PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 :
C07C 51/42, 51/43, 51/44, 51/46, 59/08

A1

(11) International Publication Number: **WO 95/03268**

(43) International Publication Date: 2 February 1995 (02.02.95)

(21) International Application Number: PCT/US94/08362

(22) International Filing Date: 25 July 1994 (25.07.94)

(30) Priority Data:
08/096,939 26 July 1993 (26.07.93) US

(71) Applicant: A.E. STALEY MANUFACTURING COMPANY [US/US]; 2200 East Eldorado Street, Decatur, IL 62525 (US).

(72) Inventors: LEHNHARDT, William, F.; 1537 W. Riverview, Decatur, IL 62522 (US). SCHANEFELT, Robert, V.; 6 Allen Bend Place, Decatur, IL 62521 (US). NAPIER, Lori, L.; 2185 Richmond Road, Decatur, IL 62521 (US).

(74) Agent: GOODMAN, Kenneth, D.; Arnold, White & Durkee, P.O. Box 4433, Houston, TX 77210 (US).

(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, HU, JP, KE, KG, KP, KR, KZ, LK, LT, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD).

Published
With international search report.

(54) Title: PROCESS FOR RECOVERING ORGANIC ACIDS

(57) Abstract

An organic acid can be recovered from a fermentation broth by clarifying the broth to remove at least a substantial portion of the impurities therein, producing a clarified feed; acidulating the clarified feed by adding a quantity of a mineral acid effective to lower the pH of the feed to between about 1.0 and about 4.5, producing an acidulated feed which is substantially saturated with respect to at least one electrolyte selected from the group consisting of $MHSO_4$, M_2SO_4, M_3PO_4, M_2HPO_4, MH_2PO_4, and MNO_3, where M is selected from the group consisting of Na, NH_4, and K; extracting the acidulated feed with an extraction mixture which includes (a) water, (b) a mineral acid, in a quantity effective to maintain the pH of the feed between about 1.0 and about 4.5, and (c) an oxygenated solvent which has limited miscibility with water and the acidulated feed, the oxygenated solvent having from 4 to 12 carbon atoms and having at least one functional group selected from the group consisting of hydroxyl, ester, keto, ether, carbonyl, and amido, with the extraction producing a solvent extract and a first raffinate; and back extracting the solvent extract with an aqueous liquid, thereby producing an organic acid-rich aqueous extract and an organic acid-depleted solvent raffinate.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria
AU	Australia
BB	Barbados
BE	Belgium
BF	Burkina Faso
BG	Bulgaria
BJ	Benin
BR	Brazil
BY	Belarus
CA	Canada
CF	Central African Republic
CG	Congo
CH	Switzerland
CI	Côte d'Ivoire
CM	Cameroon
CN	China
CS	Czechoslovakia
CZ	Czech Republic
DE	Germany
DK	Denmark
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
GE	Georgia
GN	Guinea
GR	Greece
HU	Hungary
IE	Ireland
IT	Italy
JP	Japan
KE	Kenya
KG	Kyrgystan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
KZ	Kazakhstan
LI	Liechtenstein
LK	Sri Lanka
LU	Luxembourg
LV	Latvia
MC	Monaco
MD	Republic of Moldova
MG	Madagascar
ML	Mali
MN	Mongolia
MR	Mauritania
MW	Malawi
NE	Niger
NL	Netherlands
NO	Norway
NZ	New Zealand
PL	Poland
PT	Portugal
RO	Romania
RU	Russian Federation
SD	Sudan
SE	Sweden
SI	Slovenia
SK	Slovakia
SN	Senegal
TD	Chad
TG	Togo
TJ	Tajikistan
TT	Trinidad and Tobago
UA	Ukraine
US	United States of America
UZ	Uzbekistan
VN	Viet Nam

PROCESS FOR RECOVERING ORGANIC ACIDS

The present invention relates to a process for recovering organic acids, such as lactic acid, from fermentation broths by means of extraction.

Lactic acid is an organic acid that has a number of commercial uses, for example in food manufacturing, pharmaceuticals, plastics, textiles, and as a starting material in various chemical processes. Lactic acid is commonly produced by fermentation of sugars, starch, or cheese whey, using microorganisms such as *Lactobacillus delbrueckii* to convert monosaccharides such as glucose, fructose, or galactose, or disaccharides such as sucrose or lactose, into lactic acid. The broth that results from the fermentation will contain unfermented sugars, carbohydrates, amino acids, proteins, and salts, as well as lactic acid. Some of these materials cause an undesirable color. The lactic acid must be recovered from the fermentation broth before it can be put to any substantial use.

A number of processes have been developed in the past to recover lactic acid or other organic acids from fermentation broths. Some of these processes involve precipitation of salts followed by decomposition of the salts, or extraction with certain organic solvents or water-insoluble amines.

For example, in Baniel U.S. patent 4,275,234, an acid is recovered from an aqueous solution by extracting the solution with a water-immiscible organic extractant which comprises at least one secondary or tertiary amine dissolved in a water-immiscible organic solvent. The resulting organic extract is separated from the residual aqueous liquid, and subjected to a stripping operation with an aqueous liquid for back-extracting at least a substantial part of the acid from the organic extract into the water, while leaving substantially all of the amine in the organic phase.

In King U.S. patent 5,104,492, a carboxylic acid is recovered from an aqueous solution by contacting the aqueous solution with a substantially water-immiscible but water-wettable organic solvent. Two phases are formed, one a carboxylic acid-depleted aqueous raffinate and the other a carboxylic acid enriched water-wet solvent extract. The phases are then separated and the carboxylic acid-enriched water-wet solvent extract is dewatered. This dewatering decreases the solubility of the acid in the extract solvent and generates a carboxylic acid-containing bottoms product from which the acid can be recovered as a precipitate.

However, the recovery processes which have been used in the past have tended to be relatively expensive, because of having a large number of steps, poor efficiency of recovery, or for other reasons. Therefore, a need exists for improved processes for recovery of lactic acid and other organic acids, which can provide desirable efficiency of recovery at a reduced cost.

The present invention relates to a process for the extraction of an organic acid from an aqueous solution thereof which comprises contacting such solution with a mixture of (a) water, (b) a mineral acid in a quantity effective to maintain the pH of the mixture between about 1.0 and about 4.5, and (c) an oxygenated solvent which has limited miscibility with water and the acidulated feed, the oxygenated solvent having from 5 to 12 carbon atoms and having at least one functional group selected from the group consisting of hydroxyl, ester, keto, ether, carbonyl, and amido.

In another embodiment, the invention involves a process for recovering an organic acid which includes providing an aqueous feed containing an organic acid and impurities, and clarifying the aqueous feed to remove at least a substantial portion of the impurities therein, producing a clarified feed. In this context, "at least a substantial portion" means that at least about 10% by weight of the impurities that are present are removed. The feed can optionally be subjected to microfiltration and/or nanofiltration. The clarified liquid feed is acidulated by adding a quantity of a mineral acid effective to lower the pH of the feed to between about 1.0 and about 4.5, producing an acidulated feed which is substantially saturated with respect to at least one electrolyte selected from the group consisting of $MHSO_4$, M_2SO_4, M_3PO_4, M_2HPO_4, MH_2PO_4, and MNO_3, where M is selected from the group consisting of Na, NH_4, and K.

Next, the acidulated feed is extracted with a solvent extraction mixture which includes (a) water, (b) a mineral acid, in a quantity effective to maintain the pH of the feed between about 1.0 and about 4.5, and (c) an oxygenated solvent (such as hexanol) which has limited miscibility with water and the acidulated feed, the oxygenated solvent having from 5 to 12 carbon atoms and having at least one functional group selected from the group consisting of hydroxyl, ester, keto, ether, carbonyl, and amido, with the extraction producing a solvent extract and a first raffinate. Then the solvent extract is back extracted with an aqueous liquid, thereby producing an organic acid-rich aqueous extract and an organic acid-depleted solvent raffinate.

The process can further comprise concentrating the organic acid-rich aqueous extract by removing water and solvent; and carbon-treating the extract to remove at least a portion of the impurities remaining therein.

In another embodiment the process can further comprise recovering solvent from the first raffinate by stripping solvent therefrom; and recycling the recovered solvent for use in extracting the acidulated feed. In a variation on this particular embodiment, the pH of the acidulated feed can be maintained during the extraction at a level effective to prevent substantial precipitation of phosphate, sulfate, nitrate, and chloride salts during the extraction (e.g., pH between about 1.0 and about 4.5, and preferably between about 1.0 and about 3.5); and phosphate, sulfate, nitrate, or chloride salts can be recovered from the first raffinate by evaporation after the solvent is stripped therefrom. In this context, "level effective to prevent substantial precipitation" means that no more than de minimis precipitation will occur.

In another embodiment, an aqueous salt can be recovered by crystallizing a phosphate, sulfate, or nitrate salt from the acidulated feed; washing the crystallized salt with an aqueous liquid, preferably water; and drying the washed, crystallized salt.

In one preferred embodiment, the aqueous feed is further clarified prior to acidulation by filtering the aqueous feed to remove undesirable impurities; concentrating the feed by removing a portion of the water therein; and decolorizing the feed by contacting it with a decolorizing agent. The decolorizing agent can be granular carbon, powdered carbon, or a decolorizing resin.

In another embodiment of the invention, a second solvent extraction step is added. In particular, after extracting the acidulated feed with the extraction mixture of water, mineral acid, and oxygenated solvent, and before back extracting the solvent extract with the aqueous liquid, an additional extraction is performed in which an aqueous solution which contains a quantity of the organic acid is used as the extractant of the solvent extract from the first extraction step, thereby producing a second raffinate and a purified solvent extract, with the latter subsequently being back extracted as specified above. The second raffinate can be recycled into the acidulated feed.

The quantity of the organic acid in the aqueous extraction of the oxygenated solvent is preferably adjusted such that there is no net change in the concentration of the organic acid in the aqueous or the oxygenated solvent phase at equilibrium.

In a particularly preferred embodiment of the present invention, the process comprises:

providing an aqueous feed containing lactic acid and impurities;

clarifying the aqueous feed to remove at least a substantial portion of the impurities therein, producing a clarified feed;

filtering the clarified feed to remove undesirable impurities;

concentrating the feed by removing a portion of the water therein;

decolorizing the feed by contacting it with a decolorizing agent;

acidulating the clarified feed by adding a quantity of a mineral acid effective to lower the pH of the feed to between about 1.0 and about 4.5, producing an acidulated feed which is substantially saturated with respect to at least one electrolyte selected from the group consisting of $MHSO_4$, M_2SO_4, M_3PO_4, M_2HPO_4, MH_2PO_4, and MNO_3, where M is selected from the group consisting of Na, NH_4, and K;

extracting the acidulated feed with an extraction mixture which includes (a) water, (b) a mineral acid, in a quantity effective to maintain the pH of the feed between about 1.0 and about 4.5, and (c) hexanol, with the extraction producing a first hexanol extract and a first raffinate;

extracting the first hexanol extract with an aqueous lactic acid solution, thereby producing a second raffinate and a purified hexanol extract;

back extracting the purified hexanol extract with an aqueous liquid, thereby producing a lactic acid-rich aqueous extract and a lactic acid-depleted hexanol raffinate;

recovering hexanol from the first raffinate by stripping hexanol therefrom;

recycling the recovered hexanol for use in extracting the acidulated feed;

concentrating the lactic acid-rich aqueous extract by removing water; and

carbon-treating the concentrated extract to remove at least a portion of the impurities remaining therein.

Additionally, a portion of the lactic acid-rich aqueous extract may be recycled to be used as the aqueous lactic acid solution to extract the first hexanol extract.

The organic acids which may be recovered by the process of the present invention include mono-, di-, and tricarboxylic acids comprised of 3-8 carbon atoms. Examples include, but are not limited to, lactic acid, citric acid, malic acid, maleic acid, fumaric acid, adipic acid, succinic acid, tartaric acid, α-ketoglutaric acid, and oxaloacetic acid.

One advantage of the present invention relates to performing the extraction at saturation, or substantially saturated conditions (e.g., $\geq$ 90% of saturation) with the appropriate salt of the mineral acid used for the acidulation. The higher the salt concentration, the higher is the driving force for extraction of the lactic acid into the hexanol phase.

Other advantages include the use of various recycle streams which tend to minimize the number of effluent streams. Further, working at higher concentrations of lactic acid reduces the volumes of and number of extraction stages. Thus, the present invention has advantages of simplicity, reduced cost, and reduced effluent compared to the prior art.

Figure 1 is a process flow diagram for a particular embodiment of the present invention.

Figure 2 is a plan view of a mixer-settler apparatus that can be used in the process of the present invention.

Figure 3 is a side cross sectional view of the mixer-settler of Figure 2, taken along axis X-X.

Figure 4 is a graph of the percent of lactate and phosphate that are in salt form at different pH values, and of the difference between the percentages for the two materials.

Figure 5 is a graph of the relationship between pH and the concentration of various components in the soluble phase.

Figure 6 is a graph of the relationship between pH and quantity of precipitate, supernatant, and total precipitate plus supernatant per mole of lactic acid.

Figure 7 is a graph of the relationship between pH and the distribution of soluble and insoluble phases.

Figure 8 is a graph of the relationship between pH and the moles of various components per mole of lactic acid.

Figure 9 is a graph of the relationship between pH and the moles of various components per kg of solution.

Figure 10 is a graph of the relationship between pH and the grams of various components per kg of solution.

Figure 11 is a graph of the relationship between pH and the ratio of moles of phosphoric acid to moles of lactic acid.

Figure 12 is a graph of the amount of precipitate at different pH's for a broth sample acidulated with H_2SO_4.

Figure 13 is a graph of the moles of H_2SO_4 added and precipitate formed for different samples of acidulated broth.

Figure 14 is a graph of the percentage recovery in the solvent phase of various components at varying levels of broth saturation.

Figure 15 is a graph of the percent lactic acid removed in extractions employing different acids.

Figure 16 is a graph of the percent lactic acid removed in a cross-current back extraction.

Figure 17 is a graph of the change in lactic acid content of the feed vs. that of the aqueous phase for back extractions.

Figure 18 is a graph showing calculated numbers of back extraction stages required to reach a given level of lactic acid recovery.

Figure 19 is a graph showing the percent lactic acid recovery after each of several cross-current back extractions.

The term lactic acid is used in this patent to include either optical isomer of lactic acid, as well as racemic mixtures of those optical isomers. Further, it includes mixtures of lactic acid monomers, dimers, trimers, and other lactic acid polymers of low molecular weight (generally below about 740 m.w.; e.g. a polymer of about DP 10).

Figure 1 shows a particular embodiment of a process in accordance with the present invention. Lactic acid can initially be prepared by fermentation as is known in the art. An aqueous solution containing lactic acid, in particular a fermentation broth 10, is the result of that process, and the feed for the present process.

Although the specific process embodiment of the invention described in this patent recovers lactic acid from a fermentation broth, the present invention is not limited to recovering the products of fermentation. The process of the present invention can be used in any situation where an organic acid is to be recovered from an aqueous solution or dispersion. For example, the process can be used to recover lactic acid from aqueous solutions of lactic acid-containing biopolymers, after performing the necessary process steps to free the lactic acid from the biopolymer.

The broth 10 will typically contain less than 25% by weight lactic acid. Preferably at least 80% by weight of the total lactate values in the broth are present as Na, K, or NH_4 lactates.

The fermentation broth 10 is clarified 12 by microfiltration or other procedures such as centrifugation, filter pressing, or rotary vacuum filtration, producing a particulate-free, filtered, fermentation broth 14. The biomass 16 removed by filtration can be recycled to the fermentation bioreactor, or can be dried and used, for example, as animal feed. The filtered broth 14 is further purified by ultrafiltration and/or nanofiltration 18 to further reduce the amount of undesirable organic impurities in the broth.

An example of a filtration process that can be used is as follows: Feedstock was prepared by microfiltration of fermentation broth followed by nanofiltration of the microfiltered permeate. A 0.02 micron Membralox ceramic element from U.S. Filter was used for the microfiltration. A multi-leaf spiral wound polymeric element with a 180 MW cutoff from Desalination Systems, Inc. was used for the nanofiltration process. This clean-up procedure yielded a feedstock with about 95-99% of the material having a molecular weight less than or equal to ammonium lactate.

The broth is then concentrated by standard evaporative techniques to a solids concentration of between 50% to 85% with a lactate content of between 38% to 65% respectively. The broth is then decolorized 20, by contacting the broth with granular or powdered carbon, or a decolorizing resin. Suitable commercial products for this purpose include:

powdered carbon:	Nuchar-SA, Westraco, Darco S51, ICI Chem.;
granular carbon:	Calgon CPG, Americon Norit; and

decolorizing resin: Dowex Optipore Adsorbent.

The broth may also be further concentrated 22, either after or before the decolorization step 20. The lactic acid concentration in the resulting solution is typically in the range of from about 30% to about 90% by weight.

The decolorized, concentrated broth is then acidulated 24 with an acid, such as H_3PO_4, H_2SO_4, HCl, or HNO_3, to a pH between about 1.0 and about 4.5. (Tests of acidulated broth having pH ranging from 4.3 to 3.5 showed the greatest precipitation at pH 3.5, although pH of 3.5-3.9 yielded the highest percentage of lactic acid extracted in the solvent.) At this point, the acidulated broth contains at least 35% lactic acid by weight and is substantially saturated with respect to at least one of the electrolytes $MHSO_4$, M_2SO_4, M_3PO_4, M_2HPO_4, MH_2PO_4, and MNO_3, where M is selected from the group consisting of Na, NH_4, and K.

After acidulation 24, phosphate, sulfate, and/or nitrate salts are crystallized 26, and then the salts are separated 28 from the acidulated broth by techniques typical in the industry for separation of an inorganic salt from its corresponding broth, such as solid bowl centrifugation, basket centrifugation, filtration, vacuum filtration, and the like, producing a wet crystal cake 30. The wet crystal cake 30 is then washed 32 with water 34, and dried 36 by techniques typical in the industry for drying an inorganic salt, producing a dried salt 38, for example ammonium phosphate. The water used in the washing step 32 is recycled 40 back to the concentrated broth prior to acidulation 24, and can suitably be mixed with the mineral acid 42 (e.g., phosphoric acid).

The clarified, acidulated broth 50 is then subjected to a first extraction 52 with a solvent extraction mixture 54 which includes, and preferably consists essentially of, (a) water, (b) a mineral acid, and (c) an oxygenated organic solvent. The oxygenated solvent has limited miscibility with water and the acid broth, preferably has between about 5 and about 12 carbon atoms, and carries at least one functional group selected from the group consisting of hydroxyl, ester, keto, ether, carbonyl, and amido. The oxygenated solvent more preferably has 6-8 carbon atoms. An especially preferred solvent is hexanol. The ratio of the solvent mixture 54 to the acidulated broth 50 is preferably between about 3/1 and about 6/1 by weight, preferably about 4/1.

Limiting condition extractions with the solvents hexanol, butanol, butyl acetate, isopropyl ether, 3-methyl-1-butanol, dodecanol, octanol, hexanes, and heptanol gave the following findings: butanol did not phase separate, 3-methyl-1-butanol required an equal weight addition of solvent to do so, and hexanol removed the largest quantity of lactic acid under limiting conditions.

As an example of the limited miscibility of the oxygenated organic solvent with water, Lactic Acid, Properties and Chemistry of Lactic Acid and Derivatives, by C. H. Holten, Verlag Chimie (1971), at pages 43 and 45 (which is incorporated here by reference), indicates that at 25°C the solubility of water in 1-hexanol is 7.9% and the solubility of hexanol in water is 0.5%.

The use of acid in the oxygenated organic solvent keeps the pH in a range where the lactic acid is primarily in acid form rather than salt form. As the pH goes up, a greater percentage of the lactic acid converts to the salt form, which is much less soluble in hexanol. It is preferred to keep the amount of lactic acid in the salt form at less than 30%, which indicates that the pH should preferably be kept below 3.5.

If phosphoric acid is used in the solvent extraction mixture, there is a tendency for increased salt formation and thus an increased chance of precipitation. Using a different acid such as hydrochloric acid can reduce the chance of precipitation, because ammonium chloride is formed rather than ammonium dihydrogen phosphate, the latter already being at a saturation level. However, the use of an additional acid is not entirely desirable, and it may be preferable to use other methods of reducing or eliminating precipitation.

The amount of water in the mixture 54 is preferably that of substantial saturation (i.e., at least 90% saturated), and is most preferably that of saturation. A portion of this stream will come from a back extraction step 68 and will thus carry water at a saturation level. The addition of the phosphoric acid 94 will also carry some water with it since the phosphoric acid in preferably at 75% concentration, but the addition of the phosphate will allow an increase in the quantity of water that the hexanol will hold. The acid is added in an amount effective to maintain the pH of the broth between about 1.0 and about 4.5 during the first extraction 52, in order to optimize the extraction efficiency.

Examples of suitable compositions for the process of the present invention are as follows:

acidulated broth at pH 3.0

53.14% lactic

3.52% PO_4

2.55% NH_3

28.83% water

hexanol extractant

6.0% water

0.7% H_3PO_4

93.3% hexanol

aqueous phase at equilibrium

27.67% lactic acid

47.09% water

0.25% hexanol

7.71% PO_4

3.56% NH_3

13.72% other

organic phase at equilibrium

8.04% lactic acid

0.03% PO_4

0.08% NH_3

5.81% water

86.26% hexanol

equilibrium ratio = 6.23/1 (solvent/aqueous)

The resulting first raffinate 56 is sent to a solvent recovery system, which will be discussed further below.

The first solvent extract 58 is then subjected to a second extraction 60 in order to purify the extract. An aqueous solution 62 is used which consists essentially of water and a limited quantity of pure lactic acid, preferably no more than about 25% lactic acid by weight. The ratio of the first solvent extract 58 to the aqueous lactic acid solution 62 is preferably between about 4/1 and about 20/1 by weight. This second extraction produces a second raffinate 64 which is recycled by combining it with the acidulated broth 50 for use in the first extraction 52. A purified, second solvent extract 66 is also produced, containing primarily solvent, lactic acid, and water.

The purified solvent extract 66 is then back extracted 68 with an aqueous liquid, preferably water 70, producing a lactic acid-depleted solvent raffinate 72 and a lactic acid-rich aqueous extract 74. The ratio of the purified solvent extract 66 to the water 70 is preferably between about 4/1 and about 10/1 by weight. A portion of the lactic acid-rich aqueous extract 74 is recycled 76 to the aqueous lactic acid solution 62 for use in the second extraction 60. The remainder of the lactic acid-rich aqueous extract 74 is concentrated 76, thus removing a condensate 84 which is sent to a solvent recovery system. Minor contaminants are then removed by a decolorizing treatment 78 with carbon or a decolorizing resin. After this treatment, used carbon 80 is recycled to the earlier decolorization step 20.

The final lactic acid solution 82 will typically have a concentration of between about 30%-90% by weight.

The lactic acid-depleted solvent raffinate 72 is recycled back to the first extraction 52, where it is combined with the necessary additional ingredients to make up the solvent extraction mixture 54. The first raffinate

56 and the condensate 84 are sent to a solvent stripper 86, which separates solvent 88 from aqueous waste 90. The aqueous waste 90, which will usually contain ammonium dihydrogen phosphate, other salts, proteinaceous materials, and carbohydrates, can be used as animal feed or fertilizer. The recovered solvent 88 is sent to a solvent purification unit 92. The solvent purification unit will preferably consist of a standard construction for the heterogeneous distillation of azeotropic liquids. Some or all of the lactic acid-depleted solvent raffinate 72 is also passed through the solvent purification unit 92. The desired amount of mineral acid 94 is added to the solvent recycle stream 96, together with a controlled amount of water 98 to complete the desired makeup of the solvent extraction mixture 54 for the first extraction 52.

The extraction steps can be carried out in batch operation or continuously, and may be conducted by any conventional liquid phase extraction method, including for example counter-current liquid-liquid extraction methods or extraction columns which are known to persons skilled in this field. Centrifugation can also be used. Additional extraction stages and/or steps can be used if desired.

In a particular embodiment of the present invention, the extraction steps are carried out in a multi-stage mixer-settler apparatus, such as the Robatel Model UX 1.1 mixer-settler (Robatel Inc., Pittsfield, Massachusetts). In this type of extraction apparatus, each stage includes at least a mixer and a settler. The mixer brings the solvent and the feed into intimate contact with each other. In the settler portion of each stage, a lighter phase rises to the top of the settler and overflows a weir to an adjacent stage in one direction. A heavier phase sinks to the bottom of the settler, and underflows a separate weir into a different adjacent stage in a different direction.

Figures 2 and 3 show one embodiment of a mixer-settler 100, containing eight stages 102a-102h. Each stage has a mixer 104 driven by a motor 106 and having a shaft 108 and a turbine 110. Solvent 112 can be fed in one end of the apparatus, while the feed 114 is fed into the other end. In each stage 102, the mixer 104 mixes the solvent and feed, and they then separate at least to some degree into phases. A lighter phase will overflow an overflow weir 116 into an adjacent chamber, while a heavier phase will underflow an underflow weir 118 into a separate chamber that is also adjacent. The ultimate result is an extract 120 and a raffinate 122.

In an alternate embodiment of the process, instead of crystallizing and separating the salt (e.g., ammonium dihydrogen phosphate) before extraction, the acidulated broth fed into the extraction would contain both lactic acid (in hydrogen form) and the phosphate salt. The extraction would be operated so as to be borderline saturated with ammonium dihydrogen phosphate, using pH in the same range as stated above, thereby preventing any substantial precipitation of the salt during extraction. The ammonium phosphate would be recovered from the raffinate stream 56 by stripping of the hexanol, followed by evaporation, leaving the salt.

Example 1

Calculations were performed to evaluate the pH distributions of salt and acid forms of lactic acid and phosphoric acid, using the Henderson-Hasselbach equation (pH = pK_a + log salt/acid), and the following values:

lactic acid	pK = 3.858
H_3PO_4	pK_1 = 2.15

The results are plotted in Figure 4. (Note that the above equation is generally used for dilute aqueous solutions;

the relationship may be slightly different in the system used here.) At pH 4.1, about 64% of lactic acid values will exist as ammonium lactate, with the remaining about 36% as acid. The difference between the lactate and phosphate curves will theoretically be the largest at a pH of about 3.0, and thus that pH may be preferable for the extraction.

Example 2

A clarified fermentation broth was obtained, shown in Table 1 as sample 310. A quantity of broth (C) was acidulated with a quantity of 75% phosphoric acid (D) and the resulting pH was measured (B). The supernatant was removed after centrifugation and analyzed as shown (F, G, H, I). The only assumption made was that all of the lactic acid was in the soluble phase.

Table 1A

A	B	C	D	E	F	G	H	I	J
Sample No	pH	g Sample	g 75% H3PO4	Total Wt	% NH3 Sol	% H2O Sol	% Lactic Sol	% PO4 Sol	g H3PO4
				C + D					D * 0.75
310	6.079	10.00	0	10.00	10.84	16.5	62.89	0.17	0.0000
311	5.204	10.00	1.40	11.40	9.16	19.2	58.87	2.41	1.0500
312	4.603	10.01	2.93	12.94	7.71	22.6	59.49	1.96	2.1975
313	4.204	10.02	3.98	14.00	5.95	24.7	57.93	2.04	2.9850
314	3.689	10.04	5.31	15.35	4.23	27.3	57.40	2.46	3.9825
315	3.134	10.03	6.64	16.67	2.79	29.5	55.44	3.28	4.9800
316	2.389	10.00	7.92	17.92	1.72	31.2	52.36	5.89	5.9400
317	1.600	10.08	9.33	19.41	1.43	30.8	44.86	11.14	6.9975
318	0.965	10.00	10.59	20.59	1.70	29.4	41.19	19.39	7.9425
319	0.699	10.01	11.91	21.92	1.95	28.3	35.99	26.24	8.9325

Table 1B

A	B	K	L	M	N	O	P	Q
Sample No	pH	g Lactic	%Lactic All Sol	g Soln Calc	g Ppt Calc	Moles Lactic	Moles H3PO4	M H3PO4/M Lactic
		C * 0.6289	K * 100/E	K / H * 100	E - M	K / 90.08	J / 98.00	P / O
310	6.079	6.2890	62.89			0.0698	0.0000	
311	5.204	6.2890	55.17	10.683	0.717	0.0698	0.0107	0.1535
312	4.603	6.2953	48.65	10.582	2.358	0.0699	0.0224	0.3209
313	4.204	6.3016	45.01	10.878	3.122	0.0700	0.0305	0.4354
314	3.689	6.3142	41.13	11.000	4.350	0.0701	0.0406	0.5798
315	3.134	6.3079	37.84	11.378	5.292	0.0700	0.0508	0.7257
316	2.389	6.2890	35.09	12.011	5.909	0.0698	0.0606	0.8682
317	1.600	6.3393	32.66	14.131	5.279	0.0704	0.0714	1.0146
318	0.965	6.2890	30.54	15.268	5.322	0.0698	0.0810	1.1609
319	0.699	6.2953	28.72	17.492	4.428	0.0699	0.0911	1.3042

Table 1C

A	B	R	S	T	U	V	W
Sample No	pH	Moles NH4H2PO4 Ppt	Moles NH3 Sol	Moles PO4 Sol	Moles PO4 ppt	Salt (PO4)/Acid	Moles NH4H2PO4 Sol
		N / 115.03	F*.01*M/17.03	I*.01*M/94.97	P - T	10^(B -2.15)	(V*T)/(1+V)
310	6.079						
311	5.204	0.0062	0.0575	0.0027	0.0080	1132.400	0.0027
312	4.603	0.0205	0.0479	0.0022	0.0202	283.792	0.0022
313	4.204	0.0271	0.0380	0.0023	0.0281	113.240	0.0023
314	3.689	0.0378	0.0273	0.0028	0.0378	34.594	0.0028
315	3.134	0.0460	0.0186	0.0039	0.0469	9.638	0.0036
316	2.389	0.0514	0.0121	0.0074	0.0532	1.734	0.0047
317	1.600	0.0459	0.0119	0.0166	0.0548	0.282	0.0036
318	0.965	0.0463	0.0152	0.0312	0.0499	0.065	0.0019
319	0.699	0.0385	0.0200	0.0483	0.0428	0.035	0.0017

Table 1D

A	B	X	Y	Z	AA	AB	AC
Sample No	pH	Moles H3PO4 Sol	g Solution/ Mole Lactic	g Ppt/Mole Lactic	Total g/Mole Lactic	% Precipitate	% Soluble
		T - W	M / O	N/O	Y + Z	100*Z/AA	100*Y/AA
310	6.079						
311	5.204	0.0000	153.02	10.27	163.29	6.29	93.71
312	4.603	0.0000	151.42	33.74	185.16	18.22	81.78
313	4.204	0.0000	155.50	44.63	200.13	22.30	77.70
314	3.689	0.0001	156.93	62.05	218.99	28.34	71.66
315	3.134	0.0004	162.48	75.58	238.06	31.75	68.25
316	2.389	0.0027	172.04	84.64	256.68	32.97	67.03
317	1.600	0.0129	200.80	75.01	275.81	27.20	72.80
318	0.965	0.0293	218.69	76.23	294.92	25.85	74.15
319	0.699	0.0467	250.29	63.36	313.66	20.20	79.80

Table 1E

A	B	AD	AE	AF	AG	AH
Sample No	pH	% Precipitate	Mol AmPhos PPT/Mol Lactic	Mol AmPhos Sol/Mol Lactic	Mol H3PO4 Sol/Mol Lactic	Mole AmPhos Ppt/ Kg Soln
		100 - AC	U / V	W / O	X / O	AE *1000 /Y
310	6.079					
311	5.204	6.29	0.1146	0.0388	0.0000	0.749
312	4.603	18.22	0.2896	0.0311	0.0001	1.913
313	4.204	22.30	0.4020	0.0331	0.0003	2.585
314	3.689	28.34	0.5391	0.0395	0.0011	3.435
315	3.134	31.75	0.6696	0.0508	0.0053	4.121
316	2.389	32.97	0.7615	0.0677	0.0390	4.426
317	1.600	27.20	0.7791	0.0518	0.1838	3.880
318	0.965	25.85	0.7143	0.0274	0.4191	3.266
319	0.699	20.20	0.6127	0.0236	0.6679	2.448

Table 1F

A	B	AI	AJ	AK	Al	AM	AN
Sample No	pH	Mole AmPhos Sol/ Kg Soln	Mole H3PO4/ Kg Soln	Mole Lactic/ Kg Soln	g Am Phos Sol/Kg Soln	g H3PO4 Sol/Kg Soln	g Lactic Sol/Kg Soln
		AF*1000/Y	AG*1000/Y	1*1000/Y	AI*115.03	AJ*98.0	AK*90.08
310	6.079						
311	5.204	0.254	0.000	6.535	29.16	0.02	588.70
312	4.603	0.206	0.001	6.604	23.66	0.07	594.90
313	4.204	0.213	0.002	6.431	24.49	0.18	579.30
314	3.689	0.252	0.007	6.372	28.96	0.71	574.00
315	3.134	0.313	0.032	6.155	35.99	3.18	554.40
316	2.389	0.393	0.227	5.813	45.25	22.23	523.60
317	1.600	0.258	0.915	4.980	29.67	89.68	448.60
318	0.965	0.125	1.917	4.573	14.40	187.82	411.90
319	0.699	0.094	2.669	3.995	10.87	261.51	359.90

Figures 5-11 summarize the results of this experiment graphically.

Example 3

Concentrated fermentation broth (containing 78.24% lactic acid, 3.18% water, 12.28% NH_3, 1472 ppm PO_4, and 5115 ppm Cl) was diluted with water such that the resulting lactic acid concentration was 65.41%. The pH of this diluted broth was 5.41. Portions of the broth were acidified with sulfuric acid (96.1%) such that a series of samples were produced in a pH range of 5 to 0.3. The samples were centrifuged and the supernatant was removed and analyzed for lactic acid. The only assumption made was that all of the lactic acid was in the soluble phase. See Table 2 below and Figures 12 and 13 for the results.

Table 2

g broth	g lactic	moles lactic	g H2SO4 added (96.1%)	g H2SO4	moles H2SO4	g supernate	g wet ppt	pH	g ppt	g soluble	moles ammonium sulfate	cum moles
20.04	13.026	0.1446	1	0.962	0.0098	16.68	4.36	4.96	1.35	19.69	0.010	0.01
20.02	13.013	0.1445	2.03	1.95	0.0199	15.25	6.8	4.51	2.32	19.73	0.018	0.028
20.03	13.0195	0.1445	3.02	2.91	0.0296	14.46	8.59	4.06	3.71	19.34	0.028	0.056
20.01	13.0065	0.1444	4.04	3.89	0.0396	14.02	10.03	3.51	4.18	19.87	0.032	0.087
20	13	0.1443	4.5	4.33	0.0441	14.65	9.85	3.23	5.05	19.45	0.038	0.126
20.01	13.0065	0.1444	5.03	4.84	0.0493	14.98	10.06	2.9	5.78	19.26	0.044	0.169
20	13	0.1443	5.5	5.29	0.0539	15.44	10.06	2.53	5.14	20.36	0.039	0.208
20.02	13.013	0.1445	6.05	5.82	0.0593	16.56	9.51	1.94	4.82	21.25	0.036	0.245
20.03	13.0195	0.1445	6.64	6.39	0.0651	17.39	9.28	0.73	3.46	23.21	0.026	0.271
20.03	13.0195	0.1445	7.08	6.81	0.0694	17.78	9.33	0.56	2.29	24.82	0.017	0.288
20	13	0.1443	7.56	7.27	0.0742	16.81	10.75	0.36	2.35	25.21	0.018	0.306
20.04	13.026	0.1446	8.04	7.73	0.0789	15.11	12.97	0.3	0.5	27.58	0.004	0.310

Example 4

A concentrated feed broth was acidulated with one molar equivalent of 75% H_3PO_4. Water was added to dissolve salts. The pH was 2.12 and after dilution the broth contained 16.80% lactic acid. 1.13 g of hexanol was added to 81.22 g of this feed, resulting in cloudiness. The mixture was allowed to sit; no cloudiness was observed. 5.23% lactic acid was recovered from the aqueous phase. Later ca. 0.18 g of precipitate was noted in the extracted feed.

Example 5

Several acidulated broths containing lactic acid were extracted in a cross-current process. A clarified, filtered, acidulated broth containing lactic acid designated sample 5A was extracted six times. The acidulated broth feed contained 55.03% lactic acid by weight, 3.26% PO_4, 4.33% NH_3, 30.21% water, and had a pH of 4.1. The extractant contained 100 g hexanol (95.06% by weight of the total extractant), 0.2 g of 85% H_3PO_4 (0.19% by weight), and 5.0 g water (4.78% by weight). This amount of water represented approximate saturation of the extractant mixture. Seven g of initial acidulated broth feed were extracted with 35 g of extractant (i.e., a 5/1 solvent/feed ratio by weight).

Table 3
Sample 5A

Extraction pass	Feed (g)	Extractant (g)	Extract (g)	% Lactic Acid in Extract	Comments
1	7.03	35.13	35.56	5.01	
2	5.34	35.07	35.12	1.36	precipitate forming
3	5.06	35.08	34.95	0.72	more precipitate
4	5.01	35.03	34.89	0.46	
5	4.94	35.07	34.69	0.31	
6	4.95	35.16	35.30	0.39	

The pH of the remaining aqueous phase after the sixth extraction was 5.3. The aqueous phase weighed 4.59 g and contained 12.87% lactic acid. Thus 75.5% of the lactic acid in the original feed was extracted.

It appeared that the amount of acid in the extractant was not enough to keep the pH stable during extraction, or, alternatively, that the starting pH of the acidulated broth preferably should have been lower.

Another acidulated broth containing lactic acid (designated sample 5B) was extracted. The broth prior to acidulation contained 66.09 g lactic acid (0.7337 moles) out of a total weight of 101.73 g. It was acidulated with 68.30 g of 75% H_3PO_4 (0.5227 moles), creating a pH of 3.0 and a temperature rise from 25°C to 55°C.

The resulting $NH_4H_2PO_4$ was removed by centrifugation and decantation. The sediment mixture totalled 113.82 g. The amount of $NH_4H_2PO_4$ formed was calculated by using the dilution of lactic acid concept to be 48.5 g (0.422 moles).

The clarified broth remaining after the salt was removed totaled 56.21 g, and was made up of 33.06% (weight) lactic acid, 3.73% PO_4, 2.67% NH_3, and 28.64% water.

The extractant was made up of 100 g hexanol (94.79% by weight of the total extractant), 0.5 g of 75% H_3PO_4 (0.36% by weight), and 5.0 g water (5.09% by weight). The acidulated, clarified broth was extracted six times, using 32.0 g of the extractant per cycle, in a 4/1 solvent/feed ratio by weight.

Table 4
Sample 5B

Extraction pass	Feed (g)	Extractant (g)	Extract (g)	% Lactic Acid in Extract	Comments
1	8.08	32.05	34.85	8.17	
2	5.15	32.02	32.44	2.12	
3	4.52	32.05	32.17	0.92	precipitate start
4	4.18	32.08	31.80	0.60	
5	4.25	32.14	32.17	0.44	
6	4.12	32.02	32.02	0.33	

About 4.27 g of lactic acid was extracted out of a total of about 4.39 in the feed. Thus 97.27% of the lactic acid in the original feed was extracted.

A large amount of precipitate formed during the extraction. Also, quite a bit of liquor remained with the precipitate after separation by centrifugation. This latter problem might have been minimized if filtration had been used instead of centrifugation.

Five other extractions were performed. The extraction parameters and results are shown in Table 5 below.

Table 5
Cross-Current Extraction
Cumulative % Lactic Acid Collected in Solvent

Extraction Number	Sample No.						
	5A	5B	5C	5D	5E	5F	5G
1	45.99	64.92	40.00	62.50	73.64	67.12	88.60
2	58.39	80.64	49.45	74.55	86.49	84.67	99.48
3	64.85	87.47	60.36	78.12	89.32	90.52	100.00
4	68.98	91.80	68.36	79.68	90.41	95.63	100.00
5	71.82	94.99	72.00	80.57	91.28	97.87	100.00
6	75.44	97.50	N/A	81.24	91.72	98.35	100.00
Conditions							
pH	4.10	3.00	4.10	2.91	2.65	3.00	1.31
Solvent: feed ratio	5:1	4:1	3.4:1	4:1	4:1	4:1	4:1
Solvent (Hexanol) Content							
H3PO4	0.16%	0.36%	-	-	-	0.79%	-
H2O	4.78%	4.86%	-	saturated	saturated	6.00%	saturated

Example 6

Phosphoric acid, acidulated fermentation broth (comprising 53.14% lactic acid, 3.52% PO_4, 2.55% NH_3, and 28.83% water, pH 3.0) was used "as is" or diluted with water to produce a series of solutions containing ammonium dihydrogen phosphate at 100%, 98%, 95%, 93%, 90%, and 80% of saturation. A 4:1 solvent/aqueous ratio was used. The solvent/extractant was 92.79% hexanol, 6.51% water, and 0.7% phosphoric acid. Precipitate formed in the first stage for all but the 90% and 80% samples. The percentage lactic acid recovery decreased only slightly, from 65.13% at full saturation to 62.09% recovery in the 80% saturated sample.

Table 6

Sample	Satur. Level	g broth used for dilut.	g water added	Theoret. Lactic	% Lactic	Theor. PO4	% PO4	Theor. NH3	% NH3	Theoret. Water	% Water	g dil broth used for extra c.	g lactic in	g PO4 in	g NH3 in	g water in	g solven t used
6A	100%	10	0	55.39%	53.14%	3.27%	3.52%	2.56%	2.55%	28.70%	28.83%	8.01	4.257	0.282	0.204	2.309	32
6B	98%	10	0.21	54.28%	53.18%	3.20%	3.56%	2.51%	2.49%	30.17%	30.24%	8.02	4.265	0.286	0.200	2.425	32.03
6C	95%	10	0.51	52.62%	51.32%	3.11%	3.40%	2.43%	2.48%	32.16%	32.28%	7.99	4.100	0.272	0.198	2.579	32.05
6D	93%	10	0.75	51.51%	51.11%	3.04%	3.37%	2.38%	2.33%	33.67%	33.73%	8.03	4.104	0.271	0.187	2.709	32.04
6E	90%	10	1.12	49.85%	48.76%	2.94%	2.90%	2.30%	2.32%	35.88%	36.27%	8.02	3.911	0.233	0.186	2.909	32.01
6F	80%	10	2.52	44.31%	43.30%	2.62%	3.15%	2.05%	1.97%	43.05%	43.14%	8.03	3.477	0.253	0.158	3.464	32.02

	Solvent Phase														
	g solvent out	% lactic	g lactic out	% lactic recovery	PO4 ppm	% PO4	g PO4	% PO4 recov.	% NH3	g NH3	% NH3 recovery	% water	g water in*	g water out	g water picked up from aqueous	% change in water
6A	34.48	8.04%	2.772	65.13%	279	0.0279%	0.0096	3.41%	0.076%	0.0262	12.83%	5.81%	1.92	2.0033	0.0833	4.16%
6B	34.33	8.05%	2.764	64.80%	252	0.0252%	0.0087	3.03%	0.066%	0.0227	11.35%	5.52%	1.9218	1.8950	-0.0268	-1.41%
6C	34.28	7.57%	2.595	63.29%	261	0.0261%	0.0089	3.29%	0.056%	0.0192	9.69%	5.91%	1.923	2.0259	0.1029	5.08%
6D	34.35	7.57%	2.600	63.36%	254	0.0254%	0.0087	3.22%	0.050%	0.0172	9.18%	6.02%	1.9224	2.0679	0.1455	7.03%
6E	34.15	7.03%	2.401	61.39%	196	0.0196%	0.0067	2.88%	0.037%	0.0126	6.79%	6.08%	1.9206	2.0763	0.1557	7.50%
6F	34	6.35%	2.159	62.09%	198	0.0198%	0.0067	2.66%	0.032%	0.0109	6.88%	6.35%	1.9212	2.1590	0.2378	11.01%

* 6% water in hexanol/H_3PO_4 solution

See Figure 14.

Example 7

Three cross-current extractions runs with a lactic acid solution were done with hexanol, 6% water, and the following acids: 0.7% phosphoric, 0.26% hydrochloric, and 0.46% sulfuric. The ratio of solvent to aqueous phases was 4:1.

Table 7
Hexanol Extraction with Different Acids

0.7% H_3PO_4; Extraction	g Solvent Phase	% Lactic	g Lactic	Cum g	% Lactic Acid Removed	pH	g raffinate	% lactic	g lactic remaining	% lactic remaining
1	35.13	8.72	3.06	3.06	67.11%	-				
2	32.42	2.47	0.80	3.86	84.65%	-				
3	31.84	0.84	0.27	4.13	90.57%	4.32				
4	31.92	0.73	0.23	4.36	95.61%	4.04				
5	31.73	0.32	0.10	4.46	97.81%	3.55				
6	31.64	0.07	0.02	4.48	98.25%	3	5.03	0.14%	0.007	0.05%
0.26% HCl; Extraction	g Solvent Phase	% Lactic	g Lactic	Cum g	% Lactic Acid Removed	pH	g raffinate	% lactic	g lactic remaining	% lactic remaining
1	34.95	8.8	3.08	3.08	67.54%	-				
2	32.63	2.34	0.76	3.84	84.19%	-				
3	32.02	0.25	0.08	3.92	85.95%	4.08				
4	31.99	0.13	0.04	3.96	86.84%	4.06				
5	31.90	0.44	0.14	4.10	89.92%	3.55				
6	31.81	0.08	0.03	4.13	90.57%	2.32	4.36	0.78%	0.034	0.24%
0.46% H_2SO_4	g Solvent Phase	% Lactic	g Lactic	Cum g	% Lactic Acid Removed	pH	g raffinate	% lactic	g lactic remaining	% lactic remaining
1	35.09	8.91	3.13	3.13	68.64%	4.09				
2	32.4	2.61	0.85	3.98	87.19%	4.33				
3	32	0.57	0.18	4.16	91.19%	4.25				
4	31.81	0.65	0.21	4.36	95.72%	2.92				
5	31.54	0.09	0.03	4.39	96.34%	1.96				
6	31.76	0.00003	0.00	4.39	96.34%	1.75	4.68	0.07%	0.003	0.02%

See Figure 15.

Precipitate formed with the phosphoric acid sample after stage 3 and redissolved after the fourth. Precipitate formed with the sulfuric acid sample after the third stage and redissolved after the fifth. No precipitate formed at any stage during the hydrochloric acid run. Each time the precipitate dissolved, a dramatic decrease in pH was noted.

Example 8

A concentrated fermentation broth containing lactic acid (65%) was acidulated with 75% phosphoric acid to a pH of 3.0. The acidulated suspension was clarified by filtration and a portion of the supernatant was subjected to a six by six counter-current extraction process. (Mass-Transfer Operations, 3rd Ed., Robert E. Treybal, McGraw-Hill, 1955, p. 518.) The filtered, acidulated supernatant contained 55.39% lactic acid, 3.27% phosphate, 2.56% ammonia, and 28.7% water. The supernatant was extracted at a solvent to aqueous ratio of 4:1; the solvent contained hexanol, 0.7% phosphoric acid, and 7% water.

Table 8
Counter-Current Extraction of Broth

Row 1; Stage	Aqueous Broth Feed	Solvent In	Aqueous Out	Solvent out	Aqueous Wt Loss	Solvent Wt Gain	Final Aqueous				
							% lactic	% PO4	%NH3	% Water	% Hexanol
1	8.13	32.02	5.62	34.36	2.51	2.34	-	-	-	-	-
2	5.62	32.06	5.07	32.39	0.55	0.33	-	-	-	-	-
3	5.07	32.03	5.01	31.89	0.06	-0.14	-	-	-	-	-
4	5.01	32.00	5.07	31.77	-0.06	-0.23	-	-	-	-	-
5	5.07	32.02	5.07	31.75	0	-0.27	-	-	-	-	-
6	5.07	32.04	5.07	31.82	0	-0.22	4.08%	18.76%	3.70%	60.70%	0.03%
Row 2; Stage	Aqueous Broth Feed	Solvent In	Aqueous Out	Solvent out	Aqueous Wt Loss	Solvent Wt Gain	Final Aqueous				
							% lactic	% PO4	%NH3	% Water	% Hexanol
1	7.99	32.39	4.54	35.51	3.45	3.12	-	-	-	-	-
2	4.54	31.89	4.08	32.08	0.46	0.19	-	-	-	-	-
3	4.08	31.77	3.97	31.69	0.11	-0.08	-	-	-	-	-
4	3.97	31.75	4.03	31.44	-0.06	-0.31	-	-	-	-	-
5	4.03	31.82	4.08	31.58	-0.05	-0.24	-	-	-	-	-
6	4.08	31.99	4.12	31.75	-0.04	-0.24	5.28%	18.39%	3.71%	59.30%	0.02%
Row 3; Stage	Aqueous Broth Feed	Solvent In	Aqueous Out	Solvent out	Aqueous Wt Loss	Solvent Wt Gain	Final Aqueous				
							% lactic	% PO4	%NH3	% Water	% Hexanol
1	8.02	32.08	4.54	35.35	3.48	3.27	-	-	-	-	-
2	4.54	31.69	3.89	32.13	0.65	0.44	-	-	-	-	-
3	3.89	31.44	3.70	31.49	0.19	0.05	-	-	-	-	-
4	3.7	31.58	3.74	31.37	-0.04	-0.21	-	-	-	-	-
5	3.74	31.75	3.83	31.48	-0.09	-0.27	-	-	-	-	-
6	3.83	32.03	3.86	31.75	-0.03	-0.28	9.86%	15.01%	3.91%	58.10%	0.05%

Row 1; Stage	Final Solvent					g lactic in	g lactic out Solvent	g Lactic Out Aqueous
	% lactic	%PO4	%NH3	% Water	% Hexanol			
1	7.73%	0.03%	0.07%	5.62%	-	4.503	2.656	-
2	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	-
6	-	-	-	-	-	-	-	0.207
Row 2; Stage	Final Solvent					g lactic in	g lactic out Solvent	g Lactic Out Aqueous
	% lactic	%PO4	%NH3	% Water	% Hexanol			
1	10.55%	0.04%	0.13%	6.04%	-	4.426	3.746	-
2	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	-
6	-	-	-	-	-	-	-	0.218
Row 3; Stage	Final Solvent					g lactic in	g lactic out Solvent	g Lactic Out Aqueous
	% lactic	%PO4	%NH3	% Water	% Hexanol			
1	10.66%	0.03%	0.12%	6.03%	-	4.442	3.768	-
2	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	-
6	-	-	-	-	-	-	-	0.381

Row 4; Stage	Aqueous Broth Feed	Solvent In	Aqueous Out	Solvent out	Aqueous Wt Loss	Solvent Wt Gain	Final Aqueous				
							% lactic	% PO4	%NH3	% Water	% Hexanol
1	8.02	32.13	4.36	35.59	3.66	3.46	-	-	-	-	-
2	4.36	31.49	3.72	31.96	0.64	0.47	-	-	-	-	-
3	3.72	31.37	3.53	31.72	0.19	0.35	-	-	-	-	-
4	3.53	31.48	3.52	31.3	0.01	-0.18	-	-	-	-	-
5	3.52	31.75	3.72	31.29	-0.2	-0.46	-	-	-	-	-
6	3.72	32.05	3.98	31.83	-0.26	-0.22	9.40%	14.42%	3.83%	58.40%	0.03%

Row 5; Stage	Aqueous Broth Feed	Solvent In	Aqueous Out	Solvent out	Aqueous Wt Loss	Solvent Wt Gain	Final Aqueous				
							% lactic	% PO4	%NH3	% Water	% Hexanol
1	8.00	31.96	4.68	35.09	3.32	3.13	-	-	-	-	-
2	4.68	31.72	3.80	32.07	0.88	0.35	-	-	-	-	-
3	3.80	31.30	3.77	31.06	0.03	-0.24	-	-	-	-	-
4	3.77	31.29	3.37	31.25	0.40	-0.04	-	-	-	-	-
5	3.37	31.83	3.67	31.51	-0.30	-0.32	-	-	-	-	-
6	3.67	32.08	3.63	31.61	0.04	-0.47	10.16%	14.45%	3.96%	58.00%	0.03%

Row 6; Stage	Aqueous Broth Feed	Solvent In	Aqueous Out	Solvent out	Aqueous Wt Loss	Solvent Wt Gain	Final Aqueous				
							% lactic	% PO4	%NH3	% Water	% Hexanol
1	8.02	32.07	4.39	35.49	3.63	3.42	-	-	-	-	-
2	4.39	31.06	3.85	31.56	0.54	0.5	-	-	-	-	-
3	3.85	31.25	3.45	31.32	0.40	0.07	-	-	-	-	-
4	3.45	31.51	3.40	31.42	0.05	-0.09	-	-	-	-	-
5	3.40	31.61	3.45	31.35	-0.05	-0.26	-	-	-	-	-
6	3.45	32.02	3.59	31.80	-0.14	-0.22	12.94%	12.13%	4.12%	56.10%	0.03%

Row 4; Stage	Final Solvent					g lactic in	g lactic out Solvent	g Lactic Out Aqueous
	% lactic	%PO4	%NH3	% Water	% Hexanol			
1	11.10%	0.04%	0.16%	6.04%	-	4.442	3.950	-
2	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	-
6	-	-	-	-	-	-	-	0.374

Row 5; Stage	Final Solvent					g Lactic in	g Lactic out Solvent	g Lactic Out Aqueous
	% lactic	%PO4	%NH3	% Water	% Hexanol			
1	10.69%	0.03%	0.14%	5.91%	-	4.430	3.751	-
2	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	-
6	-	-	-	-	-	-	-	0.369

Row 6; Stage	Final Solvent					g lactic in	g lactic out Solvent	g Lactic Out Aqueous
	% lactic	%PO4	%NH3	% Water	% Hexanol			
1	11.51%	0.04%	0.36%	6.08%	-	4.441	4.085	-
2	3.58%	0.00%	0.12%	4.55%	-	-	-	-
3	1.79%	0.00%	0.02%	4.43%	-	-	-	-
4	1.08%	0.00%	0.02%	4.53%	-	-	-	-
5	0.68%	0.03%	0.01%	4.75%	-	-	-	-
6	0.74%	0.03%	0.01%	5.06%	-	-	-	0.465

Example 9

A cross-current extraction was conducted to purify lactic acid. The organic phase comprised lactic acid 10.81%, water 8.08%, hexanol 78.43%, and phosphate 205 ppm, and the aqueous phase comprised lactic acid 19.09% and water 80.91%. A 10:1 organic/aqueous ratio was used.

Table 9
Cross-Current Lactic Acid Purification

Stage #	g Organic Phase In	g Organic Phase Out	g Aqueous Phase In	g Aqueous Phase Out	Aqueous Layer Analysis			mg Phos Aqueous	% of Total Phos	Cum % Phos Out
					% Water	%Lactic	% Phos			
1	30.06	30.71	3.07	2.36	72.9	21.04	0.179	4.215	68.40	68.4
2	30.71	30.48	3.01	3.11	75.84	21.38	0.065	2.022	32.81	101.21
3	30.48	30.21	3.02	3.14	76.01	21.29	0.022	0.703	11.41	112.62
4	30.21	29.89	3.08	3.22	76.78	20.61	0.012	0.399	6.48	119.1
5	29.89	29.64	3.03	3.17	77.79	20.73	0.002	0.060	0.98	120.08
6	29.64	29.4	3.02	3.11	77.15	20.31	0.000	0.000	0.00	120.08
7	29.4	29.15	3.07	3.22	76.88	19.89	0.000	0.000	0.00	120.08
8	29.15	28.94	3.13	3.22	77.21	19.82	0.000	0.000	0.00	120.08

See Figure 16.

Example 10

To find the optimum aqueous lactic acid concentration for ion removal from lactic acid in hexanol, single 10:1 solvent/aqueous extractions were performed with concentrations of 18, 21, 23, 25, 27, and 30% lactic acid in the aqueous phase. The solvent phase was 9.73% lactic acid, 330 ppm PO_4, 9.55% H_2O, and 76.22% hexanol.

Table 10

Theoretical Aqueous Conc.	Actual Aqueous Conc.	Change in Lactic Acid Conc. in Feed
18%	18.69%	-1.37%
21%	22.01%	+1.37%
23%	22.01%	+6.16%
25%	24.47%	+7.85%
27%	28.71%	+10.96%
30%	31.60%	+12.29%

Using a best fit curve (see Figure 17), 19% aqueous lactic acid should give little or no movement of lactic acid from solvent to aqueous phase during purification/ion removal.

Example 11

The effect of temperature on the back extraction of lactic acid from hexanol to water was tested. The original single phase in this experiment contained 18.31% (weight) lactic acid, 12.70% water, and 68.99% hexanol. Water was added at 20°C, 30°C, and 45° C.

Table 11

	20°C	30°C	45°C
single phase (g)	10.71	11.18	10.85
water added to reach cloud point (g)	0.3	0.32	0.39
water excess (g)	1.0	1.3	1.3
Total (g)	12.01	12.80	12.54

Table 12

quantity of phases (measured)	20°C	30°C	45°C
aqueous (g)	1.61	1.71	1.59
organic (g)	10.59	10.86	10.55

Table 13

Analysis of Phases

	Aqueous			Organic			K_s^* lactic
	% lactic	% hex.	% water	% lactic	% hex.	% water	
20°C	27.29	3.76	68.95	14.19	72.93	12.88	0.520
30°C	27.27	4.33	68.40	14.70	72.33	12.97	0.539
45°C	26.90	4.13	68.97	14.63	72.36	13.01	0.544
average	27.15	4.07	68.78	14.51	72.52	12.95	0.534

* K_s = distribution coefficient = c_s/c_w, where c_s = concentration of lactic acid in aqueous phase and c_w = concentration of lactic acid in solvent phase.

Table 14

Total Composition

	% lactic	% hexanol	% water
20°C	15.85	63.88	20.28
30°C	16.05	63.34	20.61
45°C	16.23	63.43	20.35

Thus, there appeared to be no benefit in extraction efficiency from increasing the extraction temperature from 20°C to 45°C. To the extent any trend could be discerned, increasing temperature appeared to have an adverse effect.

Example 12

First stage back extractions were performed on a lactic acid solution (11.95% lactic acid, 10.3% water, and 77.75% hexanol) with water at 4:1, 6:1, 8:1, and 10:1 organic to aqueous ratios. The lactic acid concentration was measured in the aqueous phase and the percent lactic acid removal was calculated for each of the various ratios of organic to aqueous phase. From this recovery, an estimation of the number of stages required to remove 97% of the lactic acid was made. Ratios of 4:1, 6:1, and 8:1 require 6, 9, and 11 stages respectively.

Table 15A

	g solvent	solvent % lactic	solvent in g lactic	g water	g aqueous out	g solvent out	aqueous % lactic	aqueous g lactic	% lactic removal
4:1	4	11.95%	0.48	1	1.35	3.65	14.28%	0.193	40.33%
6:1	6.01	11.95%	0.72	1	1.4	5.58	16.07%	0.225	31.33%
8:1	8	11.95%	0.96	1.01	1.43	7.6	17.64%	0.252	26.39%
10:1	10	11.95%	1.20	1.01	1.53	9.49	18.34%	0.281	23.48%

Table 15B

4:1 extraction	g lactic	% removal	g lactic removed	g lactic cum	% removed cum
1	0.478	40.33%	0.193	0.193	40.38%
2	0.285	40.33%	0.115	0.308	64.42%
3	0.170	40.33%	0.069	0.377	78.77%
4	0.101	40.33%	0.041	0.417	87.33%
5	0.061	40.33%	0.024	0.442	92.44%
6	0.036	40.33%	0.015	0.456	95.49%

Table 15C

6:1 extraction	g lactic	% removal	g lactic removed	g lactic cum	% removed cum
1	0.718	31.33%	0.225	0.225	31.34%
2	0.493	31.33%	0.155	0.380	52.86%
3	0.339	31.33%	0.106	0.486	67.63%
4	0.233	31.33%	0.073	0.558	77.78%
5	0.160	31.33%	0.050	0.609	84.75%
6	0.110	31.33%	0.034	0.643	89.54%
7	0.075	31.33%	0.024	0.666	92.82%
8	0.052	31.33%	0.016	0.683	95.08%
9	0.036	31.33%	0.011	0.694	96.63%

Table 15D

8:1 extraction	g lactic	% removal	g lactic removed	g lactic cum	% removed cum
1	0.956	26.39%	0.252	0.252	26.36%
2	0.704	26.39%	0.186	0.438	45.79%
3	0.518	26.39%	0.137	0.574	60.08%
4	0.381	26.39%	0.101	0.675	70.61%
5	0.281	26.39%	0.074	0.749	78.36%
6	0.207	26.39%	0.055	0.804	84.06%
7	0.152	26.39%	0.040	0.844	88.26%
8	0.112	26.39%	0.030	0.873	91.35%
9	0.082	26.39%	0.022	0.895	93.62%
10	0.061	26.39%	0.016	0.911	95.30%
11	0.045	26.39%	0.012	0.923	96.53%

See Figure 18.

Example 13

A cross-current six-stage back extraction was performed with a 4:1 solvent to aqueous ratio. The solvent composition was 10.82% lactic acid, 10.5% water, and 78.68% hexanol. 98.62% of the lactic acid was recovered in the aqueous stream. See Figure 19.

Example 14

A counter-current six-stage back extraction was performed with a 4:1 solvent to aqueous ratio. The solvent comprised 10.5% water, 10.82% lactic acid, and 78.62% hexanol. 16.04% of the lactic acid entering row 6 was left with the solvent stream. The final aqueous stream comprised 20.06% lactic acid and 0.7% hexanol. The final solvent stream comprised 2.03% lactic acid and 7.83% water.

* * *

The preceding description of specific embodiments of the present invention is not intended to be a complete list of every possible embodiment of the invention. Persons who are skilled in this field will recognize that modifications can be made to the specific embodiments described here that would be within the scope of the present invention.

CLAIMS:

1. A process for the extraction of an organic acid from an aqueous solution thereof which comprises contacting such solution with a mixture of (a) water, (b) a mineral acid in a quantity effective to maintain the pH of the mixture between about 1.0 and about 4.5, and (c) an oxygenated solvent which has limited miscibility with water and the aqueous solution, the oxygenated solvent having from 5 to 12 carbon atoms and having at least one functional group selected from the group consisting of hydroxyl, ester, keto, ether, carbonyl, and amido.

2. The process of claim 1, where the aqueous solution of organic acid is substantially saturated with respect to at least one electrolyte selected from the group consisting of $MHSO_4$, M_2SO_4, M_3PO_4, M_2HPO_4, MH_2PO_4, and MNO_3, where M is selected from the group consisting of Na, NH_4, and K.

3. The process of claim 1, where the oxygenated solvent has from 6 to 8 carbon atoms.

4. The process of claim 1, where the oxygenated solvent is hexanol.

5. The process of claim 1, where the contacting is performed in a mixer-settler apparatus.

6. A process for recovering an organic acid, including the steps of:

providing an aqueous feed containing an organic acid and impurities;

clarifying the aqueous feed to remove at least a substantial portion of the impurities therein, producing a clarified feed;

acidulating the clarified liquid feed by adding a quantity of a mineral acid effective to lower the pH of the feed to between about 1.0 and about 4.5, producing an acidulated feed which is substantially saturated with respect to at least one electrolyte selected from the group consisting of $MHSO_4$, M_2SO_4, M_3PO_4, M_2HPO_4, MH_2PO_4, and MNO_3, where M is selected from the group consisting of Na, NH_4, and K;

extracting the acidulated feed with an extraction mixture which includes (a) water, (b) a mineral acid, in a quantity effective to maintain the pH of the feed between about 1.0 and about 4.5, and (c) an oxygenated solvent which has limited miscibility with water and the acidulated feed, the oxygenated solvent having from 5 to 12 carbon atoms and having at least one functional group selected from the group consisting of hydroxyl, ester, keto, ether, carbonyl, and amido, with the extraction producing a solvent extract and a first raffinate; and

back extracting the solvent extract with an aqueous liquid, thereby producing an organic acid-rich aqueous extract and an organic acid-depleted solvent raffinate.

7. The process of claim 6, where the extraction of the acidulated feed is performed in a mixer-settler apparatus.

8. The process of claim 6, where the back extraction is performed in a mixer-settler apparatus.

9. The process of claim 6, where the oxygenated solvent has from 6 to 8 carbon atoms.

10. The process of claim 6, where the oxygenated solvent is hexanol.

11. The process of claim 6, where the ratio of the extraction mixture to the acidulated feed is between about 3/1 and about 6/1 by weight.

12. The process of claim 6, where the extraction mixture is substantially saturated with water.

13. The process of claim 6, further including the steps of:

concentrating the organic acid-rich aqueous extract by removing water; and

decolorizing the extract to remove at least a portion of the impurities remaining therein.

14. The process of claim 6, further including the steps of:

recovering solvent from the first raffinate by stripping solvent therefrom; and recycling the recovered solvent for use in extracting the acidulated feed.

15. The process of claim 14, further including the steps of:

maintaining the pH of the acidulated feed during the extraction at a level effective to prevent substantial precipitation of phosphate, sulfate, nitrate, and chloride salts during the extraction; and

recovering phosphate, sulfate, nitrate, or chloride salts from the first raffinate by evaporation after the solvent is stripped therefrom.

16. The process of claim 6, further including the steps of:

crystallizing a phosphate, sulfate, or nitrate salt from the acidulated feed;

washing the crystallized salt with an aqueous liquid; and

drying the washed, crystallized salt.

17. The process of claim 6, further including the steps of:

filtering the aqueous feed to remove undesirable impurities;

concentrating the feed by removing a portion of the water therein; and decolorizing the feed by contacting it with a decolorizing agent;

with the filtering, concentrating, and decolorizing of the feed being done before the feed is acidulated.

18. The process of claim 17, where the decolorizing agent is selected from the group consisting of granular carbon, powdered carbon, and decolorizing resin.

19. The process of claim 6, further including the step of:

after extracting the acidulated feed with the extraction mixture of water, mineral acid, and oxygenated solvent, and before back extracting the solvent extract with the aqueous liquid, performing an additional extraction in which an aqueous solution which contains a quantity of the organic acid is used as the extractant of the solvent extract from the first extraction step, thereby producing a second raffinate and a purified solvent extract, with the latter subsequently being back extracted as specified in claim 1.

20. The process of claim 6, where at least 20% by weight of the total organic acid values in the aqueous feed are present in the form of alkali salts of the organic acid, and where the concentration of organic acid in the feed immediately prior to acidulation is greater than about 30% by weight.

21. A process for recovering lactic acid, including the steps of:

providing an aqueous feed containing lactic acid and impurities;

clarifying the aqueous feed to remove at least a substantial portion of the impurities therein, producing a clarified feed;

acidulating the clarified feed by adding a quantity of a mineral acid effective to lower the pH of the feed to between about 1.0 and about 4.5, producing an acidulated feed which is substantially saturated with respect to at least one electrolyte selected from the group consisting of $MHSO_4$, M_2SO_4, M_3PO_4, M_2HPO_4, MH_2PO_4, and MNO_3, where M is selected from the group consisting of Na, NH_4, and K;

extracting the acidulated feed with an extraction mixture which includes (a) water, (b) a mineral acid, in a quantity effective to maintain the pH of the feed between about 1.0 and about 4.5, and (c) hexanol, with the extraction producing a hexanol extract and a first raffinate; and

back extracting the hexanol extract with an aqueous liquid, thereby producing a lactic acid-rich aqueous extract and a lactic acid-depleted hexanol raffinate.

22. The process of claim 21, where the extraction of the acidulated feed is performed in a mixer-settler apparatus.

23. The process of claim 21, where the back extraction is performed in a mixer-settler apparatus.

24. The process of claim 21, where the ratio of the extraction mixture to the acidulated feed is between about 3/1 and about 6/1 by weight.

25. The process of claim 21, where the extraction mixture is substantially saturated with water.

26. The process of claim 21, further including the steps of:

concentrating the lactic acid-rich aqueous extract by removing water; and

decolorizing the extract to remove at least a portion of the impurities remaining therein.

27. The process of claim 21, further including the steps of:

recovering hexanol from the first raffinate by stripping hexanol therefrom; and

recycling the recovered hexanol for use in extracting the acidulated feed.

28. The process of claim 27, further including the steps of:

maintaining the pH of the acidulated feed during the extraction at a level effective to prevent substantial precipitation of phosphate, sulfate, and nitrate salts during the extraction; and recovering phosphate, sulfate, or nitrate salts from the first raffinate by evaporation after the solvent is stripped therefrom.

29. The process of claim 21, further including the steps of:

crystallizing a phosphate, sulfate, or nitrate salt from the acidulated feed;

washing the crystallized salt with an aqueous liquid; and

drying the washed, crystallized salt.

30. The process of claim 21, further including the steps of:

filtering the aqueous feed to remove undesirable impurities;

concentrating the feed by removing a portion of the water therein; and

decolorizing the feed by contacting it with a decolorizing agent;

with the filtering, concentrating, and decolorizing of the feed being done before the feed is acidulated.

31. The process of claim 30, where the decolorizing agent is selected from the group consisting of granular carbon, powdered carbon, and decolorizing resin.

32. The process of claim 21, further including the step of:

after extracting the acidulated feed with the extraction mixture of water, mineral acid, and hexanol, and before back extracting the hexanol extract with the aqueous liquid, performing an additional extraction in which an aqueous solution which contains a quantity of lactic acid is used as the extractant of the hexanol extract from the first extraction step, thereby producing a second raffinate and a purified hexanol extract, with the latter subsequently being back extracted as specified in claim 1.

33. The process of claim 21, where at least 20% by weight of the total lactic acid values in the aqueous feed are present in the form of alkali lactates, and where the concentration of lactic acid in the feed immediately prior to acidulation is greater than about 30% by weight.

34. A process for recovering lactic acid, including the steps of:

providing an aqueous feed containing lactic acid and impurities;

clarifying the aqueous feed to remove at least a substantial portion of the impurities therein, producing a clarified feed;

concentrating the feed by removing a portion of the water therein;

decolorizing the feed by contacting it with a decolorizing agent;

acidulating the clarified feed by adding a quantity of a mineral acid effective to lower the pH of the feed to between about 1.0 and about 4.5, producing an acidulated feed which is substantially saturated with respect to at least one electrolyte selected from the group consisting of $MHSO_4$, M_2SO_4, M_3PO_4, M_2HPO_4, MH_2PO_4, and MNO_3, where M is selected from the group consisting of Na, NH_4, and K;

extracting the acidulated feed with an extraction mixture which includes (a) water, (b) a mineral acid, in a quantity effective to maintain the pH of the feed between about 1.0 and about 4.5, and (c) hexanol, with the extraction producing a first hexanol extract and a first raffinate;

extracting the first hexanol extract with an aqueous lactic acid solution, thereby producing a second raffinate and a purified hexanol extract;

back extracting the purified hexanol extract with an aqueous liquid, thereby producing a lactic acid-rich aqueous extract and a lactic acid-depleted hexanol raffinate;

recovering hexanol from the first raffinate by stripping hexanol therefrom;

recycling the recovered hexanol for use in extracting the acidulated feed;

concentrating the lactic acid-rich aqueous extract by removing water; and

carbon-treating the concentrated extract to remove at least a portion of the impurities remaining therein.

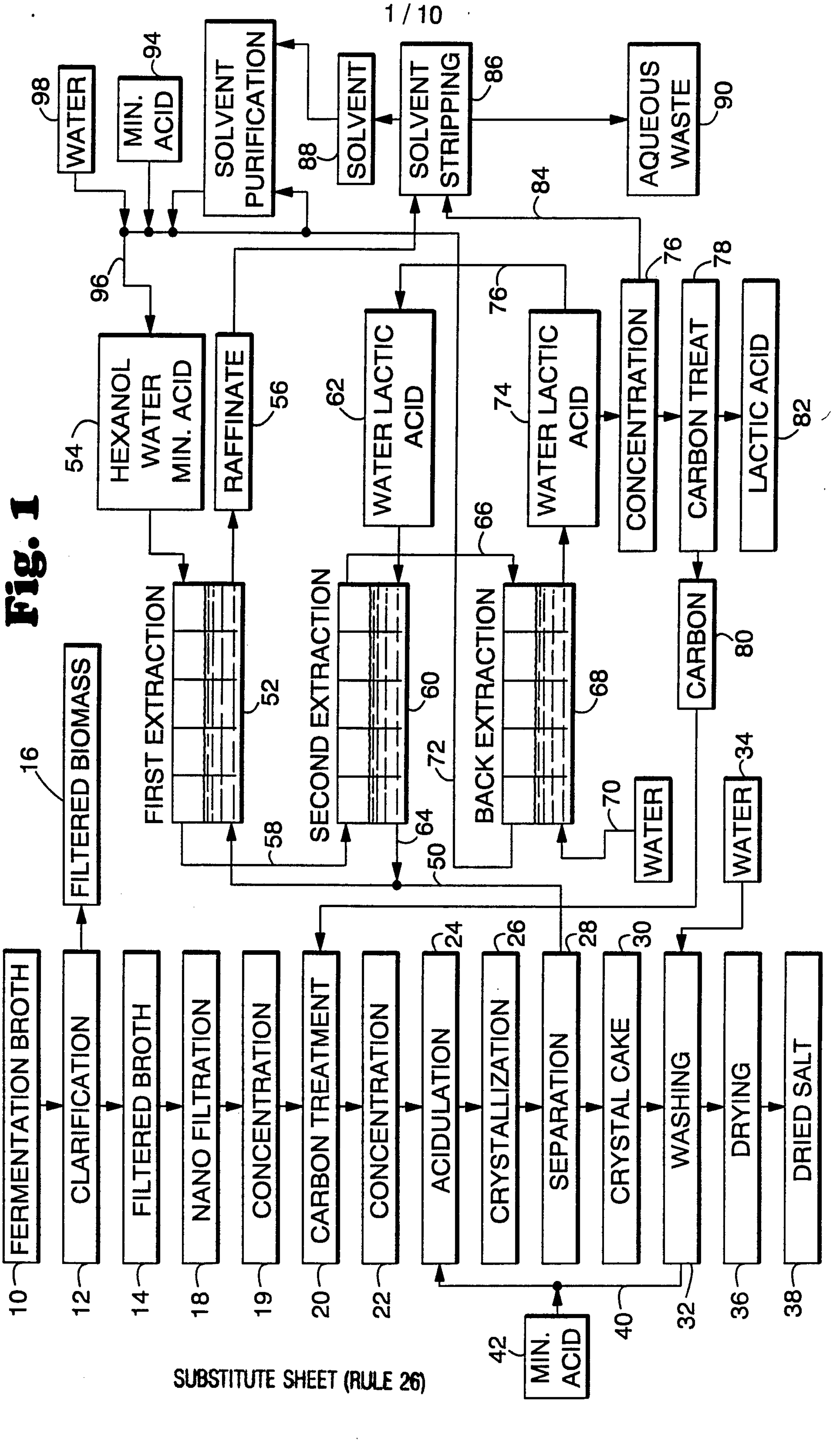
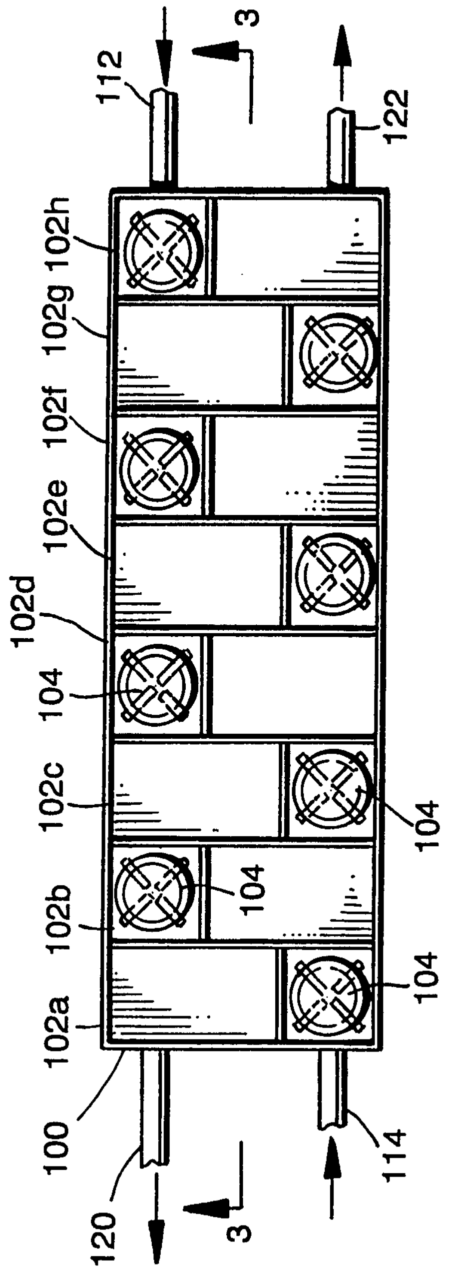

FERMENTATION BROTH
10
CLARIFICATION
12
FILTERED BIOMASS
16
FILTERED BROTH
14
NANO FILTRATION
18
CONCENTRATION
19
CARBON TREATMENT
20
CONCENTRATION
22
ACIDULATION
24
CRYSTALLIZATION
26
SEPARATION
28
CRYSTAL CAKE
30
WASHING
32
DRYING
36
DRIED SALT
38
MIN. ACID
42
40
WATER
34
FIRST EXTRACTION
52
HEXANOL WATER MIN. ACID
54
RAFFINATE
56
58
50
SECOND EXTRACTION
60
64
WATER LACTIC ACID
62
66
BACK EXTRACTION
68
72
WATER
70
WATER LACTIC ACID
74
76
CONCENTRATION
76
CARBON TREAT
78
LACTIC ACID
82
CARBON
80
84
SOLVENT STRIPPING
86
SOLVENT
88
AQUEOUS WASTE
90
SOLVENT PURIFICATION
WATER
98
MIN. ACID
94
96

Fig. 1


112
3
122
102h
102g
102f
102e
102d
104
102c
104
104
102b
104
102a
100
114
120
3

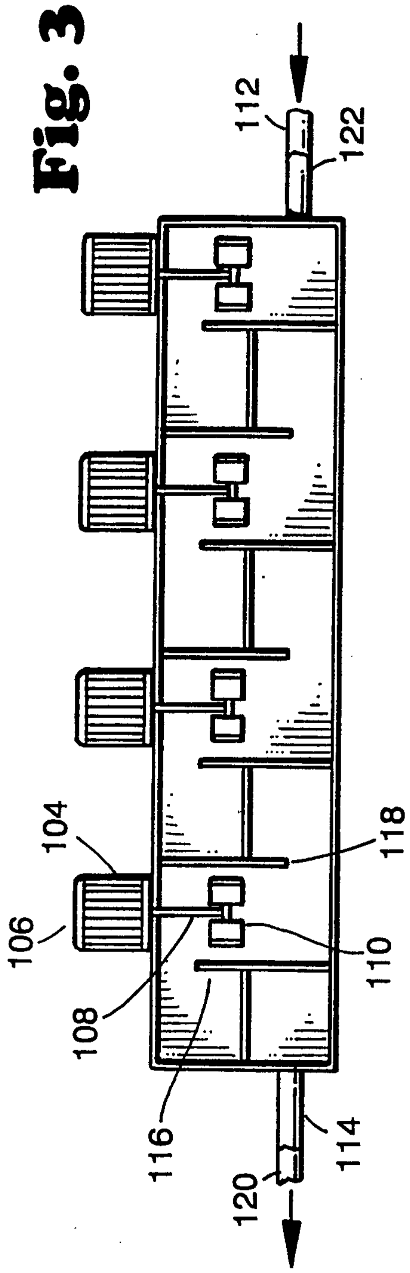

112
122
104
106
118
108
110
116
114
120

Fig. 3

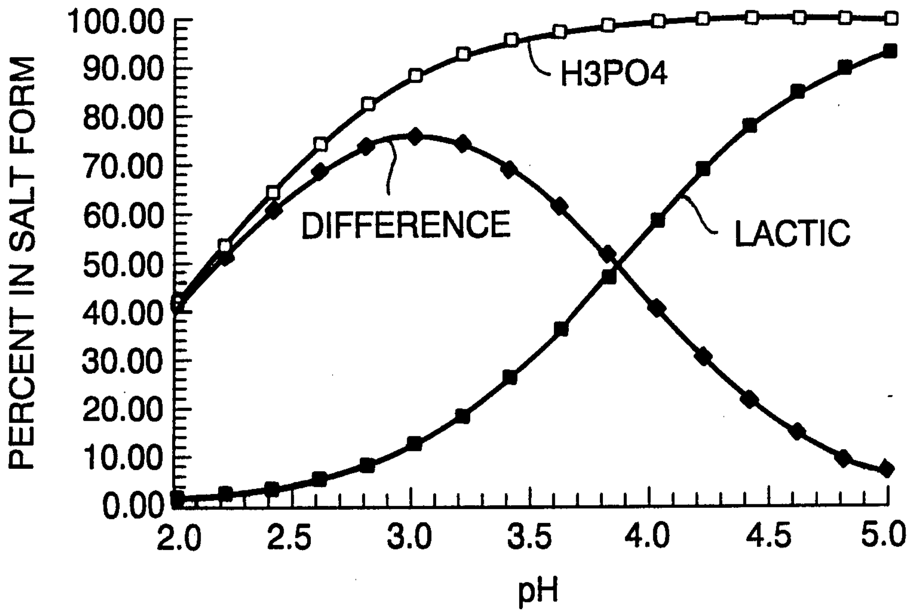

100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
PERCENT IN SALT FORM
H3PO4
DIFFERENCE
LACTIC
2.0
2.5
3.0
3.5
4.0
4.5
5.0
pH

Fig. 4

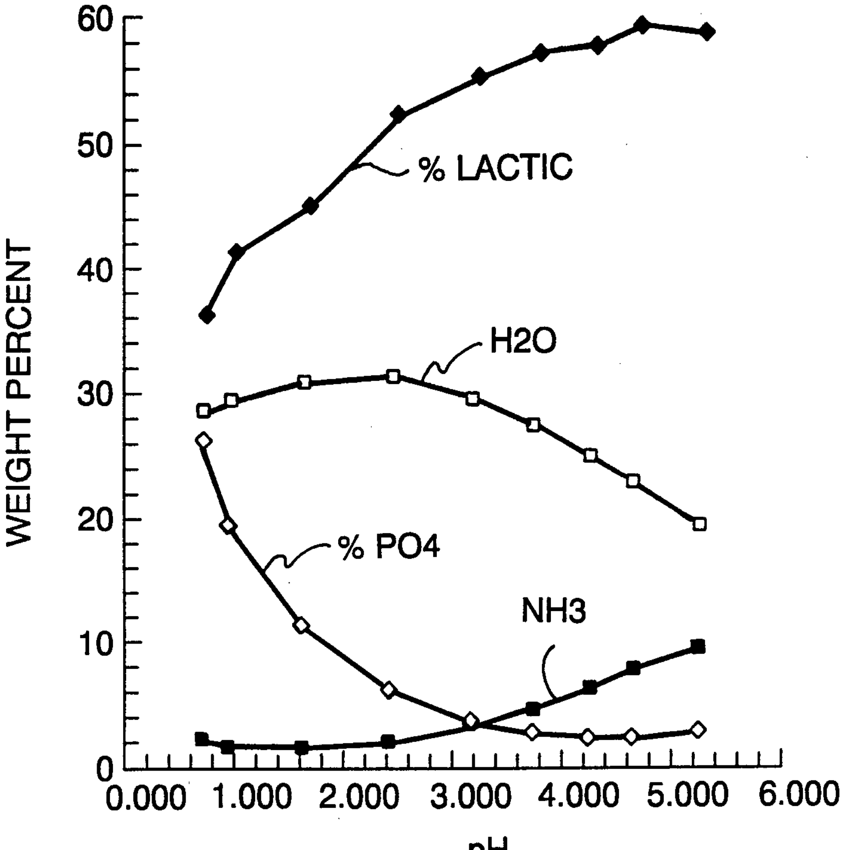

60
50
40
30
20
10
0
WEIGHT PERCENT
% LACTIC
H2O
% PO4
NH3
0.000
1.000
2.000
3.000
4.000
5.000
6.000
pH

Fig. 5

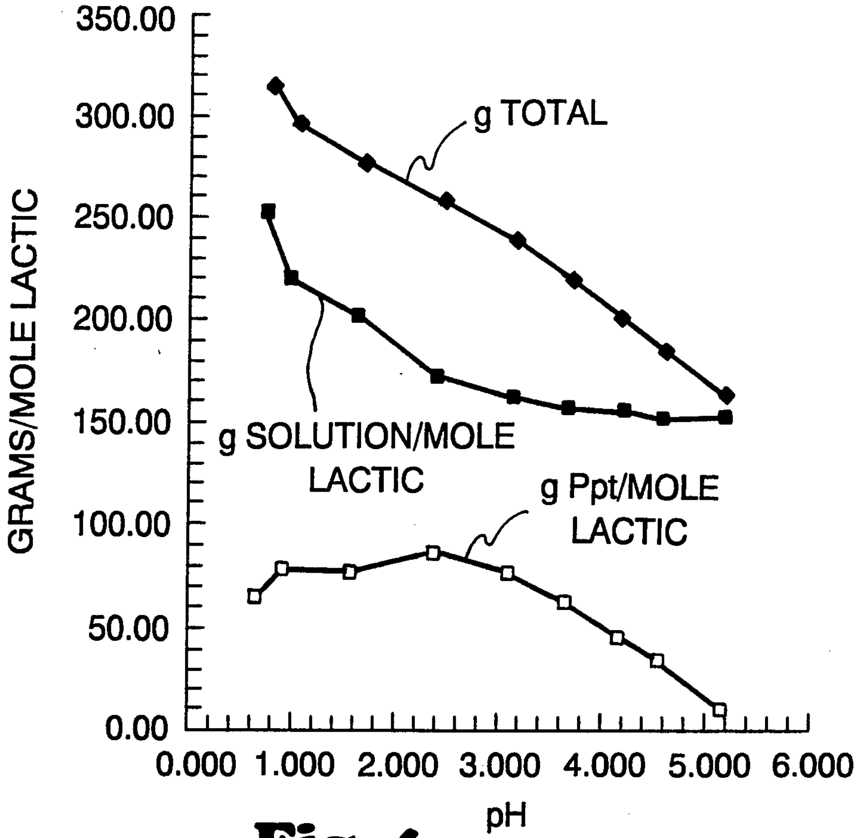

350.00
300.00
250.00
200.00
150.00
100.00
50.00
0.00
GRAMS/MOLE LACTIC
g TOTAL
g SOLUTION/MOLE LACTIC
g Ppt/MOLE LACTIC
0.000
1.000
2.000
3.000
4.000
5.000
6.000
pH

Fig. 6

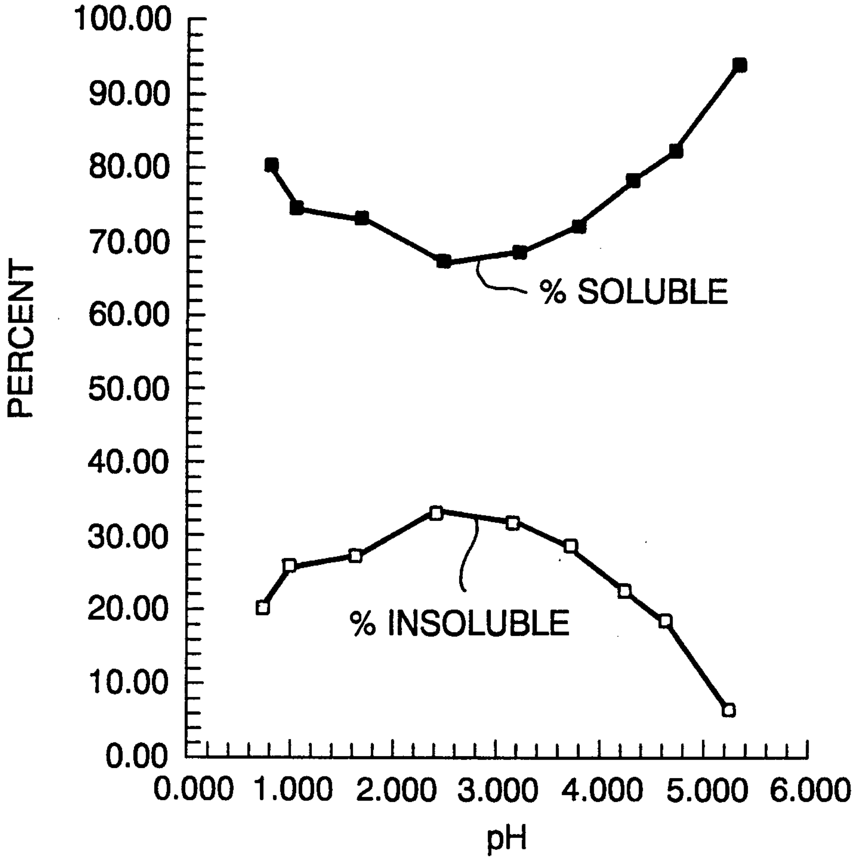
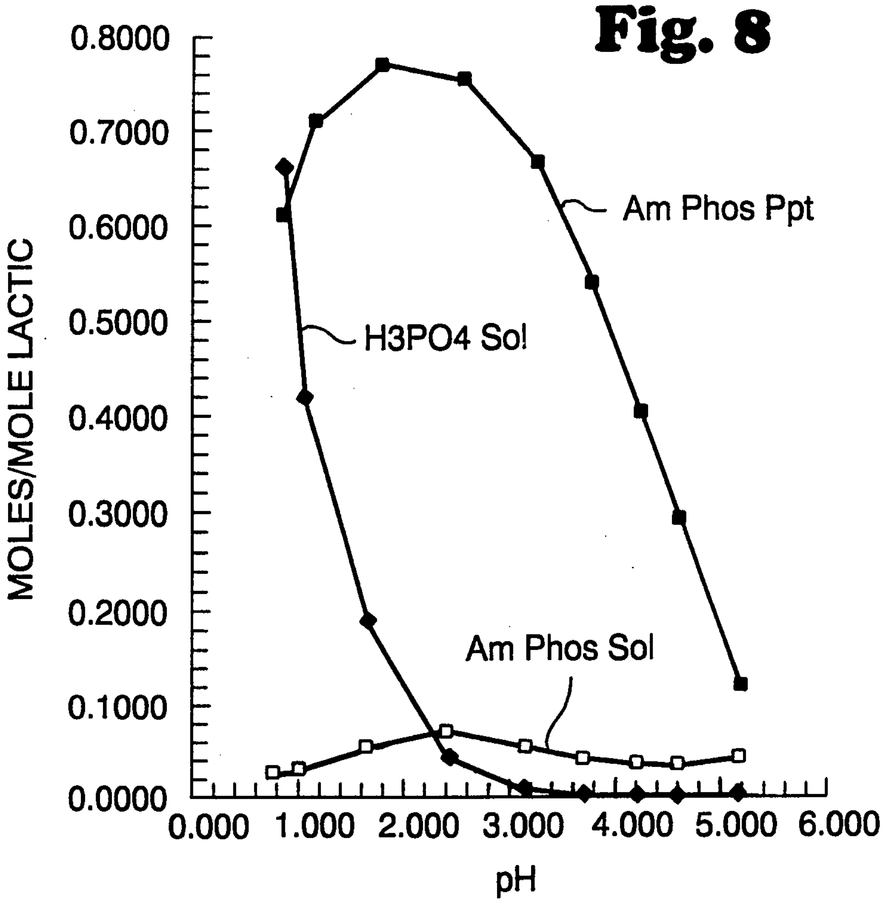

100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
PERCENT
% SOLUBLE
% INSOLUBLE
0.000
1.000
2.000
3.000
4.000
5.000
6.000
pH

Fig. 7

Fig. 8


MOLES/MOLE LACTIC
0.8000
0.7000
0.6000
0.5000
0.4000
0.3000
0.2000
0.1000
0.0000
Am Phos Ppt
H3PO4 Sol
Am Phos Sol
0.000
1.000
2.000
3.000
4.000
5.000
6.000
pH

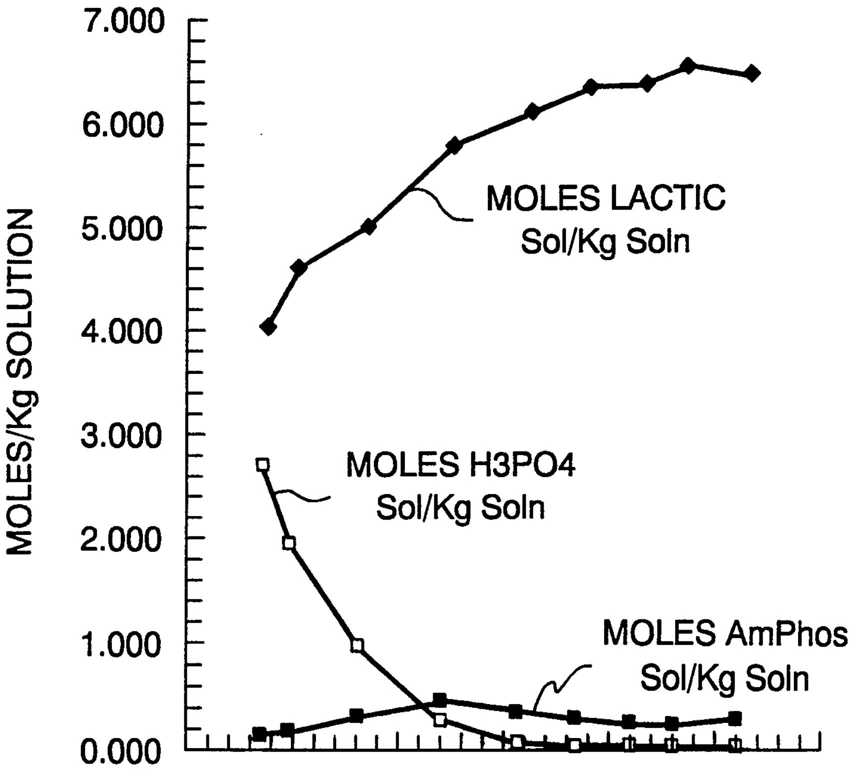

MOLES/Kg SOLUTION
7.000
6.000
5.000
4.000
3.000
2.000
1.000
0.000
MOLES LACTIC
Sol/Kg Soln
MOLES H3PO4
Sol/Kg Soln
MOLES AmPhos
Sol/Kg Soln
0.000
1.000
2.000
3.000
4.000
5.000
6.000
pH

Fig. 9

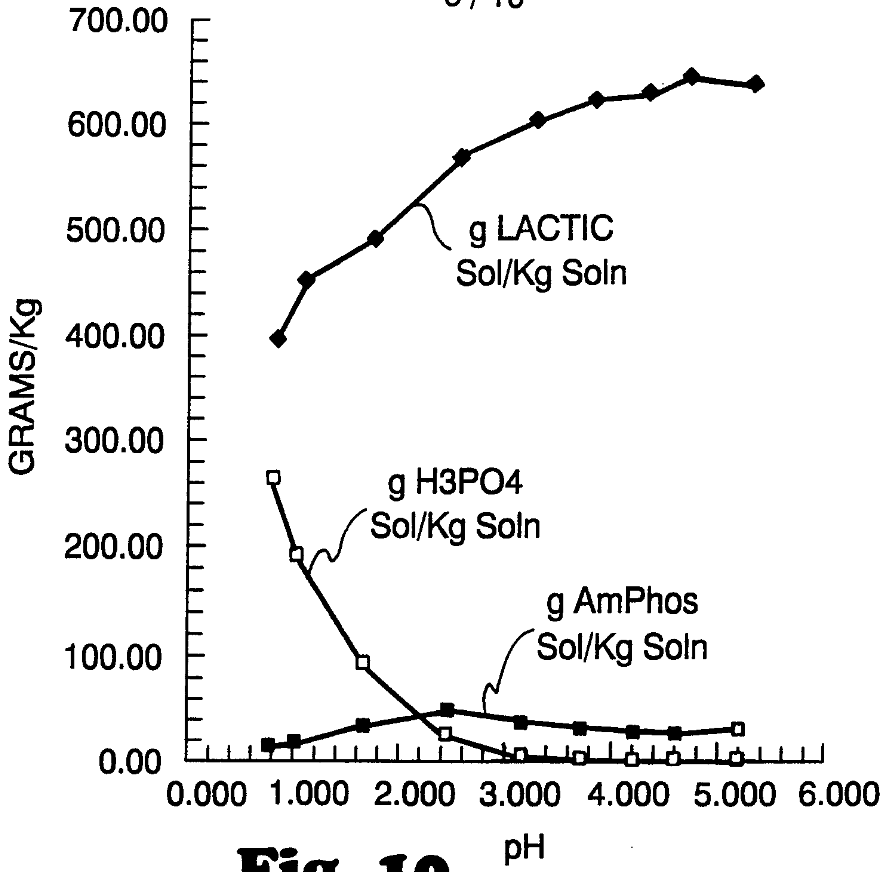

700.00
600.00
500.00
400.00
300.00
200.00
100.00
0.00
GRAMS/Kg
g LACTIC
Sol/Kg Soln
g H3PO4
Sol/Kg Soln
g AmPhos
Sol/Kg Soln
0.000
1.000
2.000
3.000
4.000
5.000
6.000
pH

Fig. 10

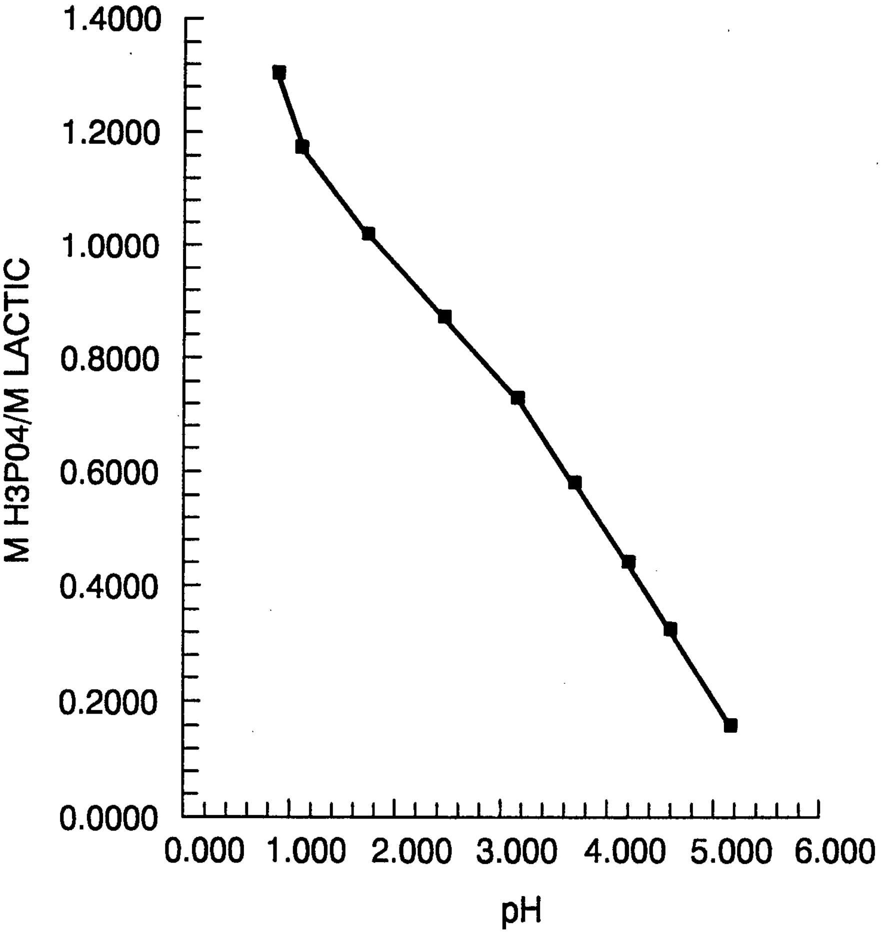

1.4000
1.2000
1.0000
0.8000
0.6000
0.4000
0.2000
0.0000
M H3P04/M LACTIC
0.000
1.000
2.000
3.000
4.000
5.000
6.000
pH

Fig. 11

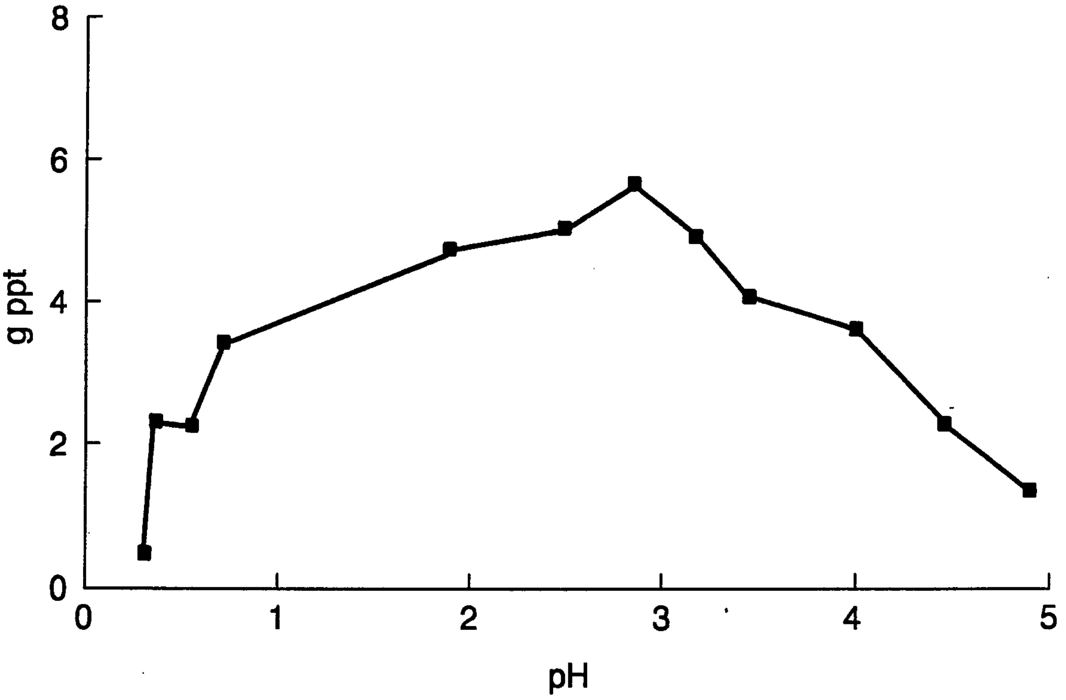

8
6
4
2
0
g ppt
0
1
2
3
4
5
pH

Fig. 12

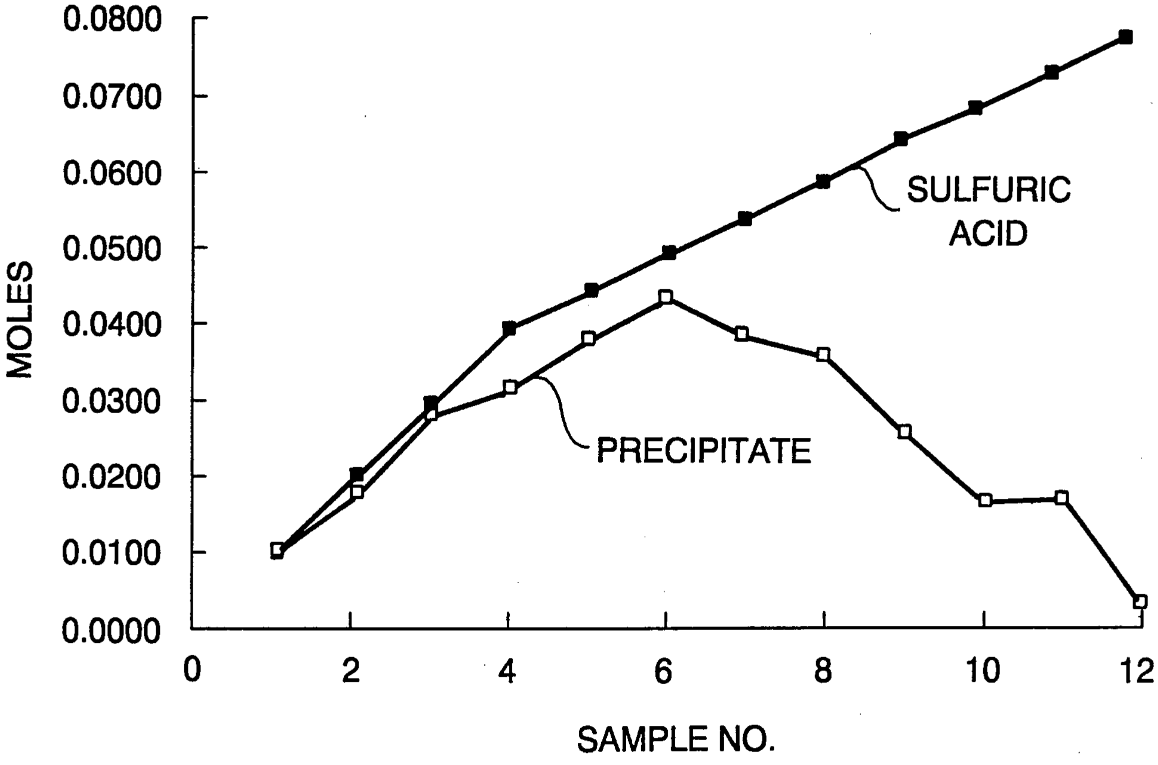

0.0800
0.0700
0.0600
0.0500
0.0400
0.0300
0.0200
0.0100
0.0000
MOLES
0
2
4
6
8
10
12
SAMPLE NO.
SULFURIC ACID
PRECIPITATE

Fig. 13

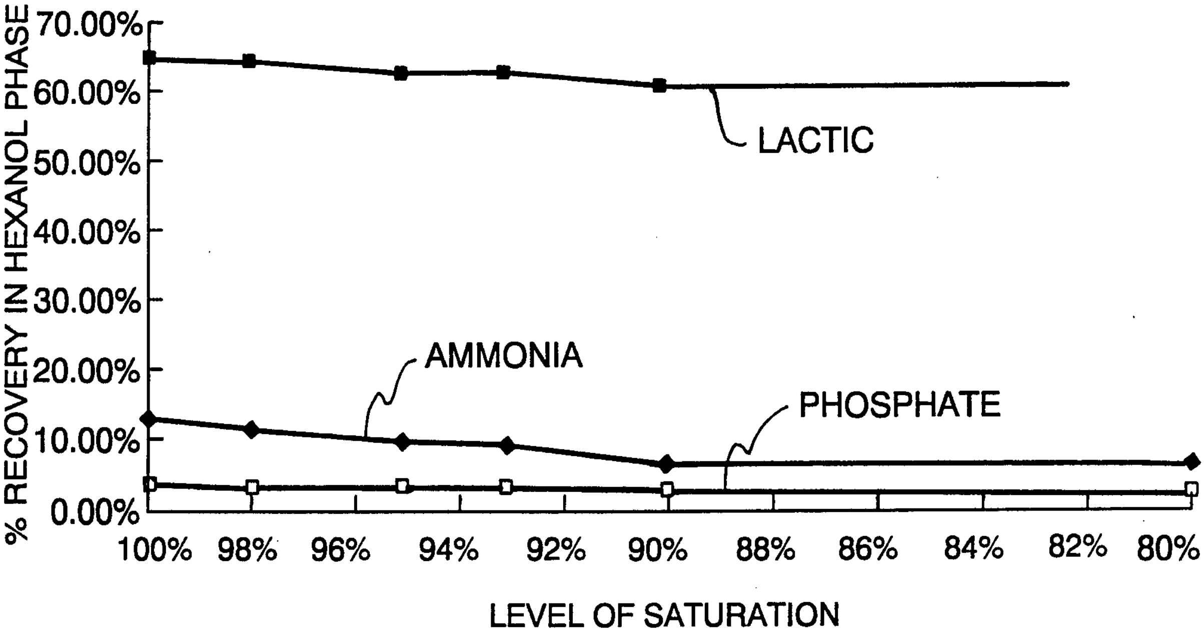

% RECOVERY IN HEXANOL PHASE
70.00%
60.00%
50.00%
40.00%
30.00%
20.00%
10.00%
0.00%
100%
98%
96%
94%
92%
90%
88%
86%
84%
82%
80%
LEVEL OF SATURATION
LACTIC
AMMONIA
PHOSPHATE

Fig. 14

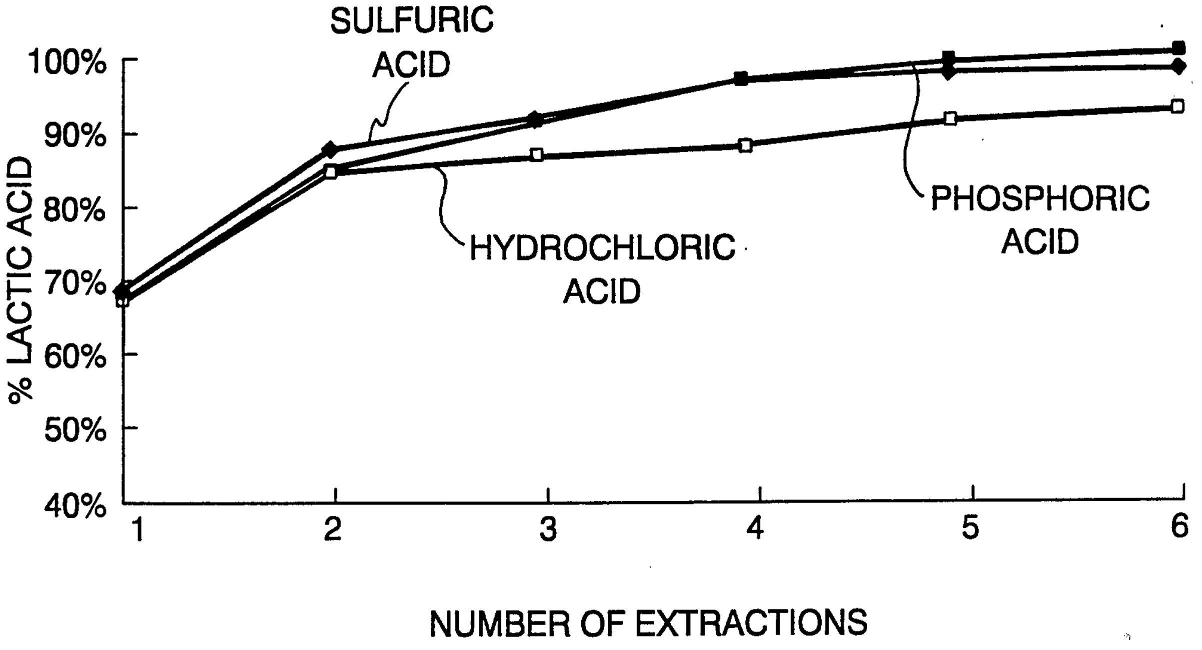

% LACTIC ACID
100%
90%
80%
70%
60%
50%
40%
1
2
3
4
5
6
NUMBER OF EXTRACTIONS
SULFURIC ACID
HYDROCHLORIC ACID
PHOSPHORIC ACID

Fig. 15

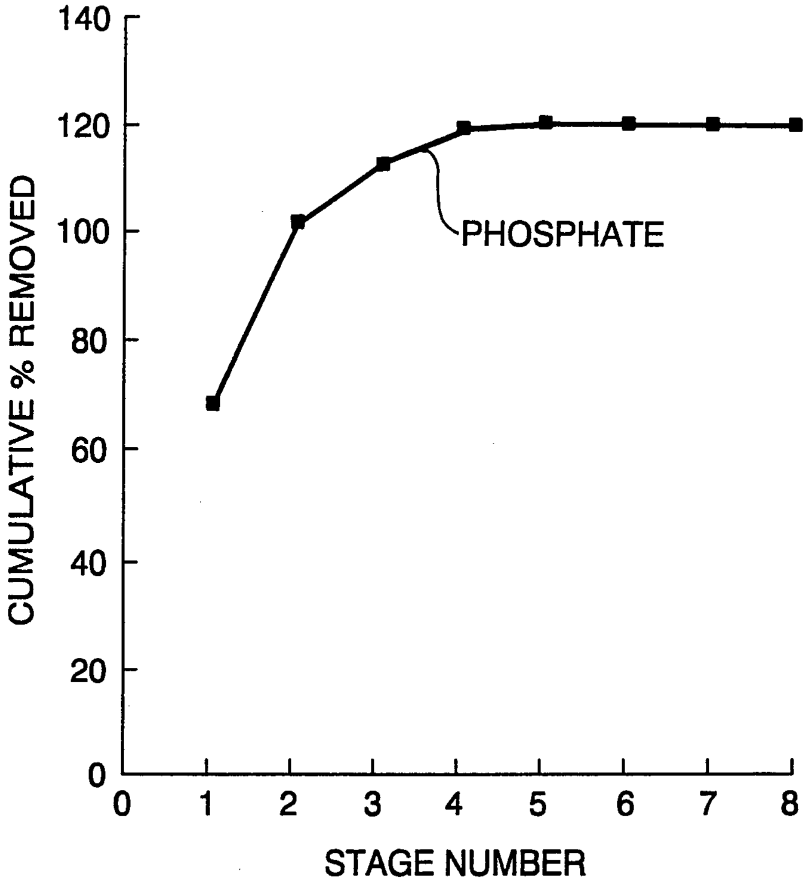

140
120
100
80
60
40
20
0
CUMULATIVE % REMOVED
PHOSPHATE
0
1
2
3
4
5
6
7
8
STAGE NUMBER

Fig. 16

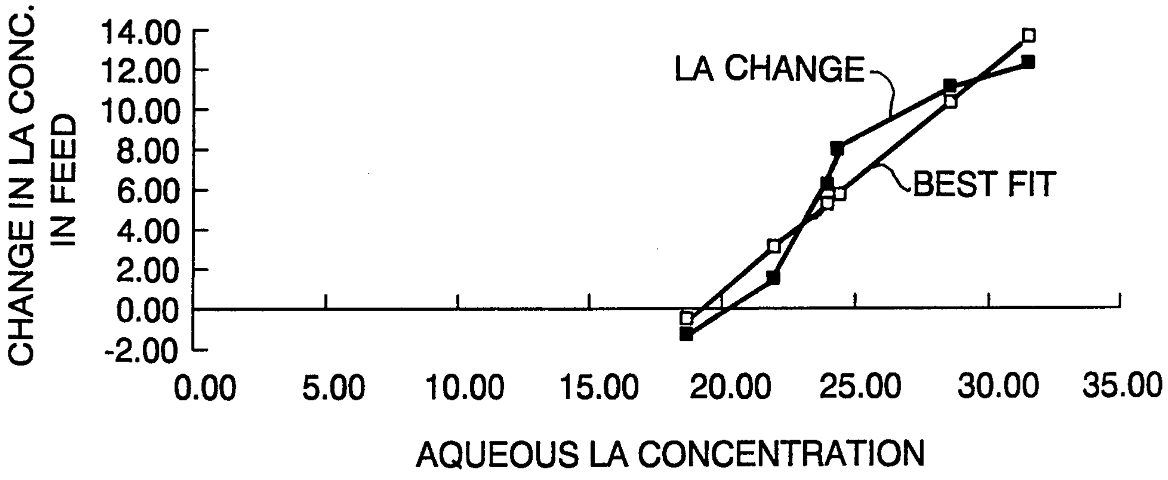

CHANGE IN LA CONC. IN FEED
14.00
12.00
10.00
8.00
6.00
4.00
2.00
0.00
-2.00
LA CHANGE
BEST FIT
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
AQUEOUS LA CONCENTRATION

Fig. 17

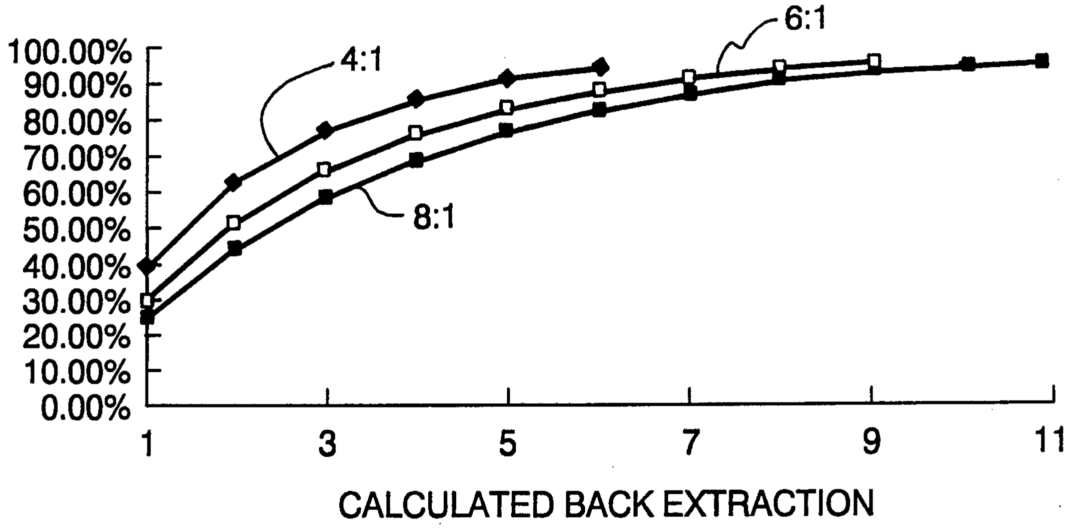

6:1
4:1
8:1
100.00%
90.00%
80.00%
70.00%
60.00%
50.00%
40.00%
30.00%
20.00%
10.00%
0.00%
1
3
5
7
9
11
CALCULATED BACK EXTRACTION

Fig. 18

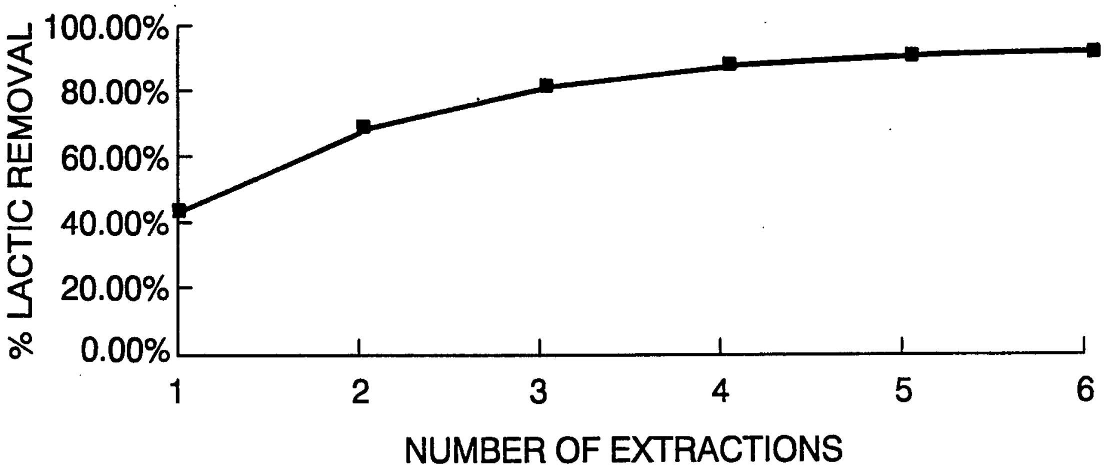

% LACTIC REMOVAL
100.00%
80.00%
60.00%
40.00%
20.00%
0.00%
1
2
3
4
5
6
NUMBER OF EXTRACTIONS

Fig. 19

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/08362

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C07C 51/42, 51/43, 51/44, 51/46, 59/08
US CL :562/578, 580, 589, 593
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 562/578, 580, 589, 593

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CAS ONLINE, APS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4,771,001 (BAILEY ET AL) 13 September 1988, claims 1 and 2.	1-34
X	US, A, 2,710,880 (FILACHIONE ET AL) 14 June 1955, column 1, lines 36-46; claim 1.	1-5

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:
"A"	document defining the general state of the art which is not considered to be of particular relevance
"E"	earlier document published on or after the international filing date
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O"	document referring to an oral disclosure, use, exhibition or other means
"P"	document published prior to the international filing date but later than the priority date claimed
"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&"	document member of the same patent family

Date of the actual completion of the international search 30 AUGUST 1994	Date of mailing of the international search report SEP 20 1994
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer BARBARA FRAZIER Telephone No. (703) 308-1235