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DISCLAIMER

CONTRACTUAL ORIGIN OF THE INVENTION

The United States Government has rights in this invention pursuant to Contract No. W-31-109-ENG-38 between the U.S. Department of Energy and The University of Chicago, representing Argonne National Laboratory.

Background Of The Invention

This invention generally relates to the bioconversion of industrial food waste containing starch to lactic acid suitable for conversion to photodegradable or biodegradable plastics. More particularly, this invention relates to an overall process for the conversion of high carbohydrate containing materials such as potato waste, cheese whey or the like into lactic acid which is thereafter polymerized to produce various degradable plastics. Cheese whey permeate which contains lactose rather than starch may also be used with slight modifications.

A huge supply of readily fermentable and generally non-toxic food waste provides an abundant and concentrated source of carbon and nitrogen for various aerobic and anaerobic bacteria. In the United States alone, totals for corn and potato waste streams are large, about 5.0 million

tons per year for potato alone, and other food streams also contain ideal substrates for enzyme and/or microbiological conversion to useful compounds. Lactic acid is one of the products which can potentially be extremely useful in industry because from it can be made various degradable plastics. Degradable plastics will assume an evermore increasing important role in replacing or partially replacing various plastic materials which forever remain in the environment or degrade so slowly that for all practical purposes are impossible to degrade in land fills or other waste collection sites throughout the United States. Lactic acid may be bioconverted directly from cheese whey permeate, cane and beet sugars using various lactic acid bacteria such as Lactobacilli in relatively high yields or indirectly by first hydrolyzing the starch in corn, potato or rice followed by bioconversions with lactic acid bacteria. Lactic acid and its sodium or calcium salts are completely non-toxic and are classified as GRAS (Generally Recognized As Safe) by the FDA.

Accordingly, an object of this invention is to provide an efficient process for producing lactic acid of sufficient purity to make a degradable plastic of lactide polymers and copolymers from a renewable biomass material in a sufficiently short process time to render the entire method economically viable.

Another object of the invention is to provide a process

for converting industrial food waste to glucose and then to lactic acid by the use of both enzyme and microbiological action, wherein the processing time to produce over 90% glucose is reduced to less than ten hours and the subsequent process time is less than about forty-eight hours to produce lactic acid from the glucose.

Yet another object of the invention is to convert industrial starchy waste into lactic acid while providing a glucose intermediate product which is substantially devoid of microbial contamination.

Yet another object of the invention is to provide a method of converting starch to a partially hydrolyzed substrate comprising providing a starch-containing material capable of conversion to a simple sugar, adding an effective amount of α-amylase enzyme to the starch-containing material to gelatinize and liquify the material, adding a stabilizing ion at a concentration in the range of from about 50 ppm to about 400 ppm, maintaining the material at a pH in the range of from about 4 to about 7, heating the material to a first elevated temperature in the range of from about 90°C to about 130°C, and maintaining the material at an elevated pressure not less than 15 psi, maintaining the material at the first elevated temperature and pressure for a time not less than about 15 minutes, cooling the temperature of the material to a second elevated temperature in the range of from about 50°C to about 70°C and adjusting

the pH to below about 6.5 and thereafter adding an effective amount of glucoamylase, and maintaining the mixture in the aforesaid condition for not less than about 4 hours.

Yet another object of the invention is to provide a method of converting starch to glucose, comprising providing a starch-containing material capable of conversion to a simple sugar, adding α-amylase enzyme in a concentration of from about 0.5x to about 100x, wherein 1x=30 units of α-amylase enzyme/gram of dry substance of starch-containing material, adding stabilizing calcium ion at a concentration in the range of from about 50 ppm to about 400 ppm, maintaining the material at a pH in the range of from about 4 to about 6, heating the material to a first elevated temperature in the range of from about 110°C to about 121°C, and maintaining the material at an elevated pressure not less than 15 psi, maintaining the material at an elevated temperature and pressure for a time not less than about 15 minutes, cooling the temperature of the material to a second elevated temperature in the range of from about 50°C to about 70°C and thereafter adding glucoamylase enzyme at a concentration of 0.5x to 100x, wherein 1x=[(13.44 unit-hour of glucoamylase)/(gram of dry substance of starting starch containing material)] $\div$ total hours of incubation, and maintaining the mixture in the aforesaid condition for a time in the range of from about 4 hours to about 24 hours to convert over 90% of the available

starch to glucose.

A final object of the invention is to provide a method of converting starch to lactic acid, comprising providing a starch-containing material capable of conversion to a simple sugar, adding an effective amount of α-amylase enzyme to the starch-containing material to gelatinize and liquify the material, adding stabilizing ion at a concentration in the range of from about 50 ppm to about 400 ppm, maintaining the material at a pH in the range of from about 4 to about 7, heating the material to a first elevated temperature in the range of from about 90°C to about 130°C, and maintaining the material at an elevated pressure not less than 15 psi, maintaining the material at an elevated temperature and pressure for a time not less than about 15 minutes, cooling the temperature of the material to a second elevated temperature in the range of from about 50°C to about 70°C and adjusting the pH to below about 6.5 and thereafter adding glucoamylase at a concentration of 0.5x to 100x, wherein 1x=[(13.44 unit-hour of glucoamylase)/(gram of dry substance of starting starch containing material)] $\div$ total hours of incubation, and maintaining the mixture in the aforesaid condition for a time in the range of not less than about 4 hours to convert more than 90% of the starch to glucose, separating the glucose from the material, introducing the glucose to a fermenter, introducing an effective amount of microorganisms selected from

homofermentative lactic acid bacterial strains to form fermentation broth to ferment the glucose to lactic acid, maintaining the microorganisms in contact with the glucose for a time sufficient to convert greater than about 90% of the glucose to lactic acid, and thereafter recovering the lactic acid from the fermentation broth.

The invention consists of certain novel features and a combination of parts hereinafter fully described, illustrated in the accompanying drawings, and particularly pointed out in the appended claims, it being understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

Brief Description of the Drawing

For the purpose of facilitating an understanding of the invention, there is illustrated in the accompanying drawing a preferred embodiment thereof, from an inspection of which, when considered in connection with the following description, the invention, its construction and operation, and many of its advantages should be readily understood and appreciated.

Figure 1 is a flow diagram of the inventive process.

Detailed Description of the Invention

Figure 1 shows a flow diagram illustrating the basic sections or stations of the inventive process. Although the process is illustrated using a substrate of potato waste,

other substrates such as cheese whey permeate, cornstarch, rice starch, barley, cane sugar, beet sugar and the like may be converted using all or part of the process herein described. The inventive process permits the conversion of more than 90% of the available starch in a potato waste to glucose in less than about eight to about ten hours and, therefore, the entire process of converting a batch of potato waste into glucose can be completed in one day. Specifically, solid potato waste and primary peel effluent are available in high volumes of more than a total of eighty thousand gallons of twelve percent starch per day per each processing plant. Other food stuffs that have in the range of between about seventy and seventy-five percent starch (dry weight) such as corn, soy gum and wheat, may also be suitable substrates for the conversion process hereinafter discussed. The substrate of potato starch in the example hereinafter set forth is blended.

The potato waste stream includes any high carbohydrate waste from a potato processing plant such as french fry plant, potato chip plant or the like and may include potato peel as well as other waste products. The potato waste, however, must be ground, blended or homogenized or otherwise size reduced by industrial blending and thereafter diluted with suitable water or deionized water until the mixture is essentially uniform. Figure 1, shows a combined processing step lasting from approximately 15 to about 30 minutes.

This step, which combines gelatinization and liquefaction of potato starch, the potato waste pH is adjusted in the range of from about 4 to about 7 but the preferred pH is about 5. Hydrochloric acid may be used to adjust the pH to 5 if the pH of the potato waste is somewhat higher. To this pH adjusted material is added an effective amount of α-amylase enzyme along with a stabilizing material in the form of calcium chloride. The α-amylase enzyme is added in a concentration of from about 1x to about 100x, wherein x = (30 units of α-amylase enzyme)/(gram of dry substance of starch-containing material). The preferred amount of α-amylase, depending to some extent upon the starting material, is about 10x. The calcium chloride is added in the range of from about 50 ppm to about 400 ppm with the preferred concentration being about 200 ppm. The pH, although preferred in this step to be about 5, may be in the range of from about 4-7, but is better maintained in the range of about 4.5 to about 6.5. In order to avoid readjustment of pH during later processing, it is preferred that the pH in the beginning α-amylase treatment remain in the range of from about 4.5 to about 5.5 with a pH of about 5 preferred.

After the calcium chloride and the α-amylase have been added to the starch and thoroughly mixed, the material is heated under pressure. This is a crucial step and one which has been found to greatly reduce the processing time

and also results in a non-microbial contaminated product. Specifically, it is preferred that the starch-containing material be uniformly exposed to an elevated temperature in the range of from about 90°C to about 130°C while the pressure is maintained at least at 15 psi for a time not less than about 15 minutes and preferably in the range of from about 20 to about 30 minutes. While the foregoing temperature range of 90°C to 130°C is available, it has been found that a temperature of about 121°C in combination with a 20 minute time span wherein the pressure is maintained at 15 psi has produced superior results. This process is important because it results in a material which has minimal microbiological activity.

Thereafter, the material is cooled to a second temperature in the range of from about 50° to about 70° and the pH is adjusted to below 6.5, if in fact it was higher for the α-amylase portion of the treatment. It has been found that the α-amylase processing for liquefaction of the starch may be accomplished at a pH as high as 7, but glucoamylase loses activity at a pH of greater than about 6.5. Accordingly, even if the initial portion of the process is conducted at a high pH, the glucoamylase is only effective at a lower pH. For this reason, it is preferred that the pH for all the enzymatic steps be maintained at about 5, even though the optimal pH for the glucoamylase enzyme is about 4.3.

After the temperature has been lowered the range of about 50°C to about 70°C with a temperature of about 60°C being preferred, the glucoamylase is added to the mixture in an effective amount, preferably at a concentration in the range of from about 0.5x to about 100x where 1x=[(13.44 unit-hour of glucoamylase)/(gram of dry substance of starting starch containing material)] - total hours of incubation. The incubation time is preferably in the range of from about 4 to about 8 hours with the shortest time for conversion to 90% to glucose being preferred. That is if the desired percent conversion occurs in the four hour time frame, then there is no substantial advantage to incubating for a longer period of time. In general, satisfactory results of over 90% conversion of the available starch to glucose has occurred in the time range of under 10 hours for the total process, with the glucoamylase digest taking approximately 4 to 8 hours. The glucoamylase portion of the conversion is conducted at atmospheric pressure. The mixture should be at a temperature of 60°C or less when the glucoamylase is added, otherwise the glucoamylase enzyme is unstable and may lose activity. For instance, 50°C is also satisfactory, and while a temperature of 70°C may be acceptable, lower temperatures are preferred. When it is desired to stop the action of the glucoamylase, the mixture is simply boiled thereby decomposing the glucoamylase and halting the saccharification reaction.

After the enzymatic hydrolysis reactions, the potato hydrolysate contains solids as well as a liquid portion containing glucose. The potato hydrolysate is passed through a filtration device wherein the solids are separated from the glucose-containing filtrate. To the filtrate from the filtration station is added nutrients to facilitate fermentation of the glucose to lactic acid.

In order for the fermentation to take place in a suitable time frame, the filtered potato hydrolysate containing the glucose must have certain nutrients in order to promote the bacterial growth necessary for the fermentation to take place in an acceptable time frame. In general, in batch tests there has been added monobasic potassium phosphate at 2 grams per liter, sodium acetate at 5 grams per liter, trypticase peptone at 10 grams per liter, tryptose at 3 grams per liter, yeast extract at 5 grams per liter, Tween 80 at 1 milliliter per liter, magnesium sulfite·7 H_2O at 0.575 grams per liter, iron sulfate·7 H_2O at 0.034 grams per liter and manganese sulfate·$2H_2O$ at 0.12 grams per liter. While these nutrient additives are adequate and satisfactory on a bench scale or laboratory test sizes, it is understood that in a production scale environment, inexpensive nutrient sources such as corn steep liquor can be used in lieu of the nutrient supplements above set forth.

The filtered potato hydrolysate containing glucose,

after the nutrients are added, is fermented in a typical industrially available fermenter for a period of about 48 hours thereby to produce or convert up to approximately 95% of the glucose to lactic acid, leaving a residual glucose concentration of less than about 0.05 grams per liter. The fermentation is conducted at a temperature in the range of from about 42°C to about 45°C and at a pH in the range of from about 5.5 to about 6.3. Preferably, the bacteria used in the fermentation step are selected from L. delbrueckii, L. lactis, L. acidophilus and L. casei, although homofermentative lactic acid bacterial strains in general are acceptable.

The pH is maintained in the fermenter with the addition, when required, of an alkali. The lactic acid produced is transformed, upon neutralization, into the lactate salt of the aforesaid alkali. Because an electrodialysis step is used for the recovery and purification of lactic acid from the fermentation broth, it is preferred to use, for pH adjustment, sodium hydroxide or other alkalies the lactate salt of which is compatible with the subsequent electrodialysis. In a continuous operation, there will be a recycle of alkali hydroxide from the electrodialysis separation of lactic acid from the fermentation broth filtrate as is obvious to one skilled in the art.

It has been found that conversions of over 95% of the

glucose to lactic acid has occurred in 48 hours of fermentation, and it has also been found that conducting the gelatinization/liquefaction and saccharification as heretofore disclosed has resulted in greater than 90% conversion of the available starch to glucose. Considering the entire process, it can be seen that there has been provided a rapid and economical process for converting various waste starch streams to lactic acid and most importantly in converting the waste starch stream to glucose with minimal microbial contamination, it being a significant advantage of the present invention that the combination of high pressure and high temperature processing kills most bacteria and produces a potato hydrolysate containing glucose that is substantially free of the usual microbial activity found in glucose feed streams. Therefore, microbial competition with the lactic acid producing bacteria in the fermenter is significantly reduced.

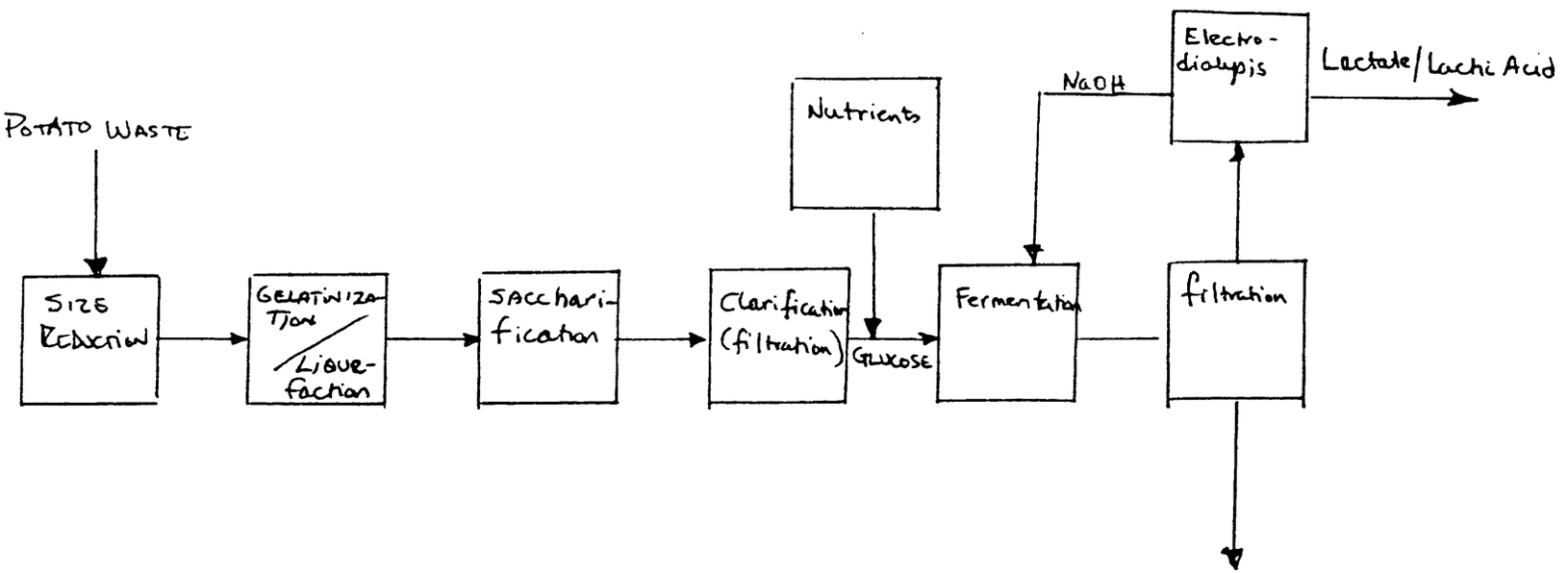
While there has been disclosed what is considered to be the preferred embodiment of the present invention, it is understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

Abstract Of The Invention

A method of converting starch to glucose and then to lactic acid starting with a starch-containing material capable of conversion to a simple sugar. Various industrial waste streams such as potato waste, cheese whey permeate and the like are disclosed. For potato waste, an effective amount of α-amylase enzyme is added to the starch-containing material to gelatinize and liquify the material along with a stabilizing ion such as calcium. The mixture is maintained at a pH in the range of from about 4 to about 7 while the temperature is elevated temperature in the range of from about 90°C to about 130°C Also, the pressure is elevated to not less than 15 psi., and the material is kept at the elevated temperature and pressure for a time not less than about 15 minutes. Thereafter the temperature of the material is lowered to about 50°C to about 70°C and the pH to below about 6.5. Then glucoamylase is added at an effective concentration and kept in the aforesaid condition for not less than about 4 hours to convert more than 90% of the starch to glucose substantially free of microbial

activity. The potato hydrolysate containing glucose is filtered and the glucose feed stream is introduced to a fermenter, with suitable microorganisms and nutrients to form a fermentation broth to ferment the glucose to lactic acid.

FIGURE 1


POTATO WASTE
SIZE REDUCTION
GELATINIZATION / LIQUEFACTION
SACCHARIFICATION
CLARIFICATION (FILTRATION)
Nutrients
GLUCOSE
FERMENTATION
NaOH
ELECTRO-DIALYSIS
Lactate/Lactic Acid
FILTRATION

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