(54) Title: RECOVERY OF FERMENTATION SALTS FROM DILUTE AQUEOUS SOLUTIONS
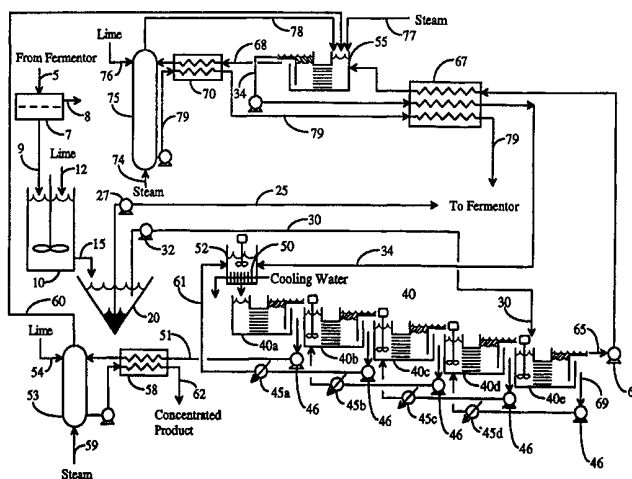
(57) Abstract

Dilute solutions of fermentation sales may be concentrated by extracting water using low–miscibility, low–molecular–weight secondary and tertiary amines, e.g. triethylamine (TEA), diisopropyl amine (DIA), N,N–diethylmethylamine (DEMA), and mixtures thereof. At 30 °C–55 °C, which coresponds to typical fermentation temperatures, these low–molecular–weight amines or their mixtures, can extract large amounts of water from dilute aqueous solutions containing fermentation salts. Thus, dilute fermentation salt solutions can be concentrated by selectively removing water. At these low temperatures, the amine phase contains 20–35 % water and a much reduced quantity of fermentation salt. When the temperature is raised, water phases out of the amine, allowing the amine to be recycled and reused to extract additional water. Using this approach, about 82,5 % of water can be removed from a 3 % dilute solution using conventional multistage, countercurrent extraction, thus providing a 15 % concentrated fermentation salt solution.

RECOVERY OF FERMENTATION SALTS FROM DILUTE
AQUEOUS SOLUTIONS

BACKGROUND OF THE INVENTION

5   **Field of the Invention**

This invention relates to a new and novel technology for isolating fermentation salts from aqueous solution. The method of this invention extracts water from the solution to concentrate fermentation salts, in particular, carboxylate salts such as calcium acetate.

10   **Review of Related Art**

Numerous manufacturing processes produce aqueous wastes or process streams containing carboxylic acid. These include the manufacture of cellulose acetate, aspirin, camphor, and RDX explosives, as well as semi-chemical wood pulping and other processes that use acetic acid as a raw material or solvent. In

15   addition, there are many manufacturing methods for acetic acid involving recovery of acetic acid from aqueous solution. For example, the principal methods to produce acetic acid are carboxylation of methanol, liquid-phase oxidation of hydrocarbons such as butane and oxidation of acetaldehyde. Earlier processes, such as alcohol fermentation and the destructive distillation of wood,

20   yielded dilute aqueous solutions. More recently, processes have been proposed to produce acetic acid, or other carboxylic acids, from biomass employing rumen microorganisms that produce dilute aqueous solutions. The concentration of acid in these processes must, of necessity, be dilute, because high acid concentrations inhibit microbial growth.

25   Several processes have been developed to recover acetic acid from aqueous solutions. These methods include liquid-liquid solvent extraction, azeotropic distillation, and extractive distillation. Simple distillation is not appropriate because (1) the relative volatility between water and acetic acid is close to unity and becomes worse for dilute aqueous acetic acid solutions, and

30   (2) water is the more volatile component, compared to acetic acid; this means all

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the water has to be vaporized from dilute acetic acid solutions, leading to a large

energy cost per unit of acetic acid recovered.

Extractive distillation was used for years in the *Suida* process to

recover acetic acid from pyroligneous acid which contains 6-7% acetic acid.

5   Recycled wood oils were used as the extractant. In acetic acid synthesis plants,

azeotropic distillation was used for higher concentration streams. Methyl and

ethyl acetates, diisopropyl ether, and benzene are commonly used entrainers for

azeotropic distillation, although other esters and ethers, ketones, chlorinated

hydrocarbons and alcohols have also been used.

10   In specific applications of acetic acid manufacturing, other processes

might be used. For example, freeze concentration has been used for years as a

backyard process for concentrating vinegar. Adsorption with carbon or anion

exchangers and chemical derivatization, followed by separation and regeneration

of the chemical derivatives, are also available. A conventional derivatization

15   method is the calcium acetate process for recovering acetic acid from

pyroligneous acid.

In the calcium acetate derivation process, calcium hydroxide reacts with

the acid to form calcium acetate, which is concentrated by evaporation. Then a

strong acid, such as sulfuric acid, is added to liberate the free acid. This

20   approach consumes chemicals such as lime and sulfuric acid and produces

gypsum as a waste aqueous salt by-product.

Recovery of carboxylic acids from water is one of the oldest

applications of solvent extraction. Solvent extraction of carboxylic acid was

proposed a century ago. With the development of more sophisticated extraction

25   techniques, such as countercurrent extraction, recovery of residual solvent from

the raffinate phase by distillation, and the use of azeotropic distillation to remove

coextracted water from the recovered acid, solvent extraction of carboxylic acids

from aqueous solutions has replaced the calcium acetate derivation process.

In general, extraction from aqueous solutions has heretofore been the

30   most favored approach to recover acetic acid, except for feeds (aqueous

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solutions) above about 80% (w/w) acetic acid content, where azeotropic

distillation is preferred. Based on the development of new extractants, extractive

processes, and the change in the economic structure, extraction is now favored

for feeds containing acetic acid below 30% (w/w); extractive distillation is

5   preferred for feeds in the 30-80% (w/w) range; and azeotropic distillation and

simple fractionation (distillation) are appropriate for more concentrated feeds.

In the literature, solvent extraction has been the main theme for

recovering carboxylic acid from dilute aqueous solutions. Because the solvents

tend to be partially water soluble, a unit operation is required to remove or

10   recover residual solvent from the raffinate. Typical extraction processes recover

carboxylic acid from water using three unit operations: the extractor, a solvent

regenerator, and a process to recover free carboxylic acid. In a conventional

extraction process, one first extracts acid into the organic phase, followed by

back-extracting acid into an aqueous phase, thus regenerating the organic phase.

15   In the regeneration process, the aqueous phase used to back extract acid from

the extract is usually an aqueous solution containing a low-boiling alkaline

solvent (e.g. trimethylamine) which can be easily evaporated. Using this

process, carboxylic acid can be separated and recovered.

Among the extractants used to recover carboxylic acid are reactive,

20   basic extractants (e.g. tertiary amines or phosphine oxides) that can be used to

gain greater solvent capacity and selectivity with respect to water and carboxylic

acid. Although solvent extraction is a potentially attractive process for

carboxylic acid recovery, it is usually deterred by the high affinity of these acids

for water. Previous workers have characterized some extractants that provide a

25   relatively high equilibrium distribution coefficient for extracting carboxylic acid

from aqueous solution. A high equilibrium distribution coefficient allows the use

of lower solvent-to-feed flow rates.

Primary amines are too soluble in water to be used with aqueous

solutions. Secondary amines are subject to amide formation upon regeneration

30   by distillation. Consequently, long-chain tertiary amines have become the most

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favored extractant for recovering carboxylic acid from dilute aqueous solutions. With the use of appropriate diluents and swings of temperature or pH, tertiary amine extractant systems have become more powerful agents for carboxylic acid recovery.

5   **Desalination**

Solvent extraction has also been proposed as a method to recover potable water from sea water or brackish water. Extracting sea water with an amine solvent produced a concentrated brine (raffinate) and an extract containing a mixture of water and amine. Clear water was recovered by heating the water-

10   laden extract to a higher temperature at which the solubility of solvent in water was greatly reduced. Previous discussions concerning the solvent extraction of water have been published by Davison et al. (see Davison, et al., "Structure and Amine-Water Solubility in Desalination by Solvent Extraction," *J. Chem. Eng. Data* 1960, 5, 420-423; Davison, et al., "Thermodynamic Cycles For Recovery

15   of Water by Solvent Extraction," *I&EC Process Design and Development,* 1964, 3, 399-404; Davison, et al., "Phase Equilibria of Desalination Solvents: Water-NaCl-Amines," *J. Chem. Eng. Data.* 1966, 2, 304-309; Davison, et al., "A Solvent Extraction Desalination Pilot Plant," *Desalination,* 1967, 3, 17-26; Davison and Hood, U. S. Patent 3,088,909; and Davison and Hood, U. S. Patent

20   3,424,675.)

Carboxylic acids from biomass

There has been increasing interest in using anaerobic bacteria to produce organic acids from biomass. A dilute aqueous stream of carboxylic acid can be produced by fermenting lignocellulosic biomass. The concentration in the

25   fermentation broths is limited by the autotoxicity of the acid to acetogenic fermentation bacteria. It may be as high as 6% (w/w), but concentrations of 2-4% are more typical. Product inhibition can be reduced by continuously removing the acid.

Extractive fermentation has been proposed to remove the inhibiting acid

30   *in situ* and thus increase the bioreactor productivity. However, at the pH where

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the microbes grow (about 6.8), only 1% is undissociated acid; the rest is salts

that will not be extracted, especially by tertiary amines. Most extractants work

efficiently only at acidic pH, yet acidogenic anaerobes generally have poor

growth rates below pH 6. Thus, extractive fermentation is not viable to remove

5   acid product *in situ.*

Moreover, after solvent-extracting carboxylic acid from the aqueous

fermentation broth using high-molecular-weight tertiary amines, the acid-amine

complexes must be broken to recover the free acid and recycle the amine

extractant, either by azeotropic distillation or back-titration. For recovering

10   carboxylic acid from dilute aqueous solutions, the extraction-regeneration

process requires both acid addition to adjust the pH and an extra solvent-

extraction process to regenerate the primary extractant. Furthermore, the

tertiary amines extractant (or phosphine oxide extractant) must necessarily have

a high molecular weight to make it immiscible in water. However, it is

15   impossible to make these extractant amines perfectly immiscible in water, so

some extractant is always present in the aqueous phase. Because of their high

molecular weight, these extractants are non-volatile and cannot be recovered by

stripping in a distillation column. Therefore, additional extractants must be

added to replace that which is lost, thus incurring additional expense.

20   Necessarily, when produced by fermentation, the acid product is

primarily present as a carboxylate salt. The pH of an aqueous solution of

carboxylic acids is ordinarily low because the acids dissociate releasing

hydronium ions in aqueous solution. To sustain active fermentation, it is

necessary to add a neutralizing agent (i.e., lime or limestone) that reacts with the

25   hydronium ion and maintains a pH near to neutrality where microbial activity is

greatest. Near neutrality, only about 1% of the product is carboxylic acid; the

remainder is present as the carboxylate salt. Therefore the traditional

technologies for recovering carboxylic acids are not easily applied, and a need

exists for developing of alternative technologies.

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SUMMARY OF THE INVENTION

Recovery of carboxylic acid from fermentation broths with conventional solvent extraction is not economical, especially when ideal extractants (i.e. those that can extract carboxylate salt into the organic phase) are not available

5   currently. Therefore, the inventors have developed a new process to concentrate fermentation broths by removing water from dilute aqueous solutions of the carboxylate salt (typically the calcium salt) rather than the conventional approach of removing acid from water. This novel extraction removes water from the aqueous phase, but selectively retains salts in the aqueous phase. As water is

10   extracted into the organic phase, salts concentrate in the aqueous phase. The water can be recovered from the organic phase by raising the temperature which causes the water to phase out of the organic phase. This recovered water can be returned to the fermentor after stripping residual organic material. In the process of the invention, residual organics are also stripped out of the concentrated

15   product.

This invention relates to a new and novel technology for isolating carboxylate salts and/or acids from an aqueous solution. Because it is difficult to extract acid from near-neutral pH fermentation broth, this invention provides method of extracting the water instead, thereby concentrating the organic acid

20   and salt solutions.

This invention further relates to the manufacture of carboxylic acid in which the improvement is to concentrate dilute aqueous carboxylate salt solutions (2-5%) produced via fermentation. In particular, this invention pertains to the manufacture of carboxylic acid wherein the salt of carboxylic acid,

25   manufactured by fermentation (i.e., by rumen microorganisms, by mixed-acid fermentation, or by pure-culture fermentation) is recovered from the aqueous solution and the extractant is conveniently and economically recycled to the extraction process. The carboxylate salts need not be monocarboxylates and may contain other functional groups, as for example, hydroxyl groups. The

30   carboxylate salts need not be derivatives of saturated hydrocarbons, but may

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contain unsaturation. Typical carboxylate salts that can be manufactured by fermentation and recovered by the method of this invention include acetates, propionates, lactates, succinates, and the like.

5   **BRIEF DESCRIPTION OF THE FIGURES**

Figure 1 shows a schematic representation of a process (Process A) for concentrating fermentation salts.

Figure 2 shows a schematic representation of a mixer/decanter that employs periodic cleaning.

10   Figure 3 shows a schematic representation of a method for achieving uniform gentle mixing of amine and water.

Figure 4 shows two possible configurations for parallel plates used to settle amine and water.

Figure 5 shows a schematic representation of a mixer/decanter that 15   employs continuous cleaning.

Figure 6 shows a simplified schematic of Process A which indicates the equipment that affects process energetics.

Figure 7 shows a simplified schematic of Process B which indicates the equipment that affects process energetics.

20   Figure 8 shows a simplified schematic of Process C which indicates the equipment that affects process energetics.

Figure 9 shows a simplified schematic of a modifiedc version of Process C.

Figure 10 shows a simplified schematic of a modified version of Process 25   B.

DETAILED DESCRIPTION OF THE INVENTION

This invention, in a preferred embodiment, is a process in which fermentation broth, which contains dilute carboxylate salt, is contacted with a low-molecular-weight secondary or tertiary amine which has a high affinity for 30   water and a low affinity for carboxylate salt. From previous work on

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desalination (Davison et al., Phase Equilibria of Desalination Solvents: Water-
NaCl-Amines. *J. Chem. Eng. Data.* 1966, 2, 304-309), two low-molecular-
weight tertiary amines, i.e. triethylamine (TEA) and *N,N*-diethylmethylamine
(DEMA), were chosen because of their superior capacity to selectively extract

5   water from aqueous salt solutions in the proper temperature ranges. The
temperature of the water-laden amine is increased by about 20-30°C which
causes the water to separate from the amine and form another phase. The
carboxylate salt remains in the fermentation broth and becomes concentrated.
Residual amines in aqueous phases are recovered by adding alkali (e.g., lime) to

10   raise the pH, thus making the amines volatile. The residual amines are then
recovered by stripping them out in a distillation column.

       In the past, extraction of water from a salt solution has been applied to
the recovery of drinking water from salt water, i.e., sea water, brackish water, or
the like. The present invention may be distinguished from this previous

15   application as follows:

       1. In the fermentation, one can select the cation which accompanies the
carboxylate. Divalent ions (i.e., calcium) are excluded from the amine extractant
more fully than monovalent ions (i.e., sodium, ammonium). Thus, by choosing a
divalent cation, the water can be more selectively removed from the salt solution.

20   In contrast, the cations in sea water or brackish water are dictated by nature and
typically are monovalent cations. As a result, the water and salt are not
separated efficiently.

       2. In the present invention, the salt is the desired product, whereas in the
previous process, the water was the desired product. The carboxylate salt is

25   much more desirable and valuable than the water, giving the present process
favorable economics. In contrast, amine extraction of water is not economically
attractive.

       3. In the drinking water process, the water product must be virtually free
of salt to be acceptable for human consumption. This requires the use of a large

30   rectification section in addition to the stripping section. These added

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rectification stages incur additional expense. In contrast, the present invention
can tolerate higher concentrations of salt in the water stream because the water
is simply recycled to the fermentor. Therefore the rectification section can have
many fewer stages or be eliminated altogether.

5   4. Complete amine recovery from all aqueous streams is critical for good
economics; otherwise, the expense of replacing the lost amine is too great. The
amine is recovered by stripping it from the aqueous stream in a distillation
column. To ensure that the amine is present as volatile free amine as opposed to
non-volatile amine salts, it is necessary to raise the pH by adding alkali. In our

10   invention, this is easily accomplished by adding lime to the aqueous streams.
There is little expense associated with this because a neutralizing agent must be
added to the fermentor anyway. Thus, there are synergies and efficiencies
associated with coupling the amine with the fermentor. In contrast, addition of
alkali to the drinking water process incurs significant expense not only for the

15   alkali, but also for its recovery; it is not acceptable for the alkali to remain in the
drinking water product. Complete amine removal from drinking water is
essential due to its potential health effects.

       Carboxylate salts which can be manufactured by fermentation and
concentrated by the method of this invention include salts of acetic acid,

20   propionic acid, lactic acid, succinic acid, and the like. This method is also
applicable to dilute aqueous solutions of carboxylate salts produced by methods
other than fermentation.

       According to the present invention, the organic phase comprises an
organic secondary or tertiary amine. Preferred amines include low-molecular-

25   weight alkyl secondary or tertiary amines or mixtures thereof. Preferred amines
are amines of the formula R_3N, wherein R is methyl, ethyl, n-propyl, or
isopropyl. Most preferred amines are triethyl amine, N, N-diethylmethyl amine,
and mixtures of these two amines. The use of various ratios of the two amines
provides an extraction system that possesses different lower critical

30   temperatures. By selecting the appropriate amine compositions, it is possible to

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operate the extraction process at any proposed temperature from 10°C to 70°C. Within this temperature range are both mesophilic and thermophilic acid-forming bacteria which gives flexibility in developing an appropriate fermentation system.

The most favored carboxylic-acid-producing microorganisms that use
5   lignocellulosic biomass are: (i) *mesophilic* (40°C) mixed cultures obtained from either cattle rumen or anaerobic sewage digesters, and (ii) thermophilic (55°C) mixed cultures from anaerobic sewage digesters. Another promising thermophile is the cellulytic organism *Clostridium thermocellum* which produces both acetic acid and ethanol generally in roughly equal amounts. Suitable fermentation
10   processes are described in greater detail in U.S. application Ser. No. 08/885,896, filed June 30, 1997, entitled "Method for Conversion of Biomass to Chemicals and Fuels," filed concurrently herewith and incorporated herein by reference.

To avoid unnecessary heating or cooling of fermentation broths, the extraction is operated at or near the fermentation temperature, as for example at
15   or near 40°C or 55°C depending on the microorganisms.

When the aqueous phase contacts the low-molecular-weight amine, the pH rises forming calcium hydroxide. Because calcium hydroxide is fairly insoluble, some precipitates thus removing calcium ions from solution. These ions are replaced with amine ions to form amine-carboxylate complexes in the
20   aqueous phase. The formation of water-soluble amine carboxylate is handled by adding calcium hydroxide to the strippers so calcium can replace the amine as the amine volatilizes.

Typically, lignocellulosic biomass is fermented to yield a dilute solution of carboxylate salts from which water may be extracted using low miscibility,
25   organic extractants. Preferably these organic extractants are low-molecular-weight secondary or tertiary amines, e.g. triethylamine (TEA), di-isopropyl amine (DIA), and N,N-diethylmethylamine (DEMA). At 40°C-55°C, which corresponds to typical fermentation temperatures, these low-molecular-weight tertiary amines or mixtures thereof can extract large amounts of water from
30   dilute aqueous solutions containing carboxylate salts. Thus, dilute carboxylate

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solutions can be concentrated by selectively removing water. At lower

temperatures, the amine phase contains 20-35% water and negligible carboxylate

salt. When the temperature is raised, water phases out of the amine, allowing the

amine to be recycled and reused to extract additional water. In a typical

5   example, using this approach, about 82.5% of water can be removed from a 3%

dilute solution using conventional multi-stage, countercurrent extraction, thus

providing a 15% concentrated carboxylate salt solution.

A typical embodiment of this invention may be described by reference to

Figure 1. Fermentation broth **5** is filtered in solids separator **7** (e.g. filter,

10   hydroclone, centrifuge, settler) to remove insoluble residues **8** (e.g. cells,

unreacted biomass). The solid-free solution **9** is sent to mixer **10** where lime **12**

is added to increase the pH to approximately 11.5. The high pH precipitates

minerals and organics (e.g. proteins, carbohydrate polymers, etc.). The slurry **15**

is sent to solids separator **20** (e.g. filter, hydroclone, centrifuge, settler) where

15   the precipitate **25** is removed by pump **27.** Figure 1 shows the precipitate being

returned to the fermentor. Alternatively, it could be processed further to

separate the minerals, protein, and carbohydrate polymers depending upon the

value of these components.

Using pump **32,** precipitate-free liquid **30** is sent to a series of

20   mixer/decanters **40** where it will be contacted countercurrently with water-lean

amine **34.** (Although Figure 1 shows a series of mixer/decanters are used to

countercurrently contact the amine and water phases, other contacting devices

may be used, such as packed columns, rotating-disc columns, oscillating-plate

columns, etc. The choice of the appropriate contactor depends upon scale;

25   mixer/decanters are preferred for large flow rates. Although Figure 1 shows five

mixer/decanters, fewer or more may be used.) Precipitate-free liquid **30** is sent

to mixer/decanter **40e** where it is mixed with amine from mixer/decanter **40d.**

The amine absorbs some water from the water phase thus increasing its salt

concentration.

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As shown in Figure 2, the amine/water mixture flows through a series of parallel plates **140** in the mixer/decanter and enters a gathering section **145** where the amine phase and water phase separate. The amine phase, having a lower density, is recovered from the top, and the water phase is recovered from

5   the bottom. Weirs **150** are set to regulate the height of the amine/water interface. Amine flows over the top and water is recovered from the underflow.

In the embodiment shown in Figure 1, water-rich amine phase **65** is sent to separator **55** to recover the absorbed water. Water phase **69** is sent to mixer/decanter **40d** where it is mixed with amine phase from mixer/decanter **40c**

10   which absorbs additional water further concentrating the water phase. This process is repeated in the other mixer/decanters. As the water phase moves from right to left, its salt concentration increases. As the amine phase moves from left to right, its water content increases.

In each of the mixer/decanters, water and amine are mixed. Because

15   there is a particularly large heat of mixing released when water-lean amine **34** is mixed with water **61,** mixing for mixer/decanter **40a** is performed in a separate vessel **52** which is provided with cooler **50.** Other mixer/decanters (**40b** through **40e**) also have a heat of mixing, but it is much less and is removed by heat exchangers **45** which regulate the temperature. Water pumps **46** cause the water

20   to flow through the heat exchangers and on to the adjacent mixer/decanter **40.** Pumps are required only for the water flow; by arranging the mixer/decanters **40** at successively declining elevations, the amine will flow by gravity eliminating the need for amine pumps.

Water stream **51,** which has the highest salt content, has dissolved amine

25   which must be removed. It is preheated in countercurrent heat exchanger **58** and is sent to stripper **53** where steam **59** vaporizes the amine. To ensure that amine is present as the volatile unionized species, rather than a nonvolatile ionized species, lime **54** is added to raise the pH. The volatile amine exits in stream **60** which also contains steam. Stream **60** is directed to separator **55** where it

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provides some of the latent heat needed to separate water and amine. Amine-free concentrated product **62** is ready for further downstream processing.

Pump **66** transports water-rich amine **65** to countercurrent heat exchanger **67** where the temperature is raised. In heat exchanger **67**, as the

5   temperature is raised, the water begins to phase out of the amine. This process is completed in separator **55** where additional heat, in the form of steam **77**, is supplied to raise the temperature and supply the latent heat necessary to separate the water from the amine. Separator **55** has a design similar to the mixer/decanters **40**, except that a mechanical mixer is not required.

10   Water phase **68** issuing from separator **55** contains dissolved amine. It is preheated in countercurrent heat exchanger **70** and sent to stripper **75** where steam **74** vaporizes the amine. To ensure that amine is present as the volatile unionized species, rather than a nonvolatile ionized species, lime **76** is added to raise the pH. The volatile amine exits in stream **78** which also contains steam.

15   Stream **78** is directed to separator **55** where it provides some of the latent heat needed to separate water and amine. Amine-free water **79**, which has a very low salt content, is cooled in countercurrent heat exchanger **70** and countercurrent heat exchanger **67** and is returned to the fermentor. If excess water must be purged from the system, a side stream of water can be removed from stream **79**

20   and sent to the waste water treatment plant for ultimate discharge. Water-lean amine **34** issuing from separator **55** is pumped through countercurrent heat exchanger **67** and mixes with water in mixer **52**.

Mixing and decanting are normally performed in separate pieces of equipment. Mixing is typically performed in a stirred tank, pump, or an in-line

25   static mixer. Decanting can be performed in a quiet tank or in a parallel plate separator. Parallel plate separators were first described by Hazen in 1904.

In a preferred embodiment, this invention provides a device that mixes raffinate and extract phases together and then decants them to achieve separation. It has been discovered that decanting occurs quickly in a horizontal

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tube. In order to capitalize on this observation, this invention provides the device shown in Figure 2. Among the unique features of this embodiment are that it combines both a mixer and decanter into a single device. Figure 2 shows a detailed sideview of the mixer decanter **40**. It is divided into four major

5   sections: mixing section **130**, settling section **135**, gathering section **145**, and weir section **150**.

In the mixing section **130**, water **110** and amine **120** are evenly mixed together using impellor **115**. Because equilibrium is quickly and easily reached, mixing can be very gentle; therefore, emulsions are not formed and the amine

10   phase quickly decants from the water phase. Even though the amine flowrate is about five or six times greater than the water flowrate, water is the continuous phase and amine is the discontinuous phase. This type of operation allows the amine residence time to be very short which reduces the amine inventory and lowers costs. Figure 2 shows an impellor providing the mixing. Figure 3 shows

15   an alternative embodiment using a series of "fingers" **230** mounted on a shaft **220** which is held in place using bearings **240**. The shafts are driven by motor **200** which rotates gears **210**. Adjacent shafts rotate in opposite directions. The fingers on adjacent shafts are interspersed allowing uniform mixing to occur in mixing section **130**. The degree of mixing is determined by the rotational speed

20   and the number of fingers per shaft. To promote even mixing, water and amine may be introduced at multiple points in the mixing section **130**.

As shown in Figure 2, the settling section **135** consists of a series of parallel plates **140**. The parallel plates have a short settling distance allowing the dispersed phases from the mixing section **130** to quickly coalesce. The short

25   amine residence time in settling section **135** reduces the amine inventory which saves capital costs. Figure 4 shows two possible embodiments of parallel plates. Both Figures 4a and 4b use rippled plates, much like those used as siding on buildings. The two versions differ only in the orientation of the parallel plates **140**. In Figure 4a, every other plate is in the same orientation and in Figure 4b,

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every plate is in the same orientation. The plate orientation shown in Figure 4b
is preferred because it allows for very close plate spacing even if there are deep
ripples. Close plate spacing ensures the flow is laminar, rather than turbulent,
which promotes coalescence. As the amine/water phases flow between the

5   parallel plates, each phase coalesces; the amine phase (being less dense) floats to
the highest point and the water phase (being more dense) sinks to the lowest
point.

       Figure 2 shows that gathering section 145 is simply a quiescent tank.
The gathering section 145 is operated with water as the continuous phase and

10   amine as the dispersed phase. As coalesced amine exits from settling section
135, it quickly floats to the top. To reduce interference with adjacent amine as it
flows to the top, parallel plates 140 are successively longer lower in the settling
section 135. Solids, such as precipitated calcium hydroxide, settle in the
gathering section and are removed by pump 190 and sent to solids separator 191

15   (e.g. filter, hydroclone, centrifuge). The solids are returned to strippers 75 or 53
to provide the lime necessary to volatilize amine.

       Figure 2 shows that weir section 150 consists of overflow weir 132 and
underflow weir 131. Overflow weir 132 sets the height of the upper surface of
the amine and underflow weir 131 sets the height of the amine/water interface.

20   Amine phase flows over overflow weir 132 and water phase flows over
underflow weir 131. To reduce the amine residence time (and hence reduce the
amine inventory), the underflow weir 131 is adjusted to minimize the thickness
of the top amine layer.

       A "rag layer" may collect at the amine/water interface, so pump 180 is

25   included to draw fluid from the amine/water interface and direct it to solids
separator 181 (e.g. filter, hydroclone, centrifuge). Amine 182 is returned to
gathering section 145. Using steam 188, separated solids 183 would be stripped
of amine in chamber 189. Exiting vapors 187 are sent to separator 55 to provide
energy needed to phase separate water from amine. Depending upon the nature

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of separated steam-stripped solids **184**, they may be returned to the fermentor, or they may be disposed of in an appropriate manner.

Because the flow through parallel plates **140** is low, solids (such as precipitated calcium hydroxide) eventually may plug settling section **135**. To

5   clean parallel plates **140**, amine flow **120** would be discontinued. Valve **126** would be opened allowing water from elevated holding tank **125** to quickly flow by gravity through parallel plates **140** causing turbulent flow that entrains any solids that settled in the parallel plates. Entrained solids **194** are collected in gathering section **145** or surge tank **195**. After the cleaning operation is

10 performed, amine flow **120** resumes and mixer/decanter **40** continues as before. During normal operation of mixer/decanter **40**, pump **185** slowly returns water to elevated tank **125** in preparation for the next cleaning cycle.

In Figure 2, tanks **125** and **195**, used to clean the parallel plates **140**, must be large in order to develop the tubulent flow required to entrain solids.

15 Figure 5 shows an alternate embodiment in which parallel plates **140-5** are continuously cleaned where, advantageously, the cleaning equipment is considerably smaller. Louvers **320-5** may be opened or closed. When closed, a section of parallel plates **140-5** is isolated allowing it to be cleaned while the remainder of the parallel plates may perform their usual function. As shown in

20 Figure 5, louvers **320-5a** and **320-5c** are open allowing the upper and lower sections of parallel plates **140-5** to perform their usual function; however, louver **320-5b** is closed, allowing the middle section of parallel plates **140-5** to be cleaned. As shown from View Z, valve **310-5b** is opened whereas other valves **310-5a** and **310-5c** are closed. This valve arrangement allows high velocity

25 water, obtained from pump **185-5**, to entrain solids in the middle section of parallel plates **140-5** and discharge the solids to gathering section **145-5** where they settle and are collected by pump **190-5**.

Compared to other technologies, the mixer/decanter described in Figures 2 to 5 provides numerous advantages. Compared to separate mixers and

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decanters, less piping is required. The degree of mixing is regulated by the agitation rate, and unlike the use of a pump as a mixer, very gentle mixing can be achieved. Furthermore, the degree of mixing is independent of the addition rate of amine and water giving greater control than an in-line static mixer. By

5   incorporating flow between parallel plates **140**, the phases separate much more quickly than in a quiet tank. To facilitate complete separation of water/amine, the water residence time can be lengthened by increasing the volume of gathering section **145**. In contrast, the amine residence time can be short by adjusting the height of weir **131** so that the amine layer is very thin.

10   Heat transfer is an important factor in optimizing this process. One preferred method for heating and cooling the amine-containing streams employs countercurrent heat exchangers **67**. Plate-and-frame heat exchangers are generally preferred for low capital cost relative to heat transfer (heat transfer coefficients of 625 Btu/(ft^2•h• °F) can be achieved). Additional energy savings

15   may be achieved by using very close approach temperatures in the hot and cold streams. For example, adding surface area to go from log-mean deltaT (LMDT) of 6.5°C to 4.1°C generates energy savings which more than pay for the increase in capital expense.

            Using countercurrent heat exchanger **67** in the amine-dewatering

20   process, only sensible heat is required on the water-lean side, but the water-rich side has both sensible and latent heat requirements. As the water-rich side warms, the water phases out of the amine, and the latent heat requirement effectively raises the heat capacity. As a consequence, the temperature difference could be, e.g., only 1°C on one end of the heat exchanger, but 10.9°C

25   at the other end.

            The process described in Figure 1 may be considered a "base case" which has the lowest capital cost, but also the lowest energy efficiency. Other process alternatives that have a higher energy efficiency are described in Table 1.

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Table 1.   Energy Costs

Process	Description	*Steam Cost ($/lb HAc)
A	Base Case	0.010
B	Single-stage vapor-compression heat pump	0.0047
C	Multiple-stage steam ejector heat pump	0.0037
* steam cost = $3/million Btu acetic acid concentration = 22 g HAc/L total acid concentration = 30 to 35 g/L		

Process A is a "base-case" that has minimal capital cost, but is not energy efficient (see Figure 1). Process B is more efficient because it employs a vapor-compression heat pump to transfer the heat of mixing (released at the absorption temperature, e.g. 40°C) to the separator (which operates at a higher temperature, e.g. 60°C). Unfortunately, because the density of the vapor is so low, very large compressors are required, incurring capital expense which may be prohibitive. Process C reduces the capital cost of heat pumps by employing low-cost steam ejectors rather than mechanical compressors. The steam is supplied from the strippers. Because steam ejectors are inefficient at high compression ratios, multiple-stage ejectors are employed allowing many of the stages to have a very low compression ratio. The multiple stages employed in Process C allow it to have the lowest energy cost. Because ejectors are very inexpensive, the capital cost of Process C is only slightly above Process A.

Figure 6 is a simplified version of Process A which shows the equipment that affects the process energetics. For simplicity, only two extraction stages are shown. Separator 55-6 is the major consumer of energy. It requires two forms of energy: (1) latent heat needed to phase water out of the amine, and (2) sensible heat needed to raise the temperature of the water-rich amine from the extraction temperature (e.g. 40°C) to the separation temperature (e.g. 60°C). By making countercurrent heat exchanger 67-6 sufficiently large, the sensible

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heat demands by separator **55-6** are minimized. The latent heat demands are mostly met by the overhead vapors from strippers **53-6** and **75-6**. Some additional energy can be provided by steam **77-6** which may result from other unit operations in the plant, such as multiple-effect evaporators or distillation

5   column condensers. Provided countercurrent heat exchanger **67-6** is sufficiently large, water-lean amine **34-6** will be cooled to approximately the extraction temperature (e.g. 40°C). Cooler **50-6** is required to remove the heat of mixing resulting from mixing water-lean amine **34-6** and water **61-6**. Ideally, given an infinitely large countercurrent heat exchanger **67-6**, the heat added to separator

10   **55-6** is removed using cooler **50-6**. In actuality, given a countercurrent heat exchanger **67-6** of finite size, some additional heat must be added to separator **50-6** to provide sensible heat. Similarly, some additional cooling must be provided by cooler **50-6** to remove sensible heat.

Figure 7 shows Process B, again emphasizing only that equipment which

15   affects process energetics. In this case, rather than rejecting the heat of mixing to cooler **50-6**, a vacuum is pulled on mixer **52-7** by compressor **300-7** which causes some amine and water to evaporate cooling the liquid to the extraction temperature (e.g. 40°C). The compressed vapors **315-7** are sent to separator **55-7** which operates at its vapor pressure. Compressed vapors **315-7** condense

20   in separator **55-7** and provide the heat required to phase the water out of the amine. Compressor **300-7** is driven by steam turbine **310-7** which is fed with high-pressure steam **320-7** and rejects low-pressure steam **325-7**. The low-pressure steam is sent to amine strippers **75-7**.

Because Process B is more energy efficient than Process A, a single

25   stripper would generate more vapors than are need by separator **55-7**. Therefore, the stripping operation is performed in multiple effects. Stripper **75-7a** is operated at a higher temperature and pressure than stripper **75-7b** which, in turn, is operated at a higher temperature and pressure than stripper **75-7c**. Figure 7 shows three strippers, but fewer or more could be used depending upon

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the cost of capital and the cost of energy. Also, stripper **53-7** could be operated in multiple effects, but it is much smaller and has less impact on process energetics. Low-pressure steam **325-7** from turbine **310-7** is sent to stripper **75-7a** which operates at the highest temperature and pressure. Overhead vapors

5   **330-7a** from stripper **75-7a** are sent to the reboiler of stripper **75-7b**. Similarly, the overhead vapors **330-7b** from stripper **75-7 b** are sent to the reboiler of stripper **75-7c.** The overhead vapors **330-7c** are sent directly to the separator **55-7** as is the overhead condensate **340-7**. The amine-stripped water **79-7** is cooled countercurrently and is returned to the fermentor.

10   Because the vapor density of amine/water is very low at an extraction temperature of 40°C, the compressor **300-7** must be very large leading to very high capital costs. This problem could be overcome by the following approaches:

          1)   A secondary refrigerant (e.g. ammonia, Freon) could be

15   compressed rather than the amine/water vapors. This approach requires heat exchangers both in the separator **55-7** and mixing vessel **52-7** which adds cost and irreversibilities that negatively impact energy efficiency.

          2)   Precipitate-free fermentation broth **30-7** could be heated to a higher temperature so the extraction occurs at a higher temperature and the

20   amine/water in mixing vessel **52-7** has a higher vapor density. This approach requires an extra countercurrent heat exchanger to prewarm fermentation broth going to the extractor and precool liquid returning to the fermentor. Also, because there is an approach temperature needed in the countercurrent heat exchanger, extra heat will be needed to fully increase the temperature of the

25   fermentation broth going to the extractor, and extra cooling will be needed to cool the water returning to the fermentors.

          3)   The fermentation could be operated at thermophilic conditions (e.g. 55°C) so the extractors operate at a higher temperature resulting in a higher vapor density in mixer **52-7**.

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4)   A highly volatile component (e.g. butane, fluorocarbon) could be added to the water-lean amine 34-7. This volatile component would raise the vapor density in mixer 52-7 allowing a more compact compressor to be employed. The highly volatile component would evaporate in mixer 52-7 and would condense in separator 55-7, so it would mostly circulate. Although some of this volatile component will be in stream 350-7 and will enter the extractors, any volatile component in the amine phase will be recycled, and any volatile component in the water phase will be removed by the strippers; therefore, very little of this volatile component will be lost.

Figure 8 shows Process C which uses multiple-stage steam ejectors as heat pumps. High-pressure steam 74-8 (e.g. 180 psig) is put into stripper 75-8a which is the first in a series of multiple-stage strippers. The vapors 330-8c exiting stripper 75-8c are at a high enough pressure (e.g. 100 psig) to provide motive force to the steam ejectors 400-8 which pull a vacuum on mixer 52-8. The vacuum evaporates amine and water from mixer 52-8 which are then compressed and condensed in contactors 410-8 causing water-rich amine 65-8 to increase in temperature. As the temperature rises, water begins to phase out of the water-rich amine, a process that is completed in separator 55-8. Because steam ejectors are inefficient at high compression ratios, the steam ejectors are staged. Steam ejector 400-8a has the lowest compression ratio because the pressure in contactor 410-8a is low. Steam ejector 400-8c has the highest compression ratio because the pressure in separator 55-8 is relatively high. Although Figure 8 shows three heat pump stages, fewer or more may be used.

Figure 9 shows a variation on Process C in which the ejectors 400-9 pull a vacuum on mixers 52-9 in multiple stages. Aqueous solution 61-9 is added to water-lean amine 34-9 in mixer 52-9c. Due to the heat of mixing, the temperature rises in mixer 52-9c, raising its vapor pressure. Using ejector 400-9c, vapors are removed from mixer 52-9c and compressed into separator 55-9. The liquid exiting mixer 52-9c is reduced in pressure and added to mixer 52-9b

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where vapors are removed using ejector **400-9b** and added to contactor **410-9b**. A similar process occurs in mixer **52-9a**. The advantage of this multi-stage flashing process is that the compression ratio of each ejector **400-9** is reduced, resulting in steam savings.

5   The energy benefits of a multiple-stage heat pump can also be realized by using multiple-stage mechanical compressors instead of the steam ejectors (see Figure 10). To raise the vapor density, a volatile component (e.g. butane, fluorocarbon, etc.) can be added directly to the water-lean amine. The volatile component would circulate between multiple-stage mixers **52-10** and the

10   separator **55-10** such that very little of the volatile component would be present in the extractors **40-10**. In the case of a hydrocarbon volatile component (e.g. butane), it will distribute primarily in the amine phase, helping to push water out in the separator **55-10**. In the case of some fluorocarbons, they are substantially immiscible in both water and amine. They have a density higher than water, so

15   they would be drawn off the bottom of the gathering section of separator **55-10** and added directly to mixer **52-10c**.

         An important consequence of Process C is that it allows recovery of dilute acids without paying a large capital or energy penalty. The liquid residence time in the fermentor is largely determined by the product

20   concentration; lower product concentrations have a short residence time because product inhibition is less. The fermentor volume decreases with shorter liquid residence time; thus, for lower product concentrations, the fermentor can be smaller.

         The energy estimates shown in Table 1 were calculated using a

25   simplifying assumption that the amount of water that phases out of the amine increases linearly with temperature. In actuality, for a single degree increase in temperature, more water phases out at low temperatures than at high temperatures. As a consequence, more of the heat pump energy will be needed at low temperatures where the compression ratio is smaller and less steam is

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needed; therefore, the simplifying linear assumption will give a worst-case

analysis. The real situation will require less energy than these projections.

The unique separation technique described in this invention provides a

commercially viable method for separating and concentrating carboxylate salts

5   formed during fermentation with recycle of all streams and minimal waste.

Concentrated solutions of carboxylate salts obtained by the method of

this invention may be further concentrated by evaporation, dried or converted to

concentrated carboxylic acid solutions as will be readily apparent to those skilled

in the art. Suitable processes for further converting of the concentrated

10   carboxylic acid salt solution of this invention into the desired product are

described in U.S. Serial No. 08/885,896, filed June 30, 1997, entitled "Method

for Conversion of Biomass to Chemicals and Fuels", filed concurrently herewith

and incorporated herein by reference in its entirety.

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We claim:

1.   A process for the manufacture of carboxylic acid wherein

(1) lignocellulosic biomass is fermented to a carboxylate salt in the presence of an aqueous solution of calcium cations,

(2) water is extracted from the carboxylate salts by contacting the aqueous solution with an organic extractant of the class consisting of low-molecular weight secondary or tertiary amine, to form a water/extractant mixture and a more concentrated solution of the carboxylate salt, and

(3) carboxylic acid is freed from the salt and purified.

2.   The process of claim 1, where the low-molecular-weight secondary or tertiary amine is an amine of the formula R_3N, wherein R is hydrogen, methyl, ethyl, n-propyl, or isopropyl, or a mixture of such amines.

3.   The process of claim 1, wherein the amine is triethylamine, N,N-diethylmethylamine, or a mixture thereof.

4.   The process of claim 1, wherein the water is extracted at about the temperature of the fermentation.

5.   The process of claim 1, wherein the organic extractant is recycled by heating the water/extractant mixture at a temperature sufficient to separate water therefrom, separating the water from the extractant, and recycling the extractant.

6.   The process of claim 5, wherein the extractant is recycled to the extraction.

7.   The process of claim 5, wherein the heating is performed in a heat exchanger.

8.   The process of claim 7, wherein the heating is performed in the heat exchanger by the presence of heated extractant therewithin.

9.   The process of claim 1, wherein lime is added to the more concentrated solution of salt and the solution is stripped of dissolved extractant.

10. The process of claim 5, wherein the water separated from the extractant is further stripped to remove extractant.

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11. The process of claim 10, wherein the water is treated with lime during the stripping process.

12. The process of claim 10, wherein the water is recycled to the fermentation process.

5

13. A process for the manufacture of a carboxylic acid wherein

(a) lignocellulosic biomass is fermented to carboxylate salts in the presence of an aqueous solution of calcium cations,

(b) water is extracted from the carboxylate salts by contacting the aqueous carboxylate salts solution with an organic extractant of the class

10   consisting of triethylamine, N,N-diethylmethylamine, and mixtures thereof, at about the temperature of the fermentation,

(c) the organic extractant is recycled by heating the water/extractant mixture in a heat exchanger to a temperature sufficient to separate water therefrom, separating the water from the extractant in a separator, and recycling

15   the extractant to the extraction,

(d) the aqueous carboxylate salts solution from step (b) is treated with lime and stripped to remove dissolved extractant from the carboxylate salts solution,

(e) the water from step (c) is treated with lime and stripped to remove

20   extractant which is recycled to the separator and the water is recycled to the fermentation,

(f) the carboxylate salts solution is acidified and carboxylic acid is purified therefrom.

14. An extraction tank comprising

25   a mixing section adapted for mixing a first fluid input stream and a second fluid input stream;

a separating section comprising a plurality of plates parallel to each other and in substantially horizontal orientation; and

a gathering section adapted for collecting an upper fluid layer and a lower

30   aqueous fluid layer, having two weirs, a first weir being in fluid communication

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with the upper fluid layer and a second weir in fluid communication with the

lower layer, the two weirs being in fluid communication with a first collection

structure and a second collection structure, respectively;

wherein one end of the parallel plates of the separating section is in fluid

5   communication with the mixing section and an other end of the parallel plates is

in fluid communication with the gathering section.

15. The extraction tank of claim 14, wherein the parallel plates are

rippled sheets.

16. The extraction tank of claim 14, wherein the end of the plurality of

10   plates in fluid communication with the gathering section slopes such that a lower

plate extends further into the gathering section than the immediately higher plate.

17. The extraction tank of claim 14, wherein the gathering section

further includes a well to collect settled solids and facilitate their removal.

15   18. The extraction tank of claim 14, where a pump removes material

from the interface of the two fluids in the gathering section, whereby

accumulated solids are removed.

19. The extraction tank of claim 14, wherein the mixing section contains

a plurality of rotating shafts having projections, projections of respective shafts

20   being interspersed such that even, gentle mixing is obtained.

20. The extraction tank of claim 14, further comprising means for

introducing a large flowrate of aqueous layer to the plurality of parallel plates

whereby settled solids are flushed therefrom, and means for collecting the

aqueous layer, wherein the solids settle for removal.

25   21. The extraction tank of claim 14, in which sections of the plurality of

parallel plates can cleaned of settled solids by isolating said sections and

introducing a large flowrate of aqueous layer, collecting the aqueous flow in the

gathering section, and recovering settled solids from the gathering section.

22. A method of extracting a solute component from a first fluid

30   containing said solute component into a second fluid, wherein said first fluid and

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said second fluid are immiscible and have different densities, said method comprising feeding said first and second fluids into the extraction tank of claim 14 and collecting the respective fluids from the first and second collection structures.

5   23. A process for concentrating an aqueous solution containing a carboxylate salt comprising

contacting the aqueous solution with an organic extractant of the class consisting of low-molecular-weight secondary or tertiary amine, to form a water/extractant mixture and a more concentrated solution of the carboxylate

10   salt; and

separating the water/extractant mixture from the more concentrated solution of the carboxylate salt.

24. A process for concentrating dilute fermentation salts comprising

(a) contacting fermentation broth with organic extractant of the class

15   consisting of low-molecular-weight secondary or tertiary amines, to form water/extractant mixture and a more concentrated solution of the fermentation salts;

(b) heating the water/extractant mixture whereby water phases out of the extractant;

20   (c) stripping the water from step (b) to remove dissolved extractant,

(d) stripping the concentrated solution of fermentation salts from step (a) to remove dissolved extractant; and

(e) recycling the extractant from step (b) to extract additional water from fermentation broth.

25   25. The process of claim 24, wherein the fermentation broth is first treated with alkali to increase the pH, thereby precipitating metal salts and dissolved organics.

26. The process of claim 25, wherein the alkali is lime.

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27. The process of claim 24, wherein the low-molecular-weight secondary or tertiary amine is an amine of the formula R_3N wherein R is hydrogen, methyl, ethyl, n-propyl or isopropyl, or a mixture of such amines.

28. The process of claim 24, wherein the amine is triethylamine, N,N-diethylmethylamine, or a mixture thereof.

29. The process of claim 24, wherein the water/extractant mixture of step (b) is heated by condensing vapors from the strippers of steps (c) and (d).

30. The process of claim 24, wherein the water/extractant mixture of step (b) is heated by condensing water/amine vapors exiting a mechanical compressor which applies suction to the contactors in which fermentation broth and organic extractant of step (a) are contacted.

31. The process of claim 30, wherein the organic extractant contains a volatile component which increases the vapor density at the suction to the compressor.

32. The process of claim 31, wherein the volatile component is a hydrocarbon or a fluorocarbon.

33. The process of claim 30, wherein the fermentation broth is preheated by a countercurrent heat exchanger, thereby raising the extraction temperature and increasing the vapor density at the suction to the compressor.

34. The process of claim 30, wherein the mechanical compressor is powered by a steam turbine, and further wherein exhaust steam from the turbine is added to the strippers of steps (c) and (d).

35. The process of claim 30, wherein the strippers of steps (c) and (d) are multiple-effect strippers, and further wherein the overhead vapors from the stripper operating at the highest pressure is sent to the reboiler of the stripper operating at the next lower pressure.

36. The process of claim 30, wherein the mechanical compressor is staged and further wherein vapors from intermediate stages are added stage-wise to the water/extractant mixture of step (b).

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37. The process of claim 24, wherein the water/extractant mixture of step (b) is heated by condensing water/amine vapors exiting a steam ejector which applies suction to the contactors of step (a).

38. The process of claim 37, further wherein the steam ejector is

5   powered by high-pressure exhaust steam from the strippers of steps (c) and (d).

39. The process of claim 38, wherein which the strippers of steps (c) and (d) are multiple-effect strippers, and further wherein the overhead vapors from the stripper operating at the highest pressure are sent to the reboiler of the stripper operating at the next lower pressure.

10 40. The process of claim 37, wherein the steam ejector is staged, and further wherein vapors from intermediate stages are added stage-wise to the water/extractant mixture of step (b).

41. The process of claim 24, wherein lime is added to the strippers described in steps (c) and (d).

15 42. The process of claim 24, wherein which the fermentation broth contains carboxylate salt.

43. The process of claim 42, wherein the carboxylate salt is a calcium salt.

44. The process of claim 24, wherein the fermentation broth consists of a

20 carboxylate salt produced by fermenting lignocellulosic biomass.

45. The process of claim 44, wherein the fermentation broth is a calcium carboxylate produced by fermenting lignocellulosic biomass.

46. The process of claim 44, wherein the lignocellulosic biomass is fermented to a carboxylate salt by a mixed culture of acid-forming

25 microorganisms.

47. The process of claim 46, wherein a calcium carboxylate salt is produced using a mixed culture of acid-forming microorganisms.

48. The process of claim 24, further comprising the steps of

condensing a secondary refrigerant in heat-exchange contact with the
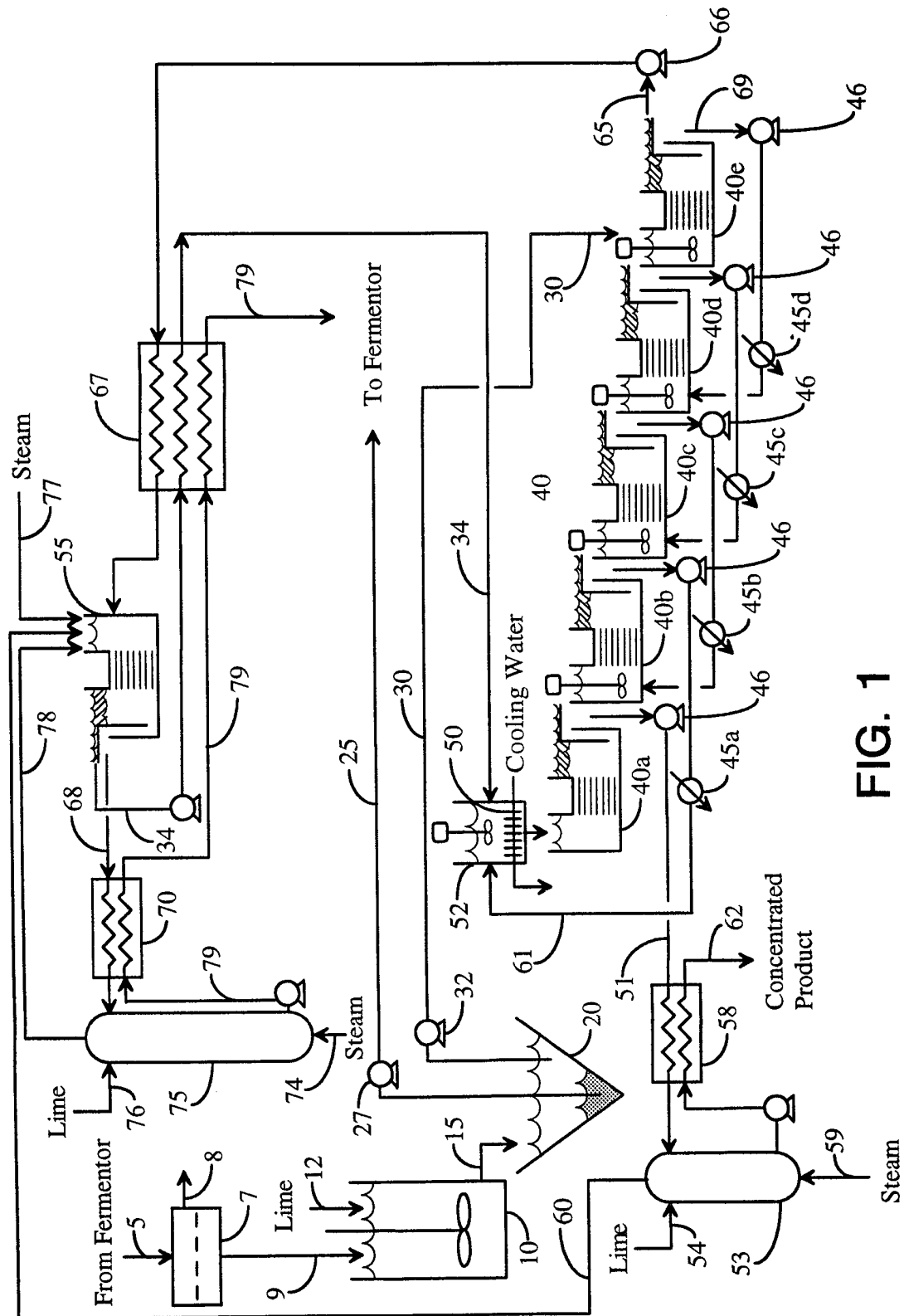
30 water/extract mixture of step (b),

30

evaporating said secondary refrigerant in heat-exchange contact with a contactor in which fermentation broth and organic extractant are contacted, and

compressing said secondary refrigerant using a mechanical compressor to apply suction to said evaporating secondary refrigerant and to apply pressure to

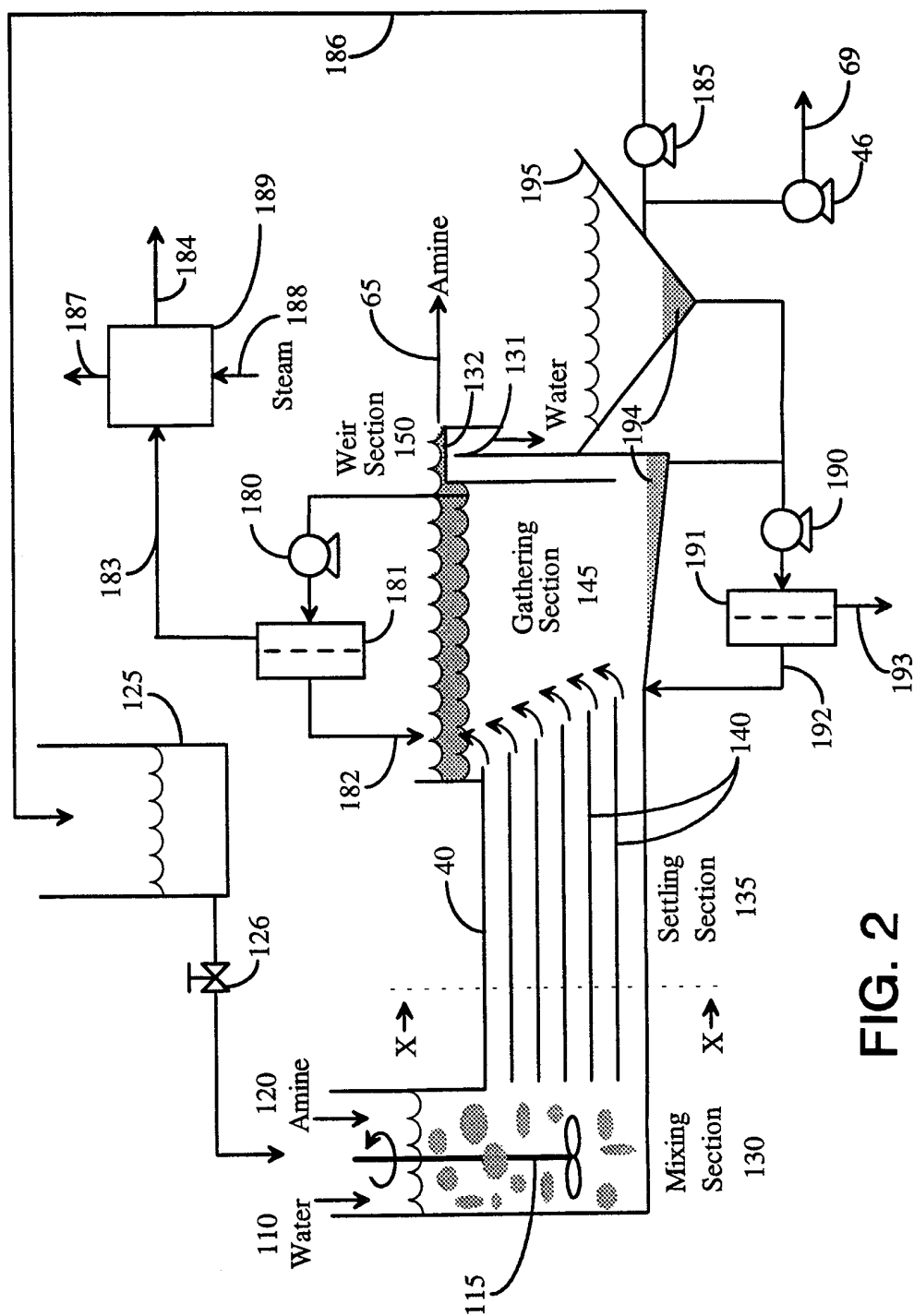5   said condensing secondary refrigerant.

49. The process of claim 48, wherein the secondary refrigerant is ammonia or Freon.

50. The process of claim 48, wherein the mechanical compressor is powered by a steam, turbine and further wherein the exhaust steam from the

10   turbine is added to the strippers of steps (c) and (d).

51. The process of claim 46, wherein the strippers of steps (c) and (d) are multiple-effect strippers, and further wherein the overhead vapors from the stripper operating at the highest pressure are sent to the reboiler of the stripper operating at the next lower pressure.

15   52. The process of claim 48, wherein the mechanical compressor is staged, and further wherein compressed vapors of secondary refrigerant from intermediate stages are in stage-wise, heat-exchange contact with the water/extractant mixture of step (b).
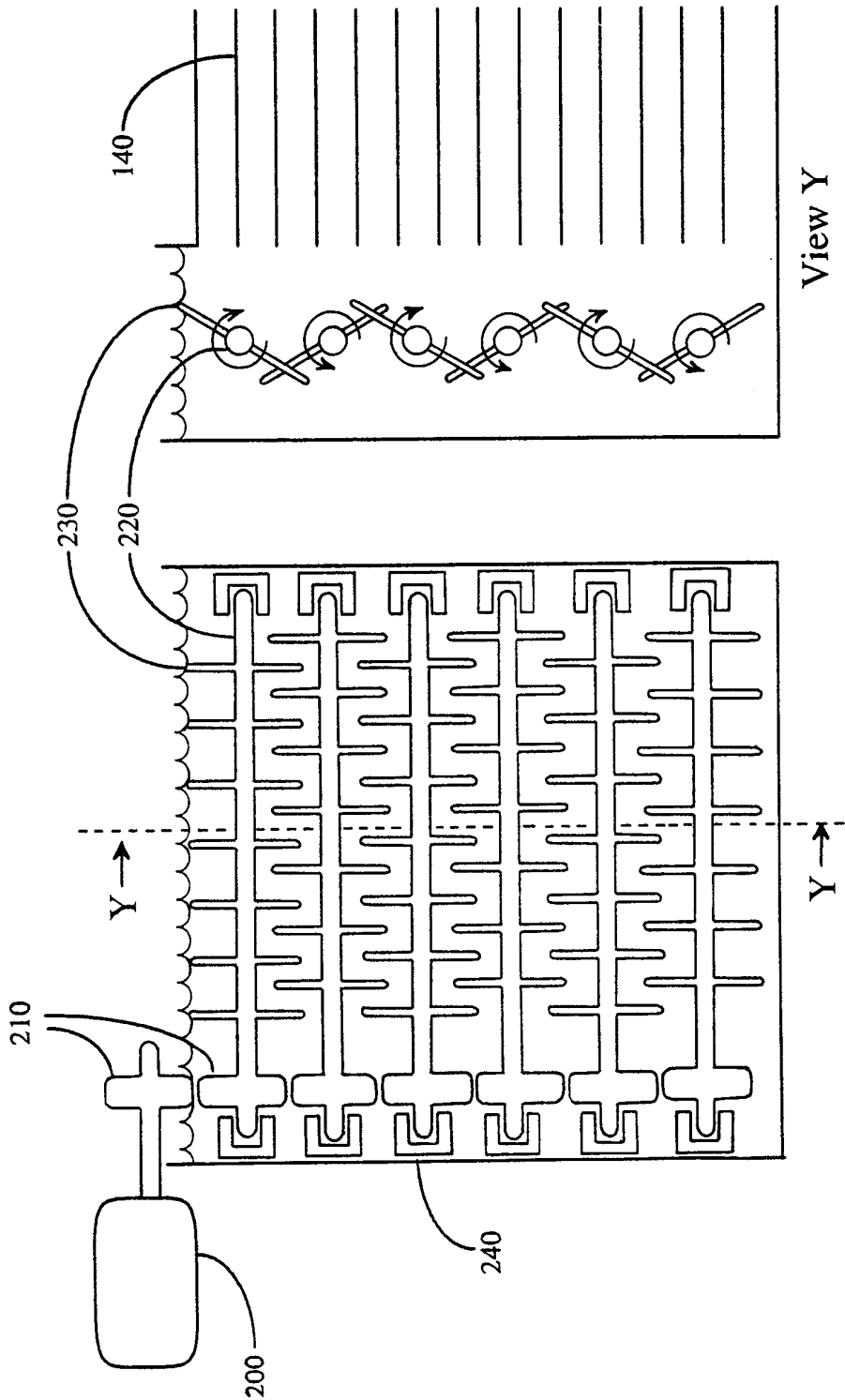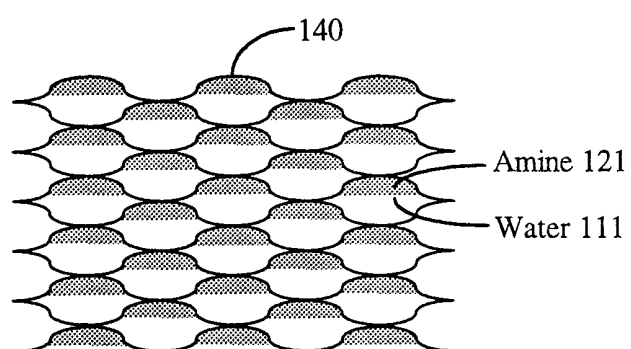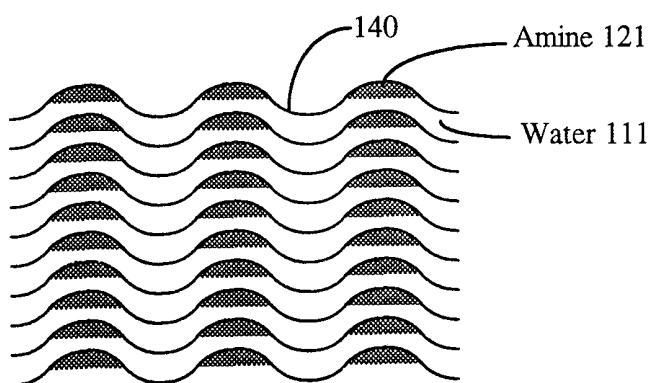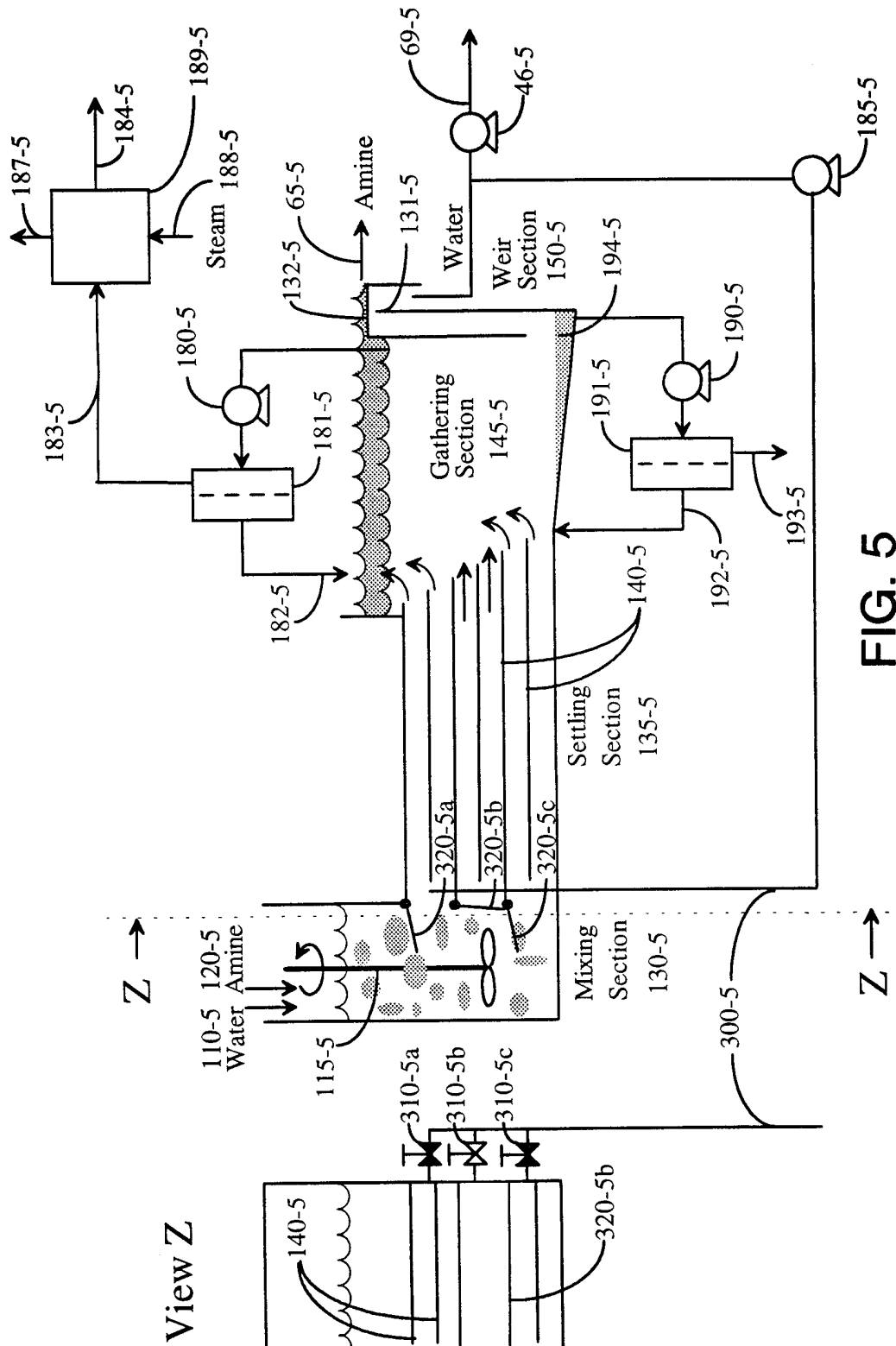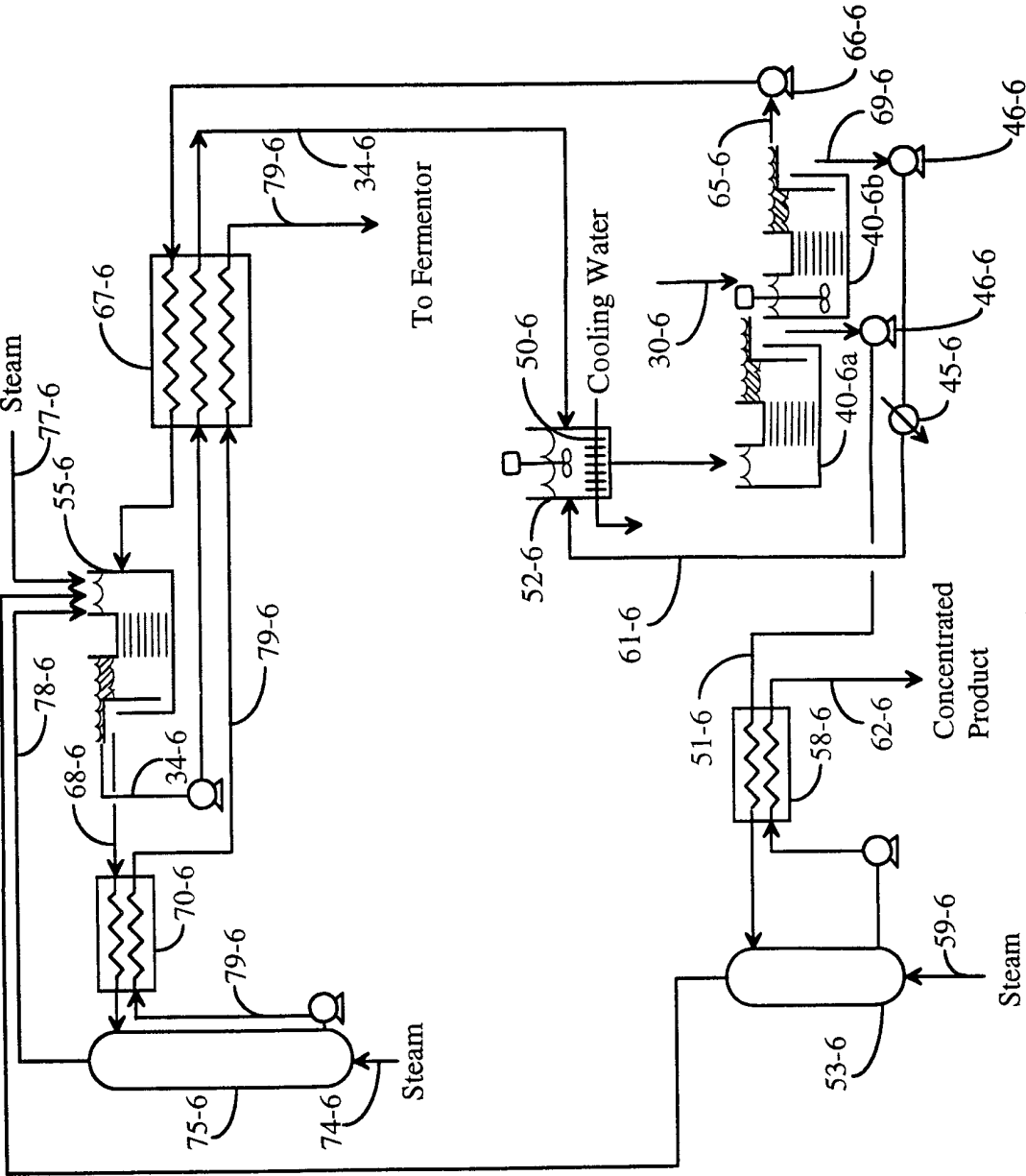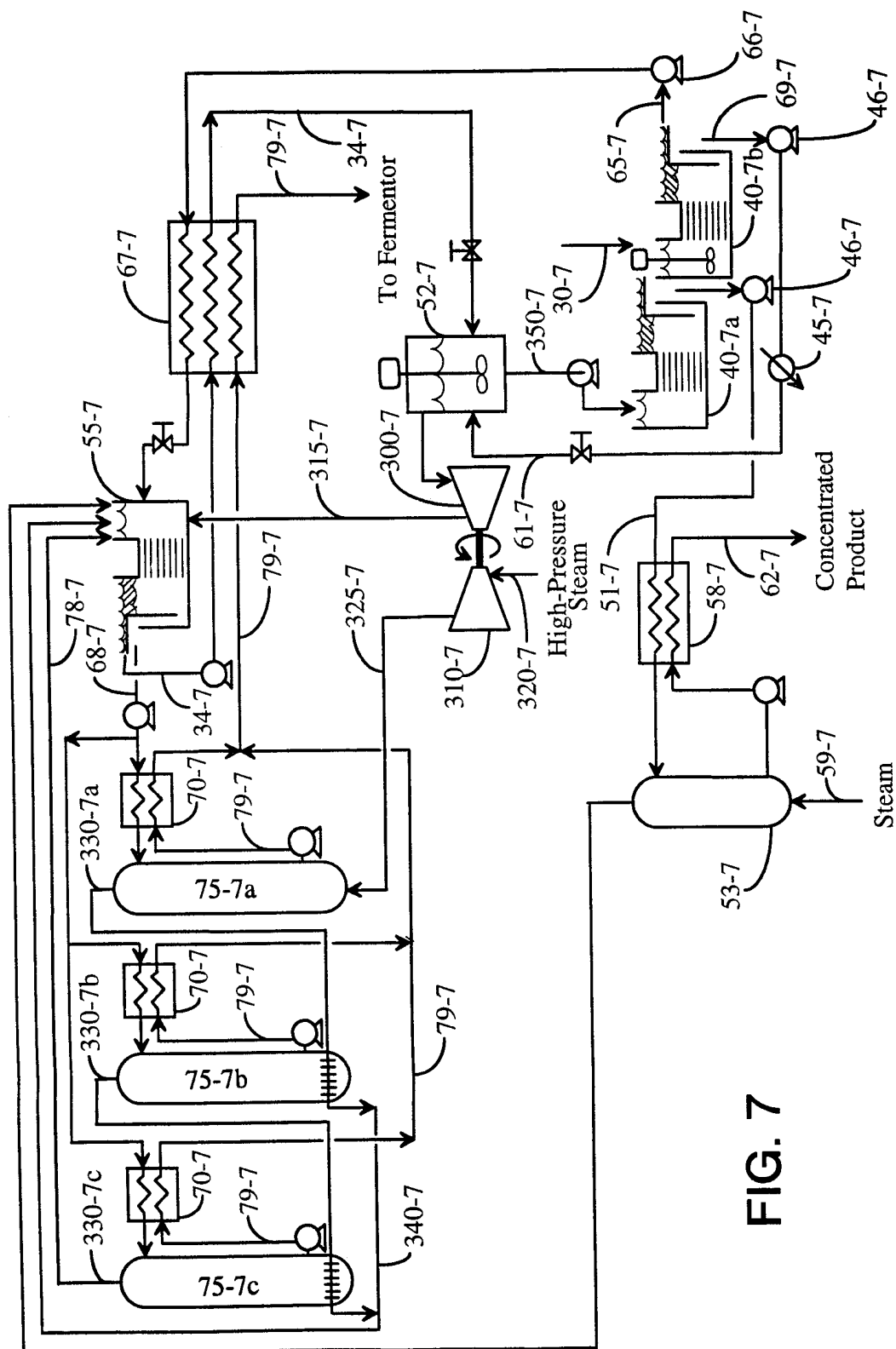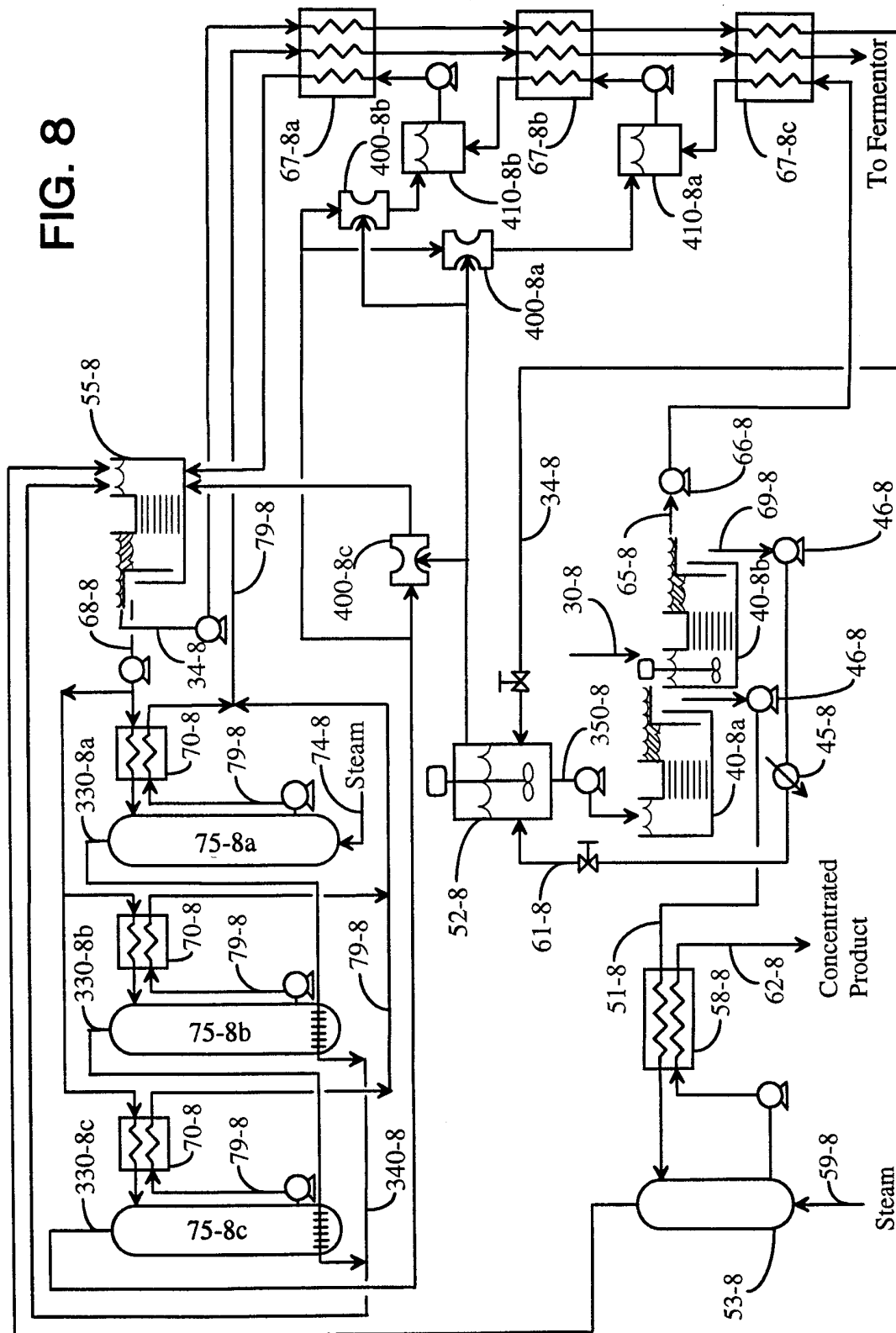
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FIG. 1

FIG. 2

View Y

FIG. 3

FIG. 4A

140

Amine 121

Water 111

View X

FIG 4B

140   Amine 121

Water 111

View X

FIG. 5

6 / 10

FIG. 6

FIG. 7

FIG. 8

FIG. 9
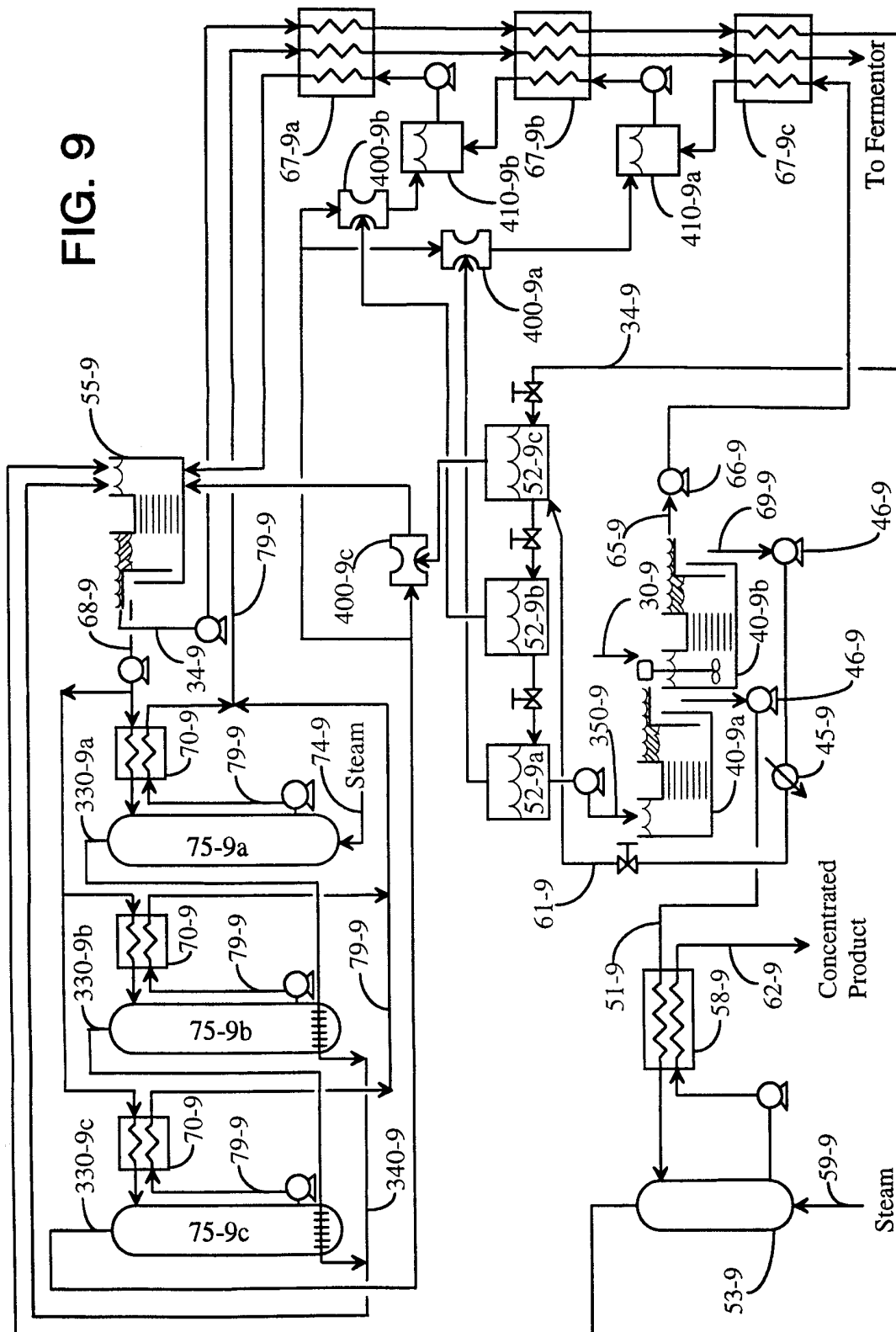
FIG. 10
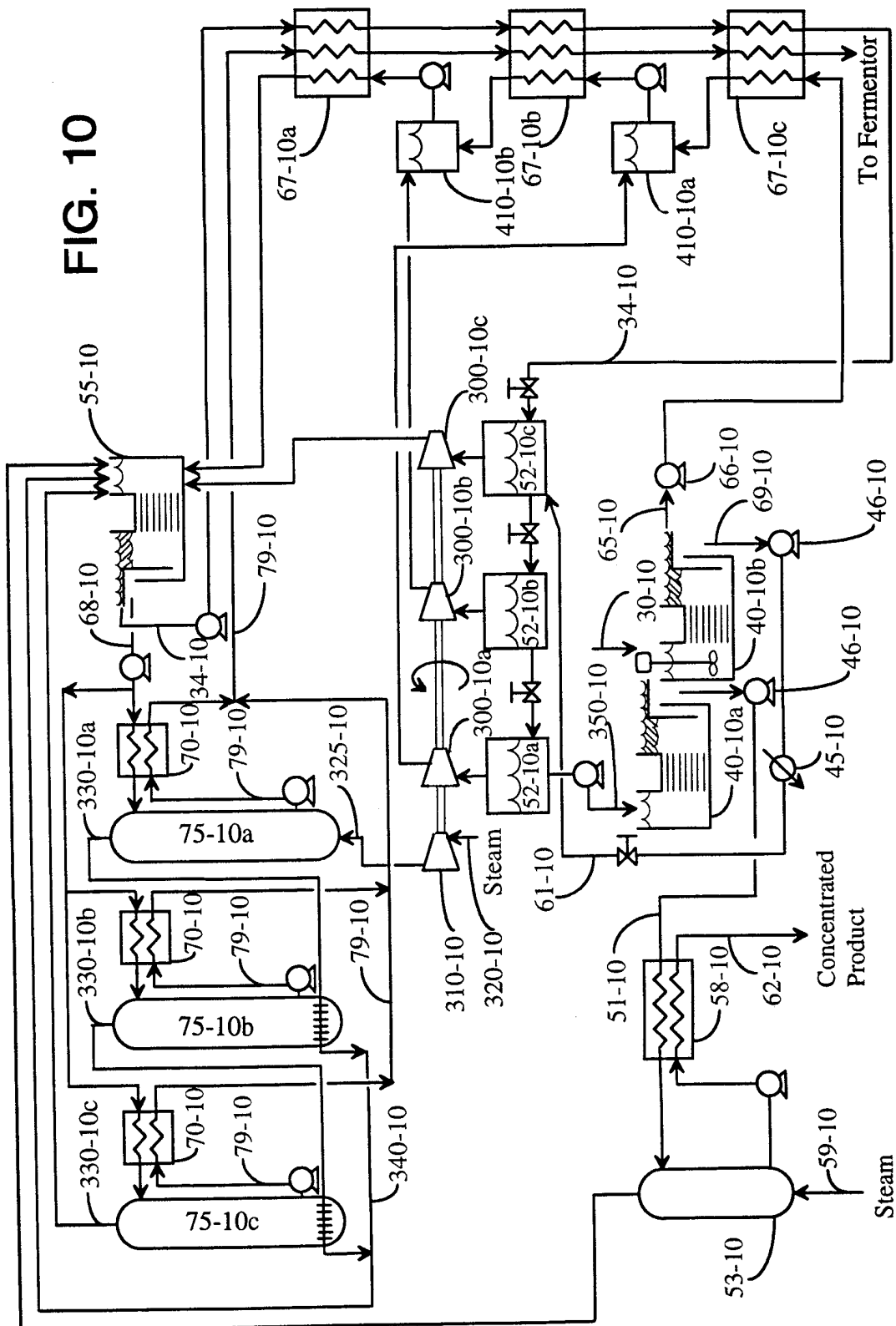
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   C07C51/48   C07C53/08   B01D11/04   C12P7/40

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)
IPC 6   C07C   B01D   C02F   C12P

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 practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DAVISON ET AL: "Phase equilibria of desalination solvents: water-NaCl-amines" JOURNAL OF CHEMICAL AND ENGINEERING DATA, vol. 2, 1966, pages 304-309, XP002082531 cited in the application	23
A	see page 304, left-hand column, paragraph 1 see tables I,II see page 309, left-hand column	1,13,24
A	EP 0 112 926 A (DAICEL CHEM) 11 July 1984 see page 7, line 13 - page 8, line 22 see example 1 see claim 1	1,13,14, 22-24

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[X] Further documents are listed in the continuation of box C. [X] Patent family members are listed in annex.

° Special categories of cited documents :

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 October 1998	11/11/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Held, P

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 635 474 A (GLITSCH INC.) 25 January 1995 see column 4, line 42 - column 5, line 29 see claims 1-4	1,13,23, 24
A	US 3 088 909 A (DAVISON ET AL) 7 May 1963 cited in the application see column 1, line 14 - line 18 see column 3, line 9 - line 51 see table 1 see claims 1,2,9,10	1,13,24
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