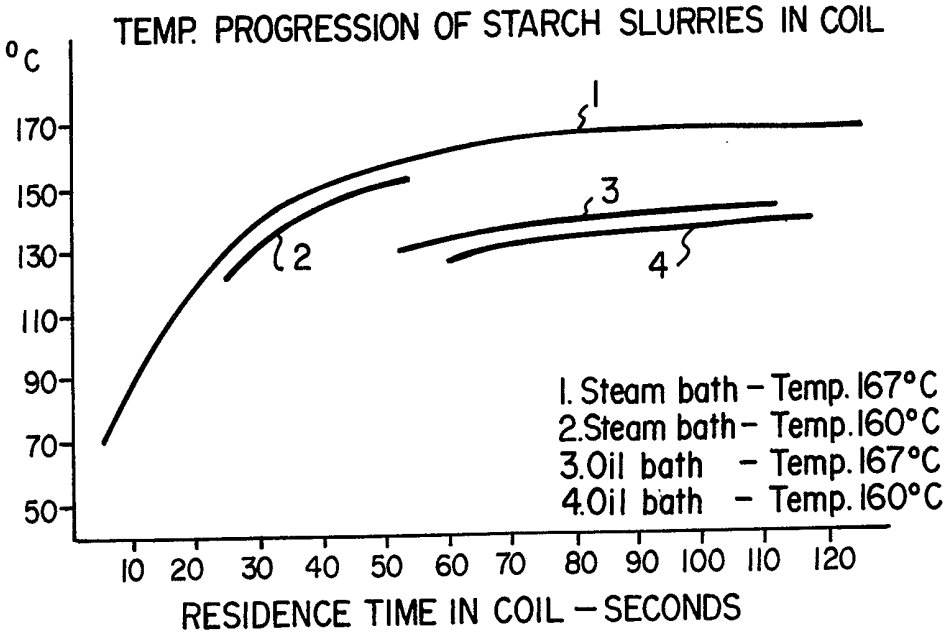
TEMP. PROGRESSION OF STARCH SLURRIES IN COIL
°C
170
150
130
110
90
70
50
1
2
3
4
1. Steam bath – Temp. 167°C
2. Steam bath – Temp. 160°C
3. Oil bath – Temp. 167°C
4. Oil bath – Temp. 160°C
10 20 30 40 50 60 70 80 90 100 110 120
RESIDENCE TIME IN COIL – SECONDS

FIG. 6

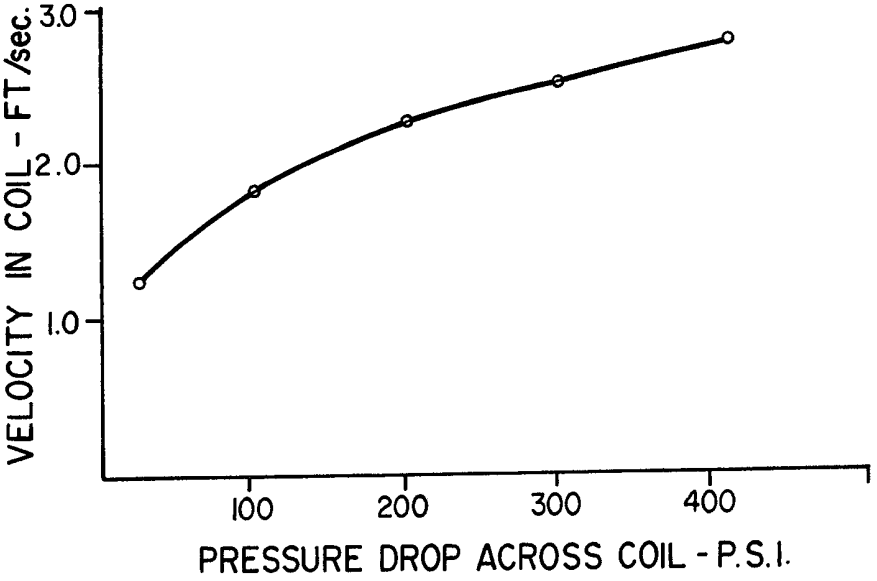
VELOCITY IN COIL - FT/sec.
3.0
2.0
1.0
100
200
300
400
PRESSURE DROP ACROSS COIL - P.S.I.

FIG. 7

SPECIFICATION

Continuous Process and Apparatus for Modifying Carbohydrate Material

This invention relates to a process for reacting a carbohydrate material with various modifying or derivatizing agents. More particularly, this invention relates to a process for producing modified starches and derivatized starches in a homogeneous fluid form.

A variety of long chain, high molecular weight carbohydrate materials are known, of which starch is typical. When these are treated with a solvent, usually under pressure, they reach a stage allowing the polymer chain to obtain and maintain many conformational states. Such a stage is normally associated with a viscosity decrease. The solvent used is usually water, although other solvents can also be used. As this relates to starch, raw starches in their usual commercial form are insoluble in water but may be formed into a colloidal or semi-colloidal dispersion by forming a slurry with water and heating the starch slurry to an elevated temperature at which the starch granules swell or burst and thus become "gelatinized". The particular temperature required for gelatinization depends upon the particular starch selected and on other conditions maintained during the gelatinization. The properties of such gelatinized dispersions depend upon many factors such as temperature and concentration, and also upon the starch material itself and the manner in which the dispersion is prepared.

This gel-forming characteristic of starch slurries when heated has always presented difficulties in processes for reacting starch with other reagents. Traditionally these starch reactions have been carried out in batch vessels over long periods of time.

There has been some degree of success with continuous starch reactions and, for instance, there are on the market continuous starch hydrolyzation systems in which the starch slurry is simply pumped through a long heating coil within which the hydrolysis takes place. Such systems are demanding on plant space, as well as energy and also have limitations as to the degree of reaction that can be achieved. Thus, in hydrolyzing starch, the maximum D.E. value that can be satisfactorily achieved in a system of the above type is in the order of about 50. When high D.E. syrups are required, e.g. at least 70 D.E. syrups, an enzyme conversion process has been required.

A significant step forward in the field of starch reactions can be found in the process of Hughes, U.S. Patent 4,137,094, in the Hughes process a starch slurry is pumped through a primary heating coil whereby it passes through the gelation stage and into the form of a hot free-flowing liquid. This liquid is then forced under high pressure through a restrictive opening into a confined tubular reaction zone and this has the effect of greatly increasing the reactivity of the starch slurry.

The Hughes apparatus operated with an oil bath and when this was operated at a moderate temperature of about 170°C, satisfactory syrups could be produced up to about 70 D.E. However, for rapid conversion this could be achieved only at excessive pressures of usually more than about 84 Kg/sq.cm. and no pumps have been found among the most sophisticated industrial pumps available which do not quickly break down under the conditions of trying to feed an acidic starch slurry at such extreme pressures.

It was found that flow rates greatly increased and pressures dropped by increasing the temperature of the oil bath, but this resulted in a decrease in quality of the syrups produced. For instance, at an oil temperature of 190°C, syrups of satisfactory quality could not be obtained above about 60 D.E. The usual commercial syrups have D.E. values up to 73 and for a commercial machine to be entirely useful, it must be capable of continuously producing a high quality syrup in the 73 D.E. range.

It is the object of the present invention to overcome the above difficulties of the Hughes process.

The present invention relates to a continuous process and apparatus for producing a modified carbohydrate material in homogeneous fluid form in which a slurry of carbohydrate material is continuously moved through a confined tubular preheat zone and heat is rapidly transferred to the slurry in the tubular zone whereby it passes through a gelation stage and forms into a hot free-flowing fluid having a temperature of at least 125°C. The heat is supplied from a steam bath containing superatmospheric steam and the temperature of the steam and the cross-sectional area of each tubular preheat zone are selected to provide a rapid heating of the slurry such as to minimize the magnitude of the zone of high viscosity gel during the gelation stage. This hot fluid thus formed is then immediately forced through a restrictive opening and into a confined tubular reaction zone accompanied by a sudden decrease in pressure whereby the carbohydrate material is made highly reactive. This highly reactive material is continuously moved, together with a reactive adjunct, through the tubular reaction zone to produce a modified carbohydrate material in fluid form.

The apparatus of the invention is a reactor comprising an elongated tubular preheater having a plurality of flow tubes passing through a heat exchange vessel, said heat exchange vessel being adapted to receive super atmospheric steam, a feed inlet to said preheater comprising a tube member connected by way of a manifold to inlets of said plurality of flow tubes, an outlet from said preheater comprising an outlet tube member connected by way of a manifold to outlets of said plurality of flow tubes, the sizes of the feed inlet tube, the outlet tube and the flow tubes being arranged such that the velocities through the tubes are substantially equal, a first flow restricting orifice connected to said single outlet tube, an elongated reaction tube having the inlet thereof flow connected to said first

orifice outlet and positive displacement pump means connected to said feed inlet tube.

The carbohydrate material may be selected from the group consisting of unmodified carbohydrate material, chemically modified carbohydrate material, derivatized carbohydrate material and mixtures thereof. The most common such material is starch, e.g. corn, potato, tapioca, sago, rice, wheat, waxy maize, grain sorghum, and waxy sorghum. They can be used in refined form or as natural components in cereal grains. It is also possible to use hemicellulose containing materials, for example, the hull fibers isolated in the wet-milling industry.

The adjunct may be selected from acids, alkalis, salts and mixtures thereof as well as enzymes to produce a modified carbohydrate. Alternatively, the adjunct may be a carbohydrate derivatizing agent such as sodium tripolyphosphate, propylene oxide, 2,3-epoxypropyl- trimethyl-ammonium chloride, sodium chloroacetate, epoxychlorohydrin, acetic anhydride, maleic anhydride, 2-chloroethyl diethylamine hydrochloride, 2,3-epoxypropyl sulfonate, triethylamine, sulfur trioxide and urea.

Some of the molecules of native starches are extremely long and it may be necessary to break these down to a manageable point in the preheat zone. This can be done by means of a cleaving agent, such as an acid, in the carbohydrate slurry.

In a process of the present type, the carbohydrate slurry must pass through a gel stage and thereafter achieve a state of equilibrium. At equilibrium, the slurry has passed through a viscosity peak and has returned to a relatively low viscosity, e.g. less than 500 cps at 90°C immediately after discharge without any substantial reaction of the carbohydrate material having taken place.

It is an important feature of this invention that the magnitude of the zone of high viscosity gel during the gelation stage is kept to a minimum, since this makes it possible to quickly achieve the state of equilibrium without the necessity of using extreme conditions of temperature and/or pressure in the preheat zone. This requires an extremely rapid heat input into the slurry in the preheat zone without substantial burning of the carbohydrate and this has been achieved according to this invention by means of individual tubular preheat zones of limited cross-sectional area which pass through a heating bath containing superatmospheric steam. The steam is generally at a pressure in the range of 7—17.5 Kg/sq.cm., with a pressure in the range of about 7—8.7 Kg/sq.cm. being particularly preferred. The 7 Kg/sq.cm. steam provides a bath temperature of 166°C, while the 8.7 Kg/sq.cm. steam provides a bath temperature of 185°C. It is also particularly desirable to use saturated steam, since it provides a greater uniformity of heating.

It is also important to have the material pass through the preheat zone as quickly as possible since it has been found that long exposures to heating tends to encourage undesirable side reactions. This is particularly important in the hydrolysis of starch, since slow reactions tend to increase the production of materials such as gentiobiose, which gives a bitter taste in the product. With the process of this invention the carbohydrate slurry is normally passed through the gel stage and brought to equilibrium conditions at reaction temperature within about 100 seconds, preferably within about 25 to 45 seconds using a 13 mm I.D. preheat tube and within about 50—100 seconds using a 25 mm I.D. preheat tube. The actual slurry velocity is usually about 15 to 120 cm/sec, preferably 30 to 90 cm/sec.

At these equilibrium conditions and desired reaction temperatures, the hot carbohydrate liquid is forced through a restrictive opening and into a confined tubular reaction zone accompanied by a sudden decrease in pressure. This has the effect of greatly increasing the reactivity of the carbohydrate so that it will very quickly react with reactive adjuncts within the tubular reaction zone. Such adjuncts may be mixed with the carbohydrate slurry before passing through the preheat zone or it may be injected directly into the highly reactive material immediately following the restrictive opening.

The tubular preheat zone can be of any desired configuration, provided it is capable of maintaining a continuous flow of material. For instance, it may be a heat exchange tube through which the material is driven by means of a continuous displacement pump. In order to achieve the desired high rate of heat exchange throughout the slurry, the individual heat exchange tubes are preferably of relatively small diameter, e.g. less than 5 cm. It has been found to be particularly advantageous to use quite small diameter tubes in the range of about 13 mm to 38 mm. With the diameters of 25 mm or more, it may be advantageous to use static mixers to provide adequate mixing within the tubes.

Moreover, additional heating and mixing of the starch slurry can be achieved by direct injection of steam into the slurry within the tube, e.g. by injecting steam in the region of the preheat zone inlet. This can serve to very quickly raise the temperature of the slurry and will, of course, have some dilution effect on the slurry. The balance of the heating to equilibrium conditions is achieved by indirect heating in a steam bath.

The restrictive opening must have a cross-sectional area significantly smaller than the cross-sectional area of the individual preheat tubes and each opening preferably has a diameter of less than about 6 mm. The restrictive opening between the preheat zone and the reaction zone can be in the form of single opening, or a plurality of adjacent openings may be used.

The temperature of the material passing through the restrictive opening is at least 125°C. and is preferably in the range of 130 to 170°C. for acid hydrolysis of starch. Of course, for other reactions the temperatures may vary significantly from this.

The pressure on the inlet side to the restrictive opening is usually at least 21 Kg/sq.cm., and preferably at least 35 to 70 Kg/sq.cm. The upper limit is largely determined by the capability of the

pump being used to pump the slurry through the system. There is a very marked pressure drop across the restrictive opening and this is preferably in the order of 21—42 Kg/sq.cm.

The confined tubular reaction zone can also be of any desired configuration, provided it is capable of maintaining a continuous flow of material. It is preferably a heat exchange tube which may pass through either the preheat steam bath or a separate heat exchange bath at the same or different temperature from the preheat steam bath. The reaction tube can be the same size as the preheat tubes or large or smaller diameter than the preheat tubes, depending on the materials being processed. Generally, the size of the reaction tube is less critical than is the size of the preheat tube since the material entering the reaction tube is already a freely flowing liquid at reaction temperature.

The residence time in the tubular reaction zone of 13 mm diameter is usually less than two minutes to produce a starch syrup having a D.E. of up to 73 and a high quality syrup of 73 D.E. has been produced according to this invention with a total residence time in a 13 mm diameter the preheat and reaction zone of less than 2 1/2 minutes.

It is desirable that the pressure within the reactor be controlled entirely by the feed pump, rather than by any form of pressure responsive recycle loop. This can be achieved by means of a variable speed positive displacement pump, such as the Moyno pump, with the pressure in the reactor being controlled by the pump speed. In this manner, the material being processed travels through the reactor as a continuous forwardly moving mass.

A better control of this system is achieved if a control is maintained over the pressure within the tubular reaction zone and this can conveniently be achieved by providing a further restrictive opening at the outlet end of the reaction zone. The pressure within the reaction zone is preferably maintained at a level sufficient to keep the material in the reaction zone in the liquid stage, e.g. about 14 Kg/sq.cm.

Certain preferred embodiments of the present invention are illustrated in the attached drawings in which:

Figure 1 is a schematic flow sheet showing apparatus for carrying out the invention;
Figure 2 is a schematic representation of one preferred embodiment of the apparatus;
Figure 3 is a detailed view of a tubular collector arrangement;
Figure 3a is a sectional view of a preferred collector arrangement;
Figure 4 is a plot of D.E. values against residence time in the reactor;
Figure 5 is a plot of glucose values against residence time in the reactor;
Figure 6 is a plot of temperature progressions for steam and oil heated reactors; and
Figure 7 is a plot of pressure drop against flow velocities for a steam reactor.

As will be seen from Figure 1, a holding tank 10 is provided for a starch slurry feed. This tank has an outlet line 11 which feeds into a Moyno pump 12. The slurry is pumped out of pump 12 to line 13 at high pressure and into a heating coil 14. The pressure within coil 14 is controlled by varying the speed of pump 12.

The main reactor of this apparatus is a closed and insulated vessel 15 which is essentially a steam vessel being supplied by a steam inlet line 16 and a steam outlet line 17. A steam control valve 30 is provided in the steam inlet line.

The tube 14 is made of stainless steel and is preferably arranged as a coil. This is the preheater for the reaction and the slurry passing through tube 14 passes through a gel stage and forms into a hot free flowing liquid. The outlet of preheat tube 14 feeds into a first restrictive opening or orifice 18 having a much smaller diameter than the diameter of tube 14. The outlet of the orifice 18 connects to a further stainless steel tube 19 which forms the tubular reaction zone of the invention. This tube in the form of a coil passes back through the steam vessel 15 and the reaction occurs during the travel of the hot liquid through coil 19.

In order to control the pressure within coil 19, a second restrictive opening or orifice 20 is provided at the outlet. The reaction product is then collected through outlet line 21.

Figure 2 shows schematically an arrangement for a high capacity apparatus. Since one of the important features of this invention is the very short heating time of the reaction materials, it is most important to bring the starch slurry through the gel stage and up to reaction temperature as quickly as possible. This is achieved in Figure 2 by connecting the slurry feed inlet 13 to a manifold consisting of two branch lines 22 and 23. Each of these branch lines is further divided into three additional branch lines 24, 25 and 26 within the heat exchange vessel. Thus, there are six preheat coils passing through vessel 15. This provides very quick heat transfer between the steam and the slurry passing through the coils.

Each group of three coils discharges into a single outlet tube 27 and 28 and these in turn feed into a single outlet line 29 which feeds into the first orifice 18. The remainder of the reaction then continues in the same manner as described above in Figure 1.

Since the viscosity of the material being processed varies widely as it passes through the preheat zone, it is most important that the sizes of the tubes be such that at any point in the process there will be a constant velocity across all of the tubes. Thus, at the outlet of tubes 24, 25 and 26, it will be seen from Figure 3 that the sizes of tubes 24, 25 and 26 on the one hand and tube 27 on the other hand must be such that the velocities in all four tubes will be constant. The same must be true for the three preheat tubes feeding into line 28 and the flow in lines 27 and 28 must also be at the same velocity so

that the materials emerging from the various tubes will all be at the same stage of processing when they enter into line 29 and the first orifice 18.

The main branch lines 22 and 23 may include valves so that either one or both lines may be used. Moreover, these lines 22 and 23, along with lines 27 and 28, may include couplings so that individual bundles of tubes 24, 25, 26 may be removed for maintenance. With a bundle removed, the remainder of the reactor can continue operating.

A preferred form of collector from the multiple preheater reaction tubes is shown in Figure 3a. A problem that can be encountered when a series of tubes discharge into a single outlet tube is that if conditions within the multiple tubes are not absolutely identical, there may be a tendency for more rapid flow through one of the tubes than the others and this will then tend to channel into the outlet tube in preference to the slower tubes, resulting in a product which lacks homogeneity.

The collector in Figure 3a is in the form of a truncated conical vessel 31 with the outlets of tubes 24, 25 and 26 connecting to the large end of vessel 31 at an angle to the axis of the vessel. In this manner the streams from tubes 24, 25 and 26 impinge upon each other within vessel 31 thereby causing a uniform mixing at this point and discouraging any tendency of any single stream from one of tubes 24, 25 and 26 to channel directly into outlet tube 27. This collector vessel can be used at any point in the system where discharges from two or more tubes are being directed into a single tube.

The above systems show the reaction tube passing through the same heat exchange bath as the preheat tubes. It is, however, to be understood that depending on the reaction being carried out, the reaction tube may be partially or totally outside the heat exchange bath or may pass through a separate bath maintained at a temperature different from the preheat bath.

The following examples are further illustrative embodiments of this invention. All parts and proportions are by weight unless otherwise specified and all pressures are gauge pressures.

Example 1

(a) The process was carried out using a reactor of the type described in Figure 1. The coils 14 and 19 were made from 13 mm I.D. stainless steel tubing with coil 14 having a length of 36.6 m. and coil 19 having a length 12.2 m. The first orifice had a diameter of 1.6 mm and the second orifice was in the form of a pair of adjacent openings, each having a diameter of 1.6 mm.

A starch slurry was formed from starch and water, this slurry containing 36.1% starch solids. 200 mls of hydrochloric acid were added to the slurry per 45 Kg of starch solids and this gave a slurry conductivity of 4100 micromhos, at 30°C. This slurry passed through the reactor at a rate of 7.5 liters per minute under the following reaction conditions:

Table 1
Reactor Conditions

Temperatures	
Steam supply	167°C
Steam after control valve	163°C
Steam bath (bottom)	160°C
Steam bath (top)	160°C
1st orifice inlet	148°C
1st orifice outlet	148°C
2nd orifice inlet	159°C
Pressures	*Kg/sq.cm.*
Steam supply	7
Steam after control valve	5.7
Feed pump outlet	70
1st orifice inlet	52.5
1st orifice outlet	32.9

The hot starch liquid immediately before the first orifice 18 had a viscosity of approximately 25 cps at 80°C. The product obtained had a D.E. of approximately 14.

(b) The above apparatus was modified to provide a preheat coil 24.4 m. long and reaction coils of varying lengths. With this arrangement, the residence time in the preheat zone was about 33 seconds and the total residence times in the reactor varied between 50 and 140 seconds.

The starch slurry feed contained 36.4% starch solids and runs were made with 140 and 200 mls of hydrochloric acid per 45 Kg of starch solids in the slurry. The steam bath temperature was 166°C, and the feed pump outlet pressure was 63 Kg/sq.cm. This produced D.E. values ranging from about 15 to about 73, with the product being of excellent quality. The D.E. results are plotted on Figure 4 and these show the very rapid generation of D.E. values within the reaction tube. Figure 5 shows a separate plot of glucose fractions in the products from the above production runs.

Example 2

(a) A series of additional tests were carried out on the same apparatus as described above to produce corn syrups having D.E. values in excess of 70.

Again using half inch tubes, a test was carried out using a preheat coil having a length of 24.4 m. feet and a reactor coil having a length of 85.3 m. The first orifice had a diameter of 1.6 mm and the second orifice consisted of two adjacent holes each having a diameter of 1.6 mm.

An aqueous starch slurry feed was prepared containing 34.8% starch solids and 190 mls of hydrochloric acid were added per 45 Kg of dry starch solids. This gave a conductivity of 3450 micromhos.

This slurry was pumped through the reactor at a flow rate of 6.8 litres per minute under the following reaction conditions:

Table 2
Reactor Conditions

Temperature	
Steam supply	165°C
Steam after control valve	165°C
Steam bath (bottom)	167°C
Steam bath (top)	165°C
1st orifice inlet	145.6°C
1st orifice outlet	145.9°C
2nd orifice inlet	162°C
Pressures	*Kg/sq.cm.*
Steam supply	6.9
Steam after control valve	6.8
Feed pump outlet	63
2nd orifice inlet	14

The product obtained was a corn syrup having excellent taste with a D.E. of approximately 74. The product had a solids content of 44 to 45%.

(b) The above test was repeated using a preheat coil having a length of 24.4 m. and a reaction coil having a length of 73.1 m. Otherwise the apparatus was unchanged.

The feed slurry was a pearl corn starch slurry containing 35.9% dry solids and 200 mls of hydrochloric acid per 45 Kg dry starch solids. This was pumped through the reactor at 6.6 liters per minute with a first orifice inlet temperature of 146°C.

The product obtained had a D.E. of about 73, containing 48.4% glucose.

(c) The process was repeated using a preheat coil having a length of 8.4 m. and a reaction coil having a length of 16.8 m. Again the remainder of the apparatus was unchanged. The feed slurry contain 35.5% dry solids of pearl corn starch and had added thereto 190 mls of hydrochloric acid per 45 Kg dry starch solids. This was fed through the reactor at a rate of 7.1 liters per minute and a first orifice inlet temperature of 161°C.

The product obtained had a D.E. of about 72 and contained 49.88% glucose and 19.37% dimers.

Example 3

A series of studies were conducted using the same apparatus as described in Example 1 above to determinerate of temperature rise of the starch slurry within the preheat coil and reaction coil. The slurry contained about 37% dry starch solids and runs were made with slurries containing 140 and 200 mls HCl. The flow velocity was about 79 cm.

These tests were conducted using a steam bath and an oil bath for heat exchange at bath temperatures of 160°C and 167°C. The results obtained are shown in Figure 6.

Example 4

A test was carried out to illustrate the importance of rapid heat input in the preheat zone. The reactor of Example 1 was used with a preheat coil having a length of 24.4 m.

The feed slurry contained 37% dry starch solids and 200 mls of HCl per 45 Kg starch. The steam bath had a temperature of 165°C. The slurry was pumped through the reactor at different velocities and the pressure drops across the system were recorded, the results being shown in Figure 7.

These show that with increasing velocities, there are very large increases in pressure drop. The very large pressure drops require very high inlet pressures with resulting heavy loads on the pump and other equipment. Thus, the faster is the heat transfer in the preheat zone, the faster the slurry passes through the gel stage and the less is the total energy required to drive the material through the tube.

Claims

1. In a continuous process for producing a modified carbohydrate material in fluid form, which

comprises continuously moving a slurry of carbohydrate material through a confined tubular preheat zone and transferring heat to the slurry whereby it passes through a gelation stage and forms into a hot free flowing liquid having a temperature of at least 125°C, immediately forcing said hot liquid through a restrictive opening and into a confined tubular reaction zone accompanied by a sudden decrease in pressure whereby the carbohydrate material is made highly reactive and continuously moving the highly reactive carbohydrate material, together with a reactive adjunct, through the tubular reaction zone to produce a modified carbohydrate material in fluid form, the improvement which comprises transferring the heat to the slurry from superatmospheric steam surrounding at least part of said tubular preheat zone, the temperature of the steam and the cross-sectional area of each tubular preheat zone being selected to rapid transfer heat from the steam throughout the slurry and minimize the magnitude of the zone of high viscosity gel formed during the gelation stage.

2. A process according to claim 1 wherein the carbohydrate material is a starch.

3. A process according to claim 1 or 2 wherein the adjunct is selected from acids, alkalis, salts, mixtures thereof and enzymes.

4. A process according to claim 1 or 2 wherein the adjunct is a carbohydrate derivatizing agent.

5. A process according to claim 2 wherein the starch material is raised to a temperature of 130 to 170°C in the preheat zone.

6. A process according to claim 1 wherein the steam is at a pressure of at least 7 Kg/sq.cm.

7. A process according to claim 6 wherein the steam is at a pressure of about 7 to 8.7 Kg/sq.cm.

8. A process according to claim 6 wherein the steam is saturated steam.

9. A process according to claim 6 wherein each tubular preheat zone has a diameter of not more than 38 cm.

10. A process according to claim 9 wherein the starch material is moved through the preheater at a speed of 15 to 120 cm/sec.

11. A process according to claim 10 wherein the starch slurry in the preheat contains 10 to 50% dry solids.

12. A process according to claim 11 wherein the hot free-flowing liquid from the preheat zone has a viscosity below 500 cps at 90°C immediately after discharge.

13. A process according to claim 12 wherein the pressure at the inlet to the preheating zone is at least 21 Kg/sq.cm.

14. A process according to claim 13 wherein the restrictive opening comprises at least one opening, each said opening having a diameter of no more than 6 mm.

15. A process according to claim 10 wherein the starch slurry is raised to a temperature of at least 130°C. within about 100 seconds in the preheat zone.

16. A process according to claim 10 wherein the starch slurry is raised to a temperature of at least 130°C within about 45 seconds in a preheat zone.

17. A continuous process for producing a modified starch material in fluid form, which comprises continuously moving a starch slurry through a confined tubular preheat zone having a diameter of no more than about 38 cm. at a speed of 15 to 120 cm/sec, transferring heat to the slurry in the preheat zone from a steam bath containing saturated steam at a pressure of least 7 Kg/sq.cm. whereby the slurry passes through a gelation stage and reaches an equilibrium stage in the form of a hot free flowing liquid having a temperature of at least 125°C, immediately forcing said hot liquid through a restrictive opening and into a confined tubular reaction zone accompanaied by a sudden decrease in pressure whereby the starch liquid is made highly reactive and continuously moving the highly reactive starch liquid, together with a reactive adjunct, through the tubular reaction zone to produce a modified starch product in fluid form.

18. A continuous process for producing starch syrups of D.E. values up to at least 73, which comprises continuously moving an acidified starch slurry through a confined tubular preheat zone having a diameter of no more than about 38 cm. at a speed of 15 to 120 cm/sec and transferring heat to the starch slurry from a steam bath containing saturated steam at a pressure of at least 7 Kg/sq.cm. whereby the starch slurry passes through a gel stage and reaches an equilibrium stage in the form of a hot free flowing liquid having a temperature of at least 125°C, immediately forcing the hot acidified starch liquid through a restrictive opening and into a confined tubular reaction zone accompanied by a sudden decrease in pressure whereby the starch is made highly reactive and continuously moving the highly reactive material through the tubular reaction zone to hydrolyze the starch into a starch syrup.

19. A reactor comprising an elongated tubular preheater having a plurality of flow tubes passing through a heat exchange vessel, said heat exchange vessel being adapted to receive super atmospheric steam, a feed inlet to said preheater comprising a tube member connected by way of a manifold to inlets of said plurality of flow tubes, an outlet from said preheater comprising an outlet tube member connected by way of a manifold to outlets of said plurality of flow tubes, the sizes of the feed inlet tube, the outlet tube and the flow tubes being arranged such that the velocities through the tubes are substantially equal, a first flow restricting orifice connected to said single outlet tube, an elongated reaction tube having the inlet thereof flow connected to said first orifice outlet and positive displacement pump means connected to said feed inlet tube.

20. A reactor according to claim 19 wherein said heat exchange vessel includes a plurality of said

inlet tube members and a plurality of said outlet tube members, each pair of inlet and outlet tube members having a plurality of said flow tubes connected therebetween.

21. A reactor according to claim 19 wherein said plurality of inlet tube members are flow connected to a single feed pump.

22. A reactor according to claim 21 wherein said pump is a variable speed pump, the speed of the pump being used as a pressure control means for the reactor.

23. A reactor according to claim 22 wherein each of said preheater flow tubes has an inside diameter of no more than about 38 mm.

24. A reactor according to claim 20 including valve means for individually closing said plurality of inlet tube members.

25. A reactor according to claim 19 wherein said elongated reaction tube passes through the heat exchange vessel containing the preheater.

26. A reactor according to claim 19 wherein said elongated reaction tube passes through a separate heat exchange vessel.

27. A reactor according to claim 19 including a continuous flow collector connected to said flow tube outlets, said collector having a truncated conical shape with a closed large end and an open small end, the open small end connecting to said outlet tube member, and said flow tubes connecting through openings in said large end, said flow tubes adjacent said openings being inclined toward the axis of the collector such that the flows from the flow tubes intersect within the collector.

28. A continuous process for producing a modified carbohydrate material in fluid form, according to claim 1 and substantially as hereinbefore described with reference to the accompanying drawings.

29. A reactor according to claim 19 and substantially as hereinbefore described with reference to the accompanying drawings.

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