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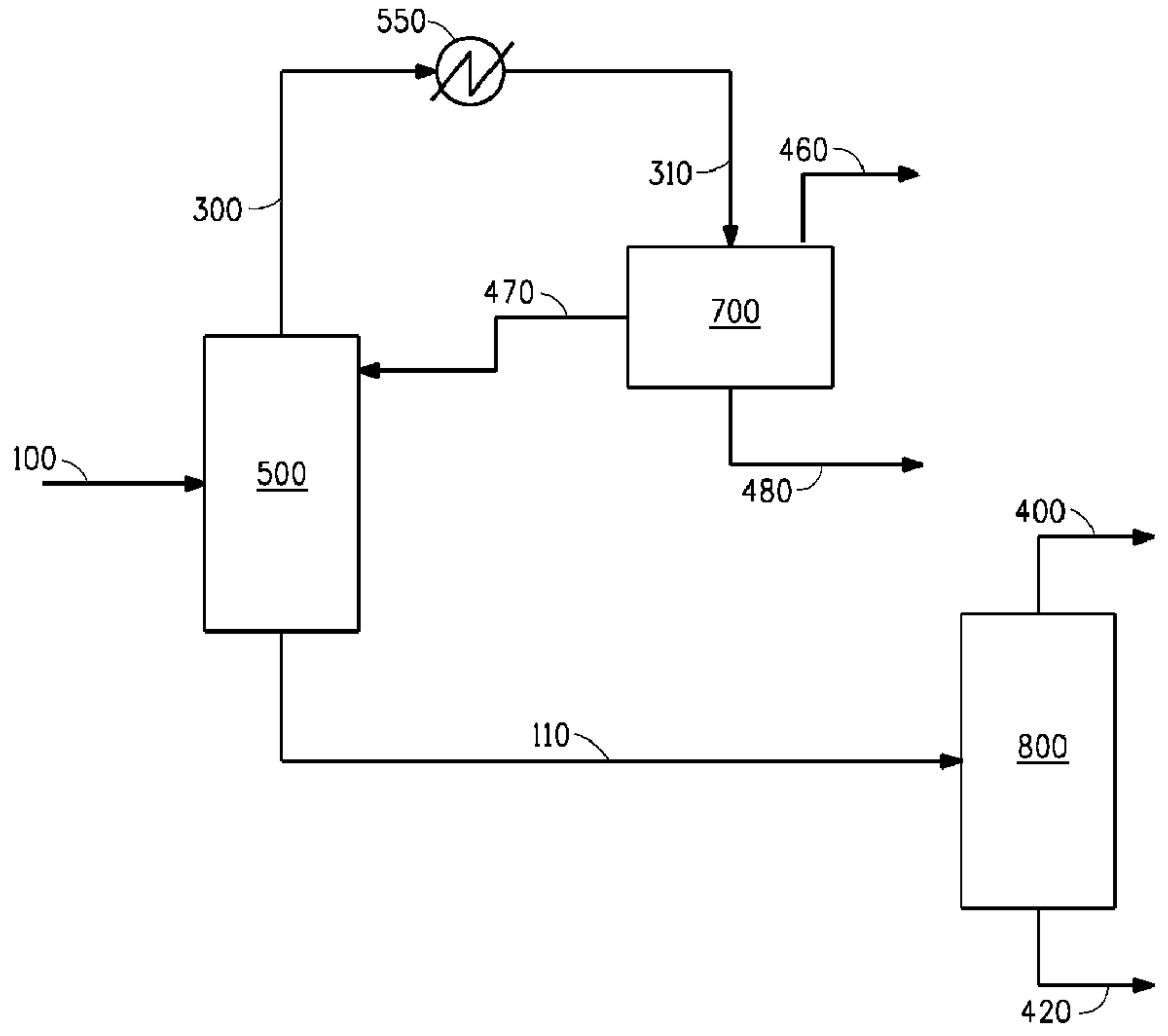
(54) **Titre** : RECUPERATION DU BUTANOL D'UN MELANGE DE BUTANOL, D'EAU ET D'UN EXTRACTANT ORGANIQUE
(54) **Title**: RECOVERY OF BUTANOL FROM A MIXTURE OF BUTANOL, WATER, AND AN ORGANIC EXTRACTANT



(57) **Abrégé/Abstract**:

A process for recovering butanol from a mixture comprising a water-immiscible organic extractant, water, butanol, and optionally a non-condensable gas, is provided. The butanol is selected from 1-butanol, isobutanol, and mixtures thereof. An overhead stream

(57) **Abrégé(suite)/Abstract(continued)**:
from a first distillation column is decanted into two liquid phases. The wet butanol phase is returned to the first distillation column as reflux. A bottom stream from the first distillation column is refined in a second distillation column to obtain a second overhead stream comprising butanol and a second bottoms stream comprising the extractant. The extractant comprises at least one solvent selected from the group consisting of C_7 to C_{22} fatty alcohols, C_7 to C_{22} fatty acids, esters of C_7 to C_{22} fatty acids, C_7 to C_{22} fatty aldehydes, and mixtures thereof.

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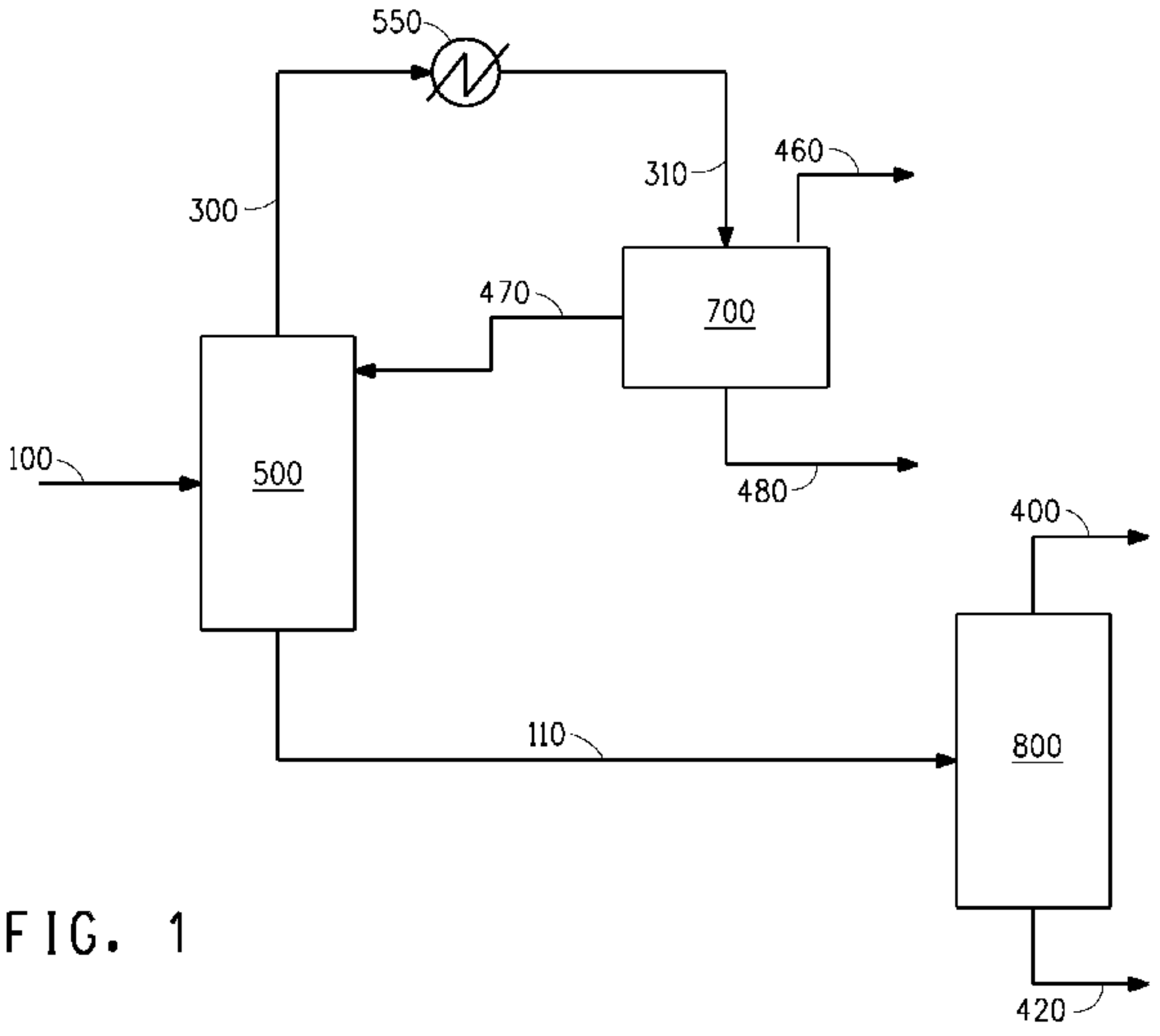

FIG. 1

(57) **Abstract**: A process for recovering butanol from a mixture comprising a water-immiscible organic extractant, water, butanol, and optionally a non-condensable gas, is provided. The butanol is selected from 1-butanol, isobutanol, and mixtures thereof. An overhead stream from a first distillation column is decanted into two liquid phases. The wet butanol phase is returned to the first distillation column as reflux. A bottom stream from the first distillation column is refined in a second distillation column to obtain a second overhead stream comprising butanol and a second bottoms stream comprising the extractant. The extractant comprises at least one solvent selected from the group consisting of C_7 to C_{22} fatty alcohols, C_7 to C_{22} fatty acids, esters of C_7 to C_{22} fatty acids, C_7 to C_{22} fatty aldehydes, and mixtures thereof.

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TITLE OF INVENTION

RECOVERY OF BUTANOL FROM A MIXTURE OF BUTANOL, WATER, AND AN ORGANIC EXTRACTANT

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of priority to U.S. Provisional Patent Application 61/225,659, filed July 15, 2009.

FIELD OF THE INVENTION

Processes for recovering butanol from a butanol-containing organic phase obtained from an extractive fermentation process are provided. Specifically, processes for separating butanol from a mixture comprising butanol, water, a water-immiscible organic extractant, and optionally a non-condensable gas, are provided.

BACKGROUND OF THE INVENTION

Butanol is an important industrial chemical with a variety of applications, such as use as a fuel additive, as a blend component to diesel fuel, as a feedstock chemical in the plastics industry, and as a foodgrade extractant in the food and flavor industry. Each year 10 to 12 billion pounds of butanol are produced by petrochemical means. As the projected demand for butanol increases, interest in producing butanol from renewable resources such as corn, sugar cane, or cellulosic feeds by fermentation is expanding.

In a fermentative process to produce butanol, in situ product removal advantageously reduces butanol inhibition of the microorganism and improves fermentation rates by controlling butanol concentrations in the fermentation broth. Technologies for in situ product removal include stripping, adsorption, pervaporation, membrane solvent extraction, and liquid-liquid extraction. In liquid-liquid extraction, an extractant is contacted with the fermentation broth to partition the butanol between the fermentation broth and the extractant phase. The butanol and the extractant are recovered by a separation process, for example by distillation. In the recovery process, the butanol can also be separated from any water, non-condensable gas, and/or fermentation by-products which may have been removed from the fermentation broth through use of the extractant.

Processes for recovering butanol from the butanol-containing extractant phase obtained by in situ product removal from a fermentation broth are sought. Economical processes for recovering butanol substantially free of water and of the extractant are desired. Also desired are separation processes which are energy efficient and provide high purity butanol product having little color. Butanol recovery processes which can be run for extended periods without equipment fouling or repeated shutdowns are also sought.

SUMMARY OF THE INVENTION

The present invention provides a process for separating a butanol selected from the group consisting of 1-butanol, isobutanol, and mixtures thereof, from a feed comprising a water-immiscible organic extractant, water, the butanol, and optionally a non-condensable gas.

In one aspect, the present invention is a process comprising the steps:

a) introducing a feed comprising:
  (i) a water-immiscible organic extractant,
  (ii) water,
  (iii) at least one isomer of butanol, and
  (iv) optionally a non-condensable gas

into a first distillation column, wherein the first distillation column comprises a stripping section and optionally a rectifying section at an introduction point above the stripping section, the first distillation column having an operating temperature, T_1 and an operating pressure P_1 at a predetermined point in the stripping section,

wherein T_1 and P_1 are selected to produce a first bottoms stream and a first vaporous overhead stream, the first bottoms stream comprising the water-immiscible organic extractant and butanol and being substantially free of water, and the first vaporous overhead stream comprising water, butanol, and the optional non-condensable gas;

b) condensing the first vaporous overhead stream to produce a gas phase and recover a first mixed condensate, wherein the first mixed condensate comprises

(i) a butanol phase comprising butanol, less than about 30 wt% water; and

(ii)an aqueous phase comprising water and less than about 10 wt% of butanol;

c) introducing at least a portion of the aqueous phase to the first distillation column;

d) introducing a first portion of the butanol phase into a second distillation column having at least a stripping section; and

e) introducing a first portion of the first bottoms stream into a second distillation column having at least a stripping section and optionally a rectifying section and operating the second distillation column to produce a second bottoms stream comprising the extractant and being substantially free of butanol, and a second vaporous overhead stream comprising butanol;

wherein the extractant preferentially dissolves butanol over water and is separable from butanol by distillation.

BRIEF DESCRIPTION OF THE FIGURES

FIG. **1** illustrates one embodiment of a system useful for practicing the process of the invention.

FIG. **2** illustrates a process schematic diagram used in modeling the process of the invention.

DETAILED DESCRIPTION OF THE INVENTION

When an amount, concentration, or other value or parameter is given as either a range, preferred range, or a list of upper preferable values and lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether ranges are separately disclosed. Where a range of numerical values is recited herein, unless otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range. It is not intended that the scope of the invention be limited to the specific values recited when defining a range.

Definitions

The following definitions are used in this disclosure:

"Butanol" as used herein refers with specificity to the butanol isomers 1-butanol (1-BuOH) and/or isobutanol (iBuOH or I-BUOH), either individually or as mixtures thereof. 2-Butanol and tert-butanol (1,1-dimethyl ethanol) are specifically excluded from the present use of the term.

"In Situ Product Removal" as used herein means the selective removal of a specific fermentation product from a biological process such as fermentation to control the product concentration in the biological process.

“Fermentation broth” as used herein means the mixture of water, sugars, dissolved solids, suspended solids, microorganisms producing butanol, product butanol and all other constituents of the material held in the fermentation vessel in which product butanol is being made by the reaction of sugars to butanol, water and carbon dioxide (CO_2) by the microorganisms present. The fermentation broth is the aqueous phase in biphasic fermentative extraction. From time to time, as used herein the term “fermentation medium” may be used synonymously with “fermentation broth”.

“Fermentation vessel” as used herein means the vessel in which the fermentation reaction by which product butanol is made from sugars is carried out. The term “fermentor” may be used synonymously herein with “fermentation vessel”.

The term “effective titer” as used herein, refers to the total amount of butanol produced by fermentation per liter of fermentation medium. The total amount of butanol includes: (i) the amount of butanol in the fermentation medium; (ii) the amount of butanol recovered from the organic extractant; and (iii) the amount of butanol recovered from the gas phase, if gas stripping is used.

The term “aqueous phase titer” as used herein, refers to the concentration of butanol in the fermentation broth.

“Stripping” as used herein means the action of transferring all or part of a volatile component from a liquid stream into a gaseous stream.

“Stripping section” as used herein means that part of the contacting device in which the stripping operation takes place.

“Rectifying” as used herein means the action of transferring all or part of a condensable component from a gaseous stream into a liquid stream in order to separate and purify lower boiling point components from higher boiling point components.

“Rectifying section” as used herein means the section of the distillation column above the feed point, i.e. the trays or packing material located above the point in the column where the feed stream enters, where the rectifying operation takes place.

The term “separation” as used herein is synonymous with “recovery” and refers to removing a chemical compound from an initial mixture to obtain the compound in greater purity or at a higher concentration than the purity or concentration of the compound in the initial mixture.

The term “water-immiscible” refers to a chemical component, such as an extractant or solvent, which is incapable of mixing with an aqueous solution, such as a fermentation broth, in such a manner as to form one liquid phase.

The term “extractant” as used herein refers to one or more organic solvents which are used to extract butanol from a fermentation broth.

The term “organic phase”, as used herein, refers to the non-aqueous phase of a biphasic mixture obtained by contacting a fermentation broth with a water-immiscible organic extractant.

The term “fatty acid” as used herein refers to a carboxylic acid having a long, aliphatic chain of C_7 to C_{22} carbon atoms, which is either saturated or unsaturated.

The term “fatty alcohol” as used herein refers to an alcohol having a long, aliphatic chain of C_7 to C_{22} carbon atoms, which is either saturated or unsaturated.

The term “fatty aldehyde” as used herein refers to an aldehyde having a long, aliphatic chain of C_7 to C_{22} carbon atoms, which is either saturated or unsaturated.

Non-condensable gas means a gas that is not condensed at an operating temperature of the process described herein.

Butanol-containing extractant streams useful as a feed in the processes of the invention include any organic phase obtained from an extractive fermentation wherein butanol is produced as a fermentation product. Typical butanol-containing extractant streams include those produced in “dry grind” or “wet mill” fermentation processes in which in situ product removal is practiced using liquid-liquid extraction of the fermentation broth with an organic extractant. After extraction, the extractant stream typically comprises butanol, water, and the extractant. The extractant stream may optionally comprise a non-condensable gas, which can be a gas that is inert or otherwise non-reactive with other feed components under the operating conditions of the present invention. Such gases can be selected from gases in the group consisting of, for example, carbon dioxide, nitrogen, hydrogen, Noble gases such as argon, or mixtures of any of these. The extractant stream may optionally further comprise fermentation by-products having sufficient solubility to partition into the extractant phase. Butanol-containing extractant streams useful as a feed in the processes of the invention include streams characterized by a butanol concentration in the feed from about 0.1 weight percent to about 40 weight percent, for example from about 2 weight percent to about 40 weight percent, for example from about 5 weight percent to about 35 weight percent, based on the weight of the feed. Depending on the efficiency of the extraction, the aqueous phase titer of butanol in the fermentation broth can be, for example, from about 5 g/L to about 85 g/L, or from about 10 g/L to about 40 g/L.

The extractant is a water-immiscible organic solvent or solvent mixture having characteristics which render it useful for the extraction of butanol from a fermentation broth. The extractant preferentially partitions butanol from the aqueous phase, for example by at least a 1.1:1 concentration ratio, such that the concentration of butanol in the extractant phase is at least 1.1 times that in the aqueous phase when evaluated in a room-temperature extraction of an aqueous solution of butanol. Preferably, the extractant preferentially partitions butanol from the aqueous phase by at least a 2:1 concentration ratio, such that the concentration of butanol in the extractant phase is at least two times that in the aqueous phase when evaluated in a room-temperature extraction of an aqueous solution of butanol. To be of practical use in the butanol recovery process, the extractant is separable from butanol by distillation, having a boiling point at atmospheric pressure which is at least about 30 degrees Celsius higher than that of the butanol to be recovered, or for example at least about 40 degrees higher, or for example at least about 50 degrees higher.

The extractant comprises at least one solvent selected from the group consisting of C_7 to C_{22} fatty alcohols, C_7 to C_{22} fatty acids, esters of C_7 to C_{22} fatty acids, C_7 to C_{22} fatty aldehydes, C_7 to C_{22} fatty amides and mixtures thereof. Suitable organic extractants are further selected from the group consisting of oleyl alcohol (CAS No. 143-28-2), behenyl alcohol (CAS No. 661-19-8), cetyl alcohol (CAS No. 36653-82-4), lauryl alcohol, also referred to as 1-dodecanol (CAS No. 112-53-8), myristyl alcohol (112-72-1), stearyl alcohol (CAS No. 112-92-5), 1-undecanol (CAS No. 112-42-5), oleic acid (CAS No. 112-80-1), lauric acid (CAS No. 143-07-7), myristic acid (CAS No. 544-63-8), stearic acid (CAS No. 57-11-4), methyl myristate CAS No. 124-10-7), methyl oleate (CAS No. 112-62-9), undecanal (CAS No. 112-44-7), lauric aldehyde (CAS No. 112-54-9), 2-methylundecanal (CAS No. 110-41-8), oleamide (CAS No. 301-02-0), linoleamide (CAS No. 3999-01-7), palmitamide (CAS No. 629-54-9) and stearylamide (CAS No. 124-26-5) and mixtures thereof. In some aspects, the extractant comprises oleyl alcohol. Suitable solvents are described in U.S. Patent Application Publication No. 2009030537 and also in U.S. Patent Publication Numbers 2010/0221802 and 2011/0097773 (both filed April 13, 2010).

These organic extractants are available commercially from various sources, such as Sigma-Aldrich (St. Louis, MO), in various grades, many of which may be suitable for use in extractive fermentation to produce or recover butanol. Technical grades contain a mixture of compounds, including the desired component and higher and lower fatty components. For example, one commercially available technical grade oleyl alcohol contains about 65% oleyl alcohol and a mixture of higher and lower fatty alcohols.

The invention provides processes for separating or recovering butanol from a feed comprising a water-immiscible organic extractant, water, the butanol, and optionally a non-condensable gas. Separation of the butanol from the feed is achieved through a combination of distillation and decantation. The distillation involves the use of at least two distillation columns. The first column, in combination with decantation, effects a separation of water from butanol and the extractant. The cooled overhead stream from the first column is decanted into two liquid phases. The organic phase is returned to the first column. The second column effects a separation of butanol from the extractant under vacuum conditions and provides a butanol stream which is substantially free of extractant. The second column also provides an extractant stream which is substantially free of water and has a reduced butanol content.

The processes of the invention can be understood by reference to **FIG. 1**, which illustrates one embodiment of a system useful for practicing the process of the invention. The feed stream **100**, obtained from a fermentation vessel (not shown) or an extractor (not shown) in a process for fermentative extraction, is introduced into a first distillation column **500,** which has a stripping section and optionally a rectifying section, at a feed point above the stripping section. The feed stream **100** is distilled to provide a first bottoms stream **110** and a first vaporous overhead stream **300** comprising water, butanol, and any non-condensable gas present in the feed. An operating temperature T_1 and an operating pressure P_1 at a predetermined point in the stripping section of column **500** are selected so as to provide the first bottoms stream **110** comprising the extractant and butanol and being substantially free of water. The distillation column **500** can be any conventional column having at least a feed inlet, an overhead vapor outlet, a bottoms stream outlet, a heating means, and a sufficient number of stages to effect the separation of the water from the extractant.

In the case where the extractant comprises oleyl alcohol, distillation column **500** should have at least 5 stages including a re-boiler.

The first bottoms stream **110** can comprise from about 0.1 to about 40 weight percent butanol, and can be substantially free of water. By "substantially free", it is meant that the bottoms stream can comprise less than about 0.1 weight percent water. For example, the bottoms stream **110** can comprise less than about 0.01 weight percent water. To ensure that the bottom stream **110** is substantially free of water, the amount of organic phase reflux and the reboiler boil-up rate can be varied.

Stream **300** is condensed in a condenser **550** to produce a first mixed condensate stream **310** comprising a liquid. The mixed stream **310** can further comprise a non-condensable gas component if the gas was present in the feed. The condenser **550** may be of any conventional design.

The mixed condensate stream **310** is introduced into a decanter **700** and allowed to separate into a gas phase optionally comprising the non-condensable gas, a liquid butanol phase, and a liquid aqueous phase. The temperature of the decanter is preferably maintained at or below about 40 ^{o}C to reduce the amount of butanol and water being stripped out by the non-condensable gas. The liquid butanol phase, the lighter liquid phase (the top liquid phase), can include about 16 to about 30 weight percent water and may further comprise any extractant which comes overhead in column **500**. The fraction of extractant in the butanol phase can be minimized by use of an optional rectification section in column **500**. The liquid aqueous phase includes about 3 to about 10 weight percent butanol. The decanter may be of any conventional design.

When a non-condensable gas such as carbon dioxide is present in the feed, the non-condensable gas is present in stream **300** and in stream **310**. At least a portion of the gas phase comprising the non-condensable gas can be purged from the process, as shown in **FIG. 1**, in which purge stream **460** comprising the non-condensable gas is shown leaving the decanter **700**.

From the decanter **700**, the aqueous phase **480** can be purged from the process, as shown in **FIG. 1**, in which the purge stream comprising the aqueous phase **480** is shown leaving the decanter **700**. Alternatively, at least a portion of the aqueous phase can be introduced to a fermentation vessel (not shown). This can provide a means to recycle some of the water from the butanol recovery process back to the extractive fermentation process. In one embodiment, at least a portion of the aqueous phase can be combined with at least a portion of the bottoms stream from the second distillation column and then introduced to a fermentation vessel, as shown in **FIG. 2** wherein the aqueous phase **48** from the decanter **70** is combined in a mixer **75** with the bottoms stream **44** from the second distillation column to provide combined stream **45**.

The butanol phase **470** from the decanter is returned to the first distillation column **500**. Stream **470** would normally be introduced as reflux to the column. Introducing stream **470** as liquid reflux will suppress extractant loss in vaporous stream **300** of column **500**. The butanol phase **470** may further comprise volatile fermentation byproducts such as acetaldehyde. Optionally, at least a portion of stream **470** may be purged from the process (not shown) to remove volatile fermentation byproducts from the butanol recovery process.

The first bottoms stream **110** is withdrawn from column **500** and introduced into a second distillation column **800,** which has a stripping section and optionally a rectifying section, at a feed point above the stripping section. The stream **110** is distilled to provide a second bottoms stream **420** comprising the extractant and a second vaporous overhead stream **400** comprising butanol. The second distillation column is operated so as to provide the bottoms stream **420** substantially free of butanol. By “substantially free of butanol” it is meant that the bottom **420** comprises less than about one weight percent butanol. The second vaporous overhead stream **400** is substantially free of the extractant. By "substantially free of extractant" it is meant that the overhead stream **400** comprises less than about 0.01 weight percent extractant. The distillation column **800** can be any conventional column having at least a feed inlet, an overhead vapor outlet, a bottoms stream outlet, a heating means, a stripping section, and a sufficient number of stages to effect the desired separation. Column **800** should have at least 6 stages a including re-boiler. Preferably, column **800** is operated at a pressure less than atmospheric to minimize the temperature of the extractant in the base of the column while enabling economical and convenient condensation of the butanol overheads.

The process may further comprise introducing bottoms stream **420** from the second distillation column into a fermentation vessel (not shown). In one embodiment, bottoms stream **420** may be combined with at least a portion of the aqueous phase **480** from the decanter before introduction into a fermentation vessel, as shown in **FIG. 2** wherein analogous streams **44** and **48** are combined in mixer **75** to provide the combined stream **45**.

A mixture of higher boiling extractants is expected to behave in a fundamentally similar way to a single extractant provided that the boiling point of the mixture, or the boiling point of the lowest boiling solvent of the mixture, is significantly higher than the boiling points of water and butanol, for example at least about 30 degrees higher.

The present processes for separating or recovering butanol provide butanol known to have an energy content similar to that of gasoline and which can be blended with any fossil fuel. Butanol is favored as a fuel or fuel additive as it yields only CO_2 and little or no SO_X or NO_X when burned in the standard internal combustion engine. Additionally, butanol is less corrosive than ethanol, the most preferred fuel additive to date.

In addition to its utility as a biofuel or fuel additive, the butanol recovered according to the present processes has the potential of impacting hydrogen distribution problems in the emerging fuel cell industry. Fuel cells today are plagued by safety concerns associated with hydrogen transport and distribution. Butanol can be easily reformed for its hydrogen content and can be distributed through existing gas stations in the purity required for either fuel cells or vehicles. Furthermore, the present processes recover butanol obtained from plant derived carbon sources, avoiding the negative environmental impact associated with standard petrochemical processes for butanol production.

One advantage of the present processes for separation or recovery of butanol is energy integration of the distillation columns, which provides energy efficiency. Relative to a distillation scheme in which the separation of butanol and extractant is made prior to the final separation of butanol and water, the present processes require less energy per unit weight of butanol obtained.

Another advantage is that the present processes provide high purity butanol having little or no color.

A further advantage is that the second bottoms stream comprising the extractant is substantially free of the butanol product, which contributes to high yield in the recovery process. Being substantially free of butanol also enables optional recycling of the second bottoms stream comprising the extractant to the fermentative process. Being substantially free of butanol also simplifies the stream’s disposition, should it not be recycled.

Yet another advantage is that the present processes allow for extended operation without equipment fouling or repeated shutdowns.

Although particular embodiments of the present invention have been described in the foregoing description, it will be understood by those skilled in the art that the invention is capable of numerous modifications, substitutions, and rearrangements without departing from the spirit of essential attributes of the invention. Reference should be made to the appended claims, rather than to the foregoing specification, as indicating the scope of the invention.

The process of the invention can be demonstrated using a computational model of the process. Process modeling is an established methodology used by engineers to simulate complex chemical processes. Process modeling software performs many fundamental engineering calculations, for example mass and energy balances, vapor/liquid equilibrium and reaction rate computations. The modeling of distillation columns is particularity well established. Calculations based on experimentally determined binary vapor/liquid equilibrium and liquid/liquid equilibrium data can predict reliably the behavior of multi-component mixtures. This capability has been expanded to allow modeling of complex multi-stage, multi-component distillation columns using rigorous algorithms like the “inside-out” algorithm developed by Joseph Boston of Aspentech, Inc. of Burlington, Mass. Commercial modeling software, such as Aspen Plus® from Aspentech, can be used in conjunction with physical property databases, such as DIPPR, available from the American Institute of Chemical Engineers, Inc., of New York, NY, to develop accurate models and assessments of processes.

EXAMPLES

The Examples were obtained through process modeling using isobutanol as the butanol isomer and oleyl alcohol as the extractant. Similar results would be expected for the analogous cases where 1-butanol or a mixture of 1-butanol and isobutanol was selected as the butanol isomer, due to the similarity of the physical property data for isobutanol and 1-butanol and the heterogeneous nature of the azeotrope between water and these butanol isomers.

Table 1 lists typical feed compositions of the rich solvent stream, obtained from extractive fermentation, entering the isobutanol product recovery area. These compositions were used in modeling the processes of the invention. In the Examples, the term “rich solvent stream” is synonymous with the term “feed stream” used above.

Table 1. Feed Compositions (in Weight Percent) of the Rich Solvent Stream from the Extractor

Feed Compositions	Example 1	Example 2
Isobutanol	11.44%	25.10%
Water	6.47%	8.23%
Carbon dioxide	0.88%	0.94%
Oleyl alcohol	81.21%	65.73%

These composition values for the rich solvent stream were established by a simulation of a dry grind facility using extractive in situ product removal technology producing 50 MM gal/year of isobutanol, and fermenter broth aqueous phase titers of 20 and 40 g/L respectively. It was assumed that the rich solvent stream was at equilibrium with the fermentation broth and that the solvent flow rate was sufficient to meet the specified annual capacity.

The parameters inputted for the simulations of the embodiments of the processes of the invention are listed in Table 2 and follow a process schematic diagram as shown in FIG. 2. In FIG. 2, "**QED06**" refers to a heat stream representing process to process heat exchange via heat

exchangers **65** and **85.** Heat exchanger 55 receives stream 40 and provides stream 49. Block **60** represents an optional mixer. Block **75**

exchangers **65** and **85**. Block **60** represents an optional mixer. Block **75** represents a mixer combining streams **48** and **44** to provide stream **45**. Certain dimensions and duty results calculated from the process model are also listed in Table 2. These parameters do not include physical property parameters, and those related to convergence and other computational options or diagnostics.

Table 2. Conditions Used for Modeling Processes of the Invention

Equipment blocks	Inputs	Example 1	Example 2	Units
Solvent Column (50)	Number of theoretical stages including re-boiler	15	15	stages
	Column top pressure	1	1	bar
	Column bottom pressure	1.1	1.1	bar
	Column internal diameter	3.71	2.91	m
	Column re-boiler duty	59612	38116	MJ/hr
	Preheated rich solvent feed (10) location	1	1	stage

	Organic reflux from decanter (47) location	1	1	stage
	Mass fraction water in bottom stream (11)	1	1	ppm
	Reflux stream temperature	40	40	deg C
	Preheated rich solvent stream (10) flow rate	177671	75171	kg/hr
	Preheated rich solvent stream (10) temperature	91.7	84.9	deg C
	Condenser duty	-48810	-33831	MJ/hr
BuOHCOL Column (80)	Number of theoretical stages including re-boiler	15	15	stages
	Column top pressure	0.1	0.1	bar
	Column bottom pressure	0.105	0.105	bar
	Column internal diameter	2.58	2.46	m
	Column re-boiler duty	9045	10951	MJ/hr
	Organic feed from solvent column (11) location	7	7	stage
	Organic feed from solvent column (11) temperature	145.6	125.1	deg C
	Column bottom temperature	147	147	deg C
	Oleyl alcohol mass fraction in top product (40)	100	100	ppm
	Isobutanol mass fraction in bottom lean solvent (42)	9000	9000	ppm
	Condenser duty	-13844	-12278	MJ/hr
Decanter (70)	Decanter pressure	1	1	atm
	Decanter temperature	40	40	deg C

Two cases were run to demonstrate the operating requirements of the processes of the invention. For each case, a particular modification was made to the rich solvent feed flow and compositions from the extractive fermentation process where two different aqueous phase titers were maintained. In each of the independent simulations, column traffic and heat exchanger duties will change because of the feed composition change. By comparing the resulting capital investment and operating costs between different cases, the impact of the rich solvent feed flow and composition on product recovery area performance was quantified. These two examples, however, should not be regarded as process operating limits of this invention.

In the Tables, the term “Solvent Column” is synonymous with the term “first distillation column” used above. The term “BUOHCOL” is synonymous with the term “second distillation column” used above. The abbreviation “OLEYLOH” refers to oleyl alcohol.

Stream results for Example 1 are listed in Table 3. BUOHCOL column traffic and liquid mass composition profiles are listed in Table 4. Solvent column traffic and liquid mass composition profiles are listed in Table 5.

Stream results for Example 2 are listed in Table 6. BUOHCOL column traffic and liquid mass composition profiles are listed in Table 7. Solvent column traffic and liquid mass composition profiles are listed in Table 8.

Other key process parameters include the following: 1) the total number of theoretical stages and the bottom stream water content in the solvent column; 2) the BUOHCOL column bottom temperature; and 3) the degree of preheating of the rich solvent stream before feeding it to the solvent column. These parameters can be manipulated to achieve optimum separation performance.

EXAMPLE 1

In this Example, 177,671 kg/hr rich solvent feed (**9**) containing 11.44 weight percent isobutanol is heated from 32.2 to 91.7 °C by a process to process heat exchanger and the resulting stream (**10**) is fed to the solvent column (**50**) at stage 1. This rich solvent feed condition corresponds to 20 g/liter aqueous phase titer in the fermentor which is maintained during the extractive fermentation process. The separation is realized by a larger diameter solvent column, higher solvent column bottom temperature, and higher solvent column re-boiler and condenser duties. Stream (**40**) is essentially 100 weight percent isobutanol. Stream (**42**) contains 0.9 weight percent isobutanol and 99.1 weight percent oleyl alcohol.

EXAMPLE 2

In this Example, 75,171 kg/hr rich solvent feed (**9**) is heated from 32.2 to 84.9 °C by a process to process heat exchanger and the resulting stream (**10**) is fed to the solvent column (**50**) at stage 1. This rich solvent feed condition corresponds to 40 g/liter aqueous phase titer in the fermenter which is maintained during the extractive fermentation process. The separation is realized by a smaller diameter solvent column, lower solvent column bottom temperature, and lower solvent column re-boiler and condenser duties. Stream (**40**) is essentially 100 weight percent isobutanol. Stream (**42**) contains 0.9 weight percent isobutanol and 99.1 weight percent oleyl alcohol.

Table 3. Simulated Stream Outputs for Example 1.

	9	10	11	30	31	40	42	44	45	46	47	48	49
Temperature C	32.2	91.7	145.6	92.6	92.6	56.5	147	45	44.3	40	40	40	40
Pressure atm	1.09	1.04	1.09	0.99	0.99	0.1	0.11	1.26	1	1	1	1	0.1
Vapor Frac	0	0.157	0	1	1	0	0	0	0	1	0	0	0
Mole Flow kmol/hr	1485.305	1485.305	798.584	1075.55	1075.55	243.483	555.101	555.101	1203.014	38.774	388.863	647.913	24[illegible].83
Mass Flow kg/hr	177671.064	177671.1	163638.7	32370.384	32370.384	18047.763	145590.98	145591	157963.271	1659.511	18338.586	12372.288	18[illegible].76
Volume Flow l/hr	212216.149	6.88E+06	219236	3.23E+07	3.23E+07	23409.954	193029.09	175750.7	1.88E+05	9.91E+05	2.25E+04	12691.227	22984.34
Enthalpy MMBtu/hr	-546.773	-515.113	-315.653	-256.916	-256.916	-75.628	-244.574	-276.233	-451.502	-13.946	-113.965	-175.268	-76.401
Mass Flow kg/hr													
I-BUOH	20332.4088	20332.41	19356.11	15863.657	15863.657	18045.795	1310.3189	1310.319	2222.04846	64.7054968	14887.2216	911.729612	18045.79
WATER	11496.2539	11496.25	0.163639	14842.689	14842.689	0.1636388	2.67E-10	2.67E-10	11444.7055	50.7448995	3347.23881	11444.7055	0.163639
CO2	1559.93142	1559.931	3.18E-23	1656.2064	1656.2064	0	0	0	15.8524187	1544.06067	96.2933369	15.8524187	0
OLEYLOH	144282.47	144282.5	144282.5	7.8319222	7.8319222	1.8047763	144280.67	144280.7	144280.665	1.02E-06	7.83188542	3.58E-05	1.804776
Mass Frac													
I-BUOH	0.11443849	0.114438	0.118286	0.490067	0.490067	0.9998909	0.009	0.009	0.01406686	0.03899069	0.8117977	0.07369127	0.999891
WATER	0.06470526	0.064705	1.00E-06	0.4585268	0.4585268	9.07E-06	1.83E-15	1.83E-15	0.07245168	0.03057822	0.18252437	0.92502744	9.07E-06
CO2	0.00877988	0.00878	1.94E-28	0.0511643	0.0511643	0	0	0	0.00010035	0.93043108	0.00525085	0.00128128	0
OLEYLOH	0.81207635	0.812076	0.881713	0.0002419	0.0002419	0.0001	0.991	0.991	0.91338109	6.15E-10	0.00042707	2.89E-09	0.0001

Table 4. Simulated BUOHCOL Column Traffic and Liquid Mass Composition Profile Outputs for Example 1.

Stage	Temperature C	Pressure atm	Heat duty MJ/hr	Liquid flow kg/hr	Vapor flow kg/hr	Liquid feed kg/hr	Vapor feed kg/hr	Mixed feed kg/hr	Liquid produc kg/hr	Vapor product kg/hr
1	56.5011602	0.1	-13844.4	2793.2042	0	0	0	0	18047.7632	0
2	66.1270606	0.100357	0	267.02946	20840.967	0	0	0	0	0
3	120.88619	0.100714	0	229.71305	18314.793	0	0	0	0	0
4	122.750144	0.101071	0	229.1764	18277.476	0	0	0	0	0
5	122.786979	0.101429	0	228.44906	18276.94	0	0	0	0	0
6	122.794813	0.101786	0	227.72417	18276.212	0	17089.858	0	0	0
7	122.802293	0.102143	0	146776.65	1185.6295	146548.89	0	0	0	0
8	122.815489	0.1025	0	146784.87	1185.6706	0	0	0	0	0
9	122.828661	0.102857	0	146793.08	1193.8891	0	0	0	0	0
10	122.841823	0.103214	0	146801.28	1202.0929	0	0	0	0	0
11	122.854977	0.103571	0	146809.47	1210.2909	0	0	0	0	0
12	122.868132	0.103929	0	146817.66	1218.485	0	0	0	0	0
13	122.88251	0.104286	0	146825.93	1226.6759	0	0	0	0	0
14	123.082079	0.104643	0	146866.29	1234.9444	0	0	0	0	0
15	147.019984	0.105	9045.051	145590.98	1275.3011	0	0	0	145590.984	0

Stage	I-BUOH	WATER	OLE[illegible]OH
1	0.999891	9.07E-06	[illegible]01
2	0.245012	1.93E-07	0.7[illegible]87
3	0.017676	1.37E-08	0.982324
4	0.016748	1.32E-08	0.983252
5	0.01679	1.32E-08	0.98321
6	0.016848	1.33E-08	0.983152
7	0.016906	2.59E-09	0.983094
8	0.016961	4.80E-10	0.983039
9	0.017015	8.85E-11	0.982985
10	0.01707	1.63E-11	0.98293
11	0.017124	2.98E-12	0.982876
12	0.017178	5.43E-13	0.982822
13	0.017232	9.86E-14	0.982768
14	0.017188	1.75E-14	0.982812
15	0.009	1.83E-15	0.991

Table 5. Simulated Solvent Column Traffic and Liquid Mass Composition Profile Outputs for Example 1.

Stage	Temperature C	Pressure atm	Heat duty MJ/hr	Liquid flow kg/hr	Vapor flow kg/hr	Liquid feed kg/hr	Vapor feed kg/hr	Mixed feed kg/hr	Liquid produc kg/hr	Vapor product kg/hr	1st liquid flow kg/hr	2nd liquid flow kg/hr
1	92.5578171	0.986923	0	190930.5	32370.903	189058.21	6951.4374	0	0	32369.8779	187271.886	3658.6179
2	93.6721095	0.993973	0	191294.94	27291.757	0	0	0	0	0	187484.04	3810.90195
3	93.875775	1.001022	0	191366.91	27656.195	0	0	0	0	0	187538.31	3828.59527
4	94.0607027	1.008072	0	191435.46	27728.158	0	0	0	0	0	187593.472	3841.98237
5	94.2425765	1.015121	0	191518.88	27796.707	0	0	0	0	0	187673.645	3845.23649
6	94.4133652	1.022171	0	191695.12	27880.134	0	0	0	0	0	187907.591	3787.53341
7	94.5220752	1.02922	0	192452.05	28056.375	0	0	0	0	0	189102.216	3349.83052
8	94.2567509	1.036269	0	197295.41	28813.3	0	0	0	0	0	197295.407	0
9	97.1873422	1.043319	0	211117.51	33656.66	0	0	0	0	0	211117.509	0
10	106.390013	1.050368	0	230900.1	47478.762	0	0	0	0	0	230900.098	0
11	114.300372	1.057418	0	244353.88	67261.351	0	0	0	0	0	244353.875	0
12	117.024529	1.064467	0	248884.39	80715.128	0	0	0	0	0	248884.391	0
13	117.793003	1.071517	0	249926.35	85245.644	0	0	0	0	0	249926.346	0
14	118.611501	1.078566	0	243744.67	86287.599	0	0	0	0	0	243744.673	0
15	145.617646	1.085616	59612.44	163638.75	80105.926	0	0	0	163638.747	0	163638.747	0

Stage	I-BUOH	WATER	CO2	OLE[illegible]H
1	0.175304	0.068834	0.000144	0.75[illegible]3
2	0.176064	0.069654	2.77E-06	0.75[illegible]9
3	0.176227	0.069777	5.31E-08	0.75[illegible]6
4	0.176394	0.069879	1.02E-09	0.753726
5	0.176655	0.069947	1.97E-11	0.753398
6	0.177494	0.069801	3.82E-13	0.752705
7	0.18192	0.068339	7.49E-15	0.749741
8	0.211661	0.057001	0	0.731338
9	0.284384	0.032138	0	0.683478
10	0.364523	0.010521	0	0.624956
11	0.406922	0.002509	0	0.590569
12	0.419647	0.000527	0	0.579826
13	0.422474	0.000107	0	0.57742
14	0.40689	2.04E-05	0	0.593089
15	0.118286	1.00E-06	0	0.881713

Table 6. Simulated Stream Outputs for Example 2.

	9	10	11	30	31	40	42	44	45	46	47	48	49
Temperature C	32.2	84.9	125.2	90.6	90.6	56.5	147	45	44	40	40	40	40
Pressure atm	1.09	1.04	1.09	0.99	0.99	0.1	0.11	1.26	1	1	1	1	0.1
Vapor Frac	0	0.063	0	1	1	0	0	0	0	1	0	0	0
Mole Flow kmol/hr	797.981	797.981	431.612	727.821	727.821	241.521	190.091	190.091	538.959	17.528	361.426	348.867	241.521
Mass Flow kg/hr	75171.2	75171.2	67759.48	24453.15	24453.15	17902.59	49856.89	49856.89	56518.78	750.182	17041.08	6661.889	17902.59
Volume Flow l/hr	90271.19	1.50E+06	90110.59	2.17E+07	2.17E+07	23221.75	66101.83	60184.94	66985.58	447766.1	20937.83	6833.643	22799.48
Enthalpy MMBtu/hr	-273.088	-262.246	-157.514	-174.532	-174.532	-75.019	-83.753	-94.595	-188.968	-6.304	-105.921	-94.373	-75.786
Mass Flow kg/hr													
I-BUOH	18869.86	18869.86	18349.44	14357.87	14357.87	17900.73	448.712	448.712	939.7063	29.25273	13837.62	490.9942	17900.73
WATER	6184.856	6184.856	0.067759	9296.486	9296.486	0.067759	4.32E-14	4.32E-14	6162.359	22.93916	3111.188	6162.359	0.067759
CO2	706.512	706.512	0	795.989	795.989	0	0	0	8.536	697.99	89.463	8.536	0
OLEYLOH	49409.97	49409.97	49409.97	2.811	2.811	1.79	49408.18	49408.18	49408.18	0	2.811	0	1.79
Mass Frac													
I-BUOH	0.251025	0.251025	0.270803	0.587158	0.587158	0.999896	0.009	0.009	0.016626	0.038994	0.812015	0.073702	0.999896
WATER	0.082277	0.082277	1.00E-06	0.380175	0.380175	3.78E-06	8.67E-19	8.67E-19	0.109032	0.030578	0.18257	0.925017	3.78E-06
CO2	0.009399	0.009399	1.49E-28	0.032552	0.032552	0	0	0	0.000151	0.930428	0.00525	0.001281	0
OLEYLOH	0.657299	0.657299	0.729196	0.000115	0.000115	0.0001	0.991	0.991	0.87419	2.38E-10	0.000165	1.12E-09	0.0001

Table 7. Simulated BUOHCOL Column Traffic and Liquid Mass Composition Profile Outputs for Example 2.

Stage	Temperatu C	Pressure atm	Heat duty MJ/hr	Liquid flow kg/hr	Vapor flow kg/hr	Liquid feec kg/hr	Vapor feec kg/hr	Mixed feec kg/hr	Liquid proc kg/hr	Vapor product kg/hr
1	56.50411	0.1	-12277.7	580.4229	0	0	0	0	17902.59	0
2	66.12733	0.100357	0	8.058413	18483.01	0	0	0	0	0
3	78.95627	0.100714	0	6.737	17910.65	0	0	0	0	0
4	78.99224	0.101071	0	6.69776	17909.32	0	0	0	0	0
5	78.9936	0.101429	0	6.660182	17909.29	0	0	0	0	0
6	78.99491	0.101786	0	6.622855	17909.25	0	12857.16	0	0	0
7	78.99731	0.102143	0	54908.56	5052.046	54902.32	0	0	0	0
8	79.04864	0.1025	0	54918.21	5051.663	0	0	0	0	0
9	79.09983	0.102857	0	54927.84	5061.317	0	0	0	0	0
10	79.15088	0.103214	0	54937.45	5070.946	0	0	0	0	0
11	79.20184	0.103571	0	54947.02	5080.554	0	0	0	0	0
12	79.25394	0.103929	0	54956.15	5090.13	0	0	0	0	0
13	79.3555	0.104286	0	54948.29	5099.253	0	0	0	0	0
14	81.40961	0.104643	0	54559.54	5091.393	0	0	0	0	0
15	147.02	0.105	10950.61	49856.89	4702.649	0	0	0	49856.89	0

Stage	I-BUOH	WATER	OL[illegible]LOH
1	0.999896	3.78E-06	[illegible]001
2	0.245	8.07E-08	[illegible].755
3	0.098561	2.81E-08	0.901439
4	0.098808	2.82E-08	0.901192
5	0.09925	2.83E-08	0.900749
6	0.099694	2.85E-08	0.900306
7	0.100134	3.18E-09	0.899866
8	0.100292	2.63E-10	0.899708
9	0.100449	2.17E-11	0.899551
10	0.100607	1.79E-12	0.899394
11	0.100763	1.48E-13	0.899237
12	0.100912	1.23E-14	0.899088
13	0.100775	1.01E-15	0.899225
14	0.090278	0	0.909722
15	0.009	0	0.991

Table 8. Simulated Solvent Column Traffic and Liquid Mass Composition Profile Outputs for Example 2.

Stage	Temperatu C	Pressure atm	Heat duty MJ/hr	Liquid flow kg/hr	Vapor flow kg/hr	Liquid feec kg/hr	Vapor feec kg/hr	Mixed feec kg/hr	Liquid proc kg/hr	Vapor proc kg/hr	1st liquid fl kg/hr	2nd liquid flow kg/hr
1	90.62398	0.986923	0	93278.67	24452.8	90384.63	1827.657	0	0	24453.68	90909.07	2369.606
2	91.46275	0.993973	0	93442.51	25519.19	0	0	0	0	0	91034.75	2407.763
3	91.65498	1.001022	0	93481.11	25683.03	0	0	0	0	0	91070.53	2410.574
4	91.83796	1.008072	0	93520.73	25721.63	0	0	0	0	0	91109.71	2411.021
5	92.0175	1.015121	0	93598.2	25761.25	0	0	0	0	0	91213.06	2385.141
6	92.16465	1.022171	0	94198.65	25838.72	0	0	0	0	0	92221.08	1977.569
7	92.40016	1.02922	0	98158.28	26439.17	0	0	0	0	0	98158.28	0
8	95.35407	1.036269	0	107889.8	30398.8	0	0	0	0	0	107889.8	0
9	102.9854	1.043319	0	119982.9	40130.34	0	0	0	0	0	119982.9	0
10	109.7331	1.050368	0	127742.4	52223.47	0	0	0	0	0	127742.4	0
11	112.4066	1.057418	0	130587.3	59982.94	0	0	0	0	0	130587.3	0
12	113.2472	1.064467	0	131403	62827.79	0	0	0	0	0	131403	0
13	113.5887	1.071517	0	131648.5	63643.56	0	0	0	0	0	131648.5	0
14	113.9111	1.078566	0	129620	63889.04	0	0	0	0	0	129620	0
15	125.1555	1.085616	38116.05	67759.48	61860.52	0	0	0	67759.48	0	67759.48	0

Stage	I-BUOH	WATER	CO2	C[illegible]YLOH
1	0.362857	0.107294	0.000112	[illegible]9736
2	0.363393	0.107798	1.41E-06	[illegible]8808
3	0.363534	0.107877	1.77E-08	[illegible]2859
4	0.363698	0.107936	2.22E-10	[illegible]8366
5	0.36426	0.107812	2.81E-12	0.527929
6	0.370412	0.105027	3.59E-14	0.524561
7	0.410794	0.085803	0	0.503402
8	0.494394	0.047597	0	0.458009
9	0.571843	0.016292	0	0.411865
10	0.608865	0.004277	0	0.386858
11	0.620548	0.001017	0	0.378435
12	0.623678	0.000235	0	0.376087
13	0.624558	5.40E-05	0	0.375388
14	0.618452	1.21E-05	0	0.381536
15	0.270803	1.00E-06	0	0.729196

CLAIMS

What is claimed is:

1. A process comprising the steps:
   a) introducing a feed comprising:
      (i) a water-immiscible organic extractant,
      (ii) water,
      (iii) at least one isomer of butanol, and
      (iv) optionally a non-condensable gas

into a first distillation column, wherein the first distillation column comprises a stripping section and optionally a rectifying section at an introduction point above the stripping section, the first distillation column producing a first bottoms stream and a first vaporous overhead stream, the first bottoms stream comprising the water-immiscible organic extractant and butanol and being substantially free of water, and the first vaporous overhead stream comprising water, butanol, and the optional non-condensable gas;

b) condensing the first vaporous overhead stream to produce a gas phase and recover a first mixed condensate, wherein the first mixed condensate comprises

(i) a butanol phase comprising butanol, less than about 30 wt% water; and

(ii) an aqueous phase comprising water and less than about 10 wt% of butanol;

c) introducing at least a portion of the butanol phase to the first distillation column; and

d) introducing a first portion of the first bottoms stream into a second distillation column having a stripping section and optionally a rectifying section and operating the second distillation column to produce a second bottoms stream comprising the extractant and being substantially free of butanol, and a second vaporous overhead stream comprising butanol;

wherein the extractant preferentially dissolves butanol over water and is separable from butanol by distillation.

2. The process of claim 1, further comprising introducing at least a portion of the aqueous phase to a fermentation vessel.

3. The process of claim 1, further comprising withdrawing the bottoms stream from the second distillation column and introducing at least a portion of the withdrawn bottoms stream into a fermentation vessel.

4. The process of claim 3, further comprising introducing at least a portion of the aqueous phase to a fermentation vessel.

5. The process of claim 4, wherein at least a portion of the withdrawn bottoms stream and at least a portion of the aqueous phase are combined before introduction to a fermentation vessel.

6. The process of claim 1, wherein a non-condensable gas is present in the feed and the process further comprises purging at least a portion of the gas phase comprising the non-condensable gas from the process.

7. The process of claim 1, wherein the non-condensable gas comprises carbon dioxide.

8. The process of claim 1, wherein the feed comprises an organic phase obtained from an extractive fermentation.

9. The process of claim 1, wherein the butanol concentration in the feed is from about 0.1 weight percent to about 40 weight percent, based on the weight of the feed.

10. The process of claim 1, wherein the butanol comprises 1-butanol.

11. The process of claim 1, wherein the butanol comprises isobutanol.

12. The process of claim 1, wherein the extractant comprises at least

one solvent selected from the group consisting of C_7 to C_{22} fatty alcohols, C_7 to C_{22} fatty acids, esters of C_7 to C_{22} fatty acids, C_7 to C_{22} fatty aldehydes, and mixtures thereof.

13. The process of claim 12, wherein the extractant comprises oleyl alcohol.

14. The process of claim 13, wherein the butanol consists essentially of 1-butanol.

15. The process of claim 13, wherein the butanol consists essentially of isobutanol.

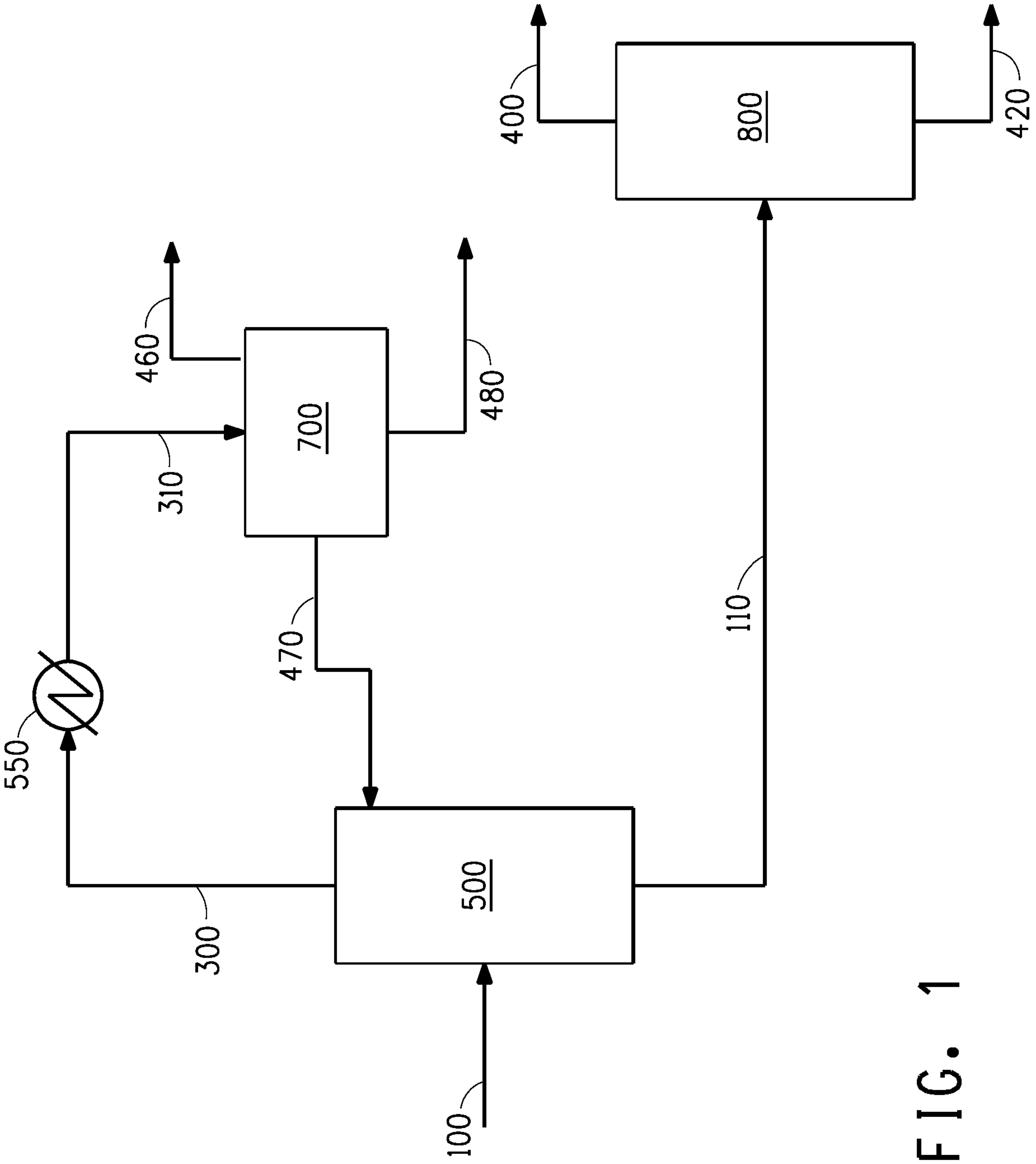
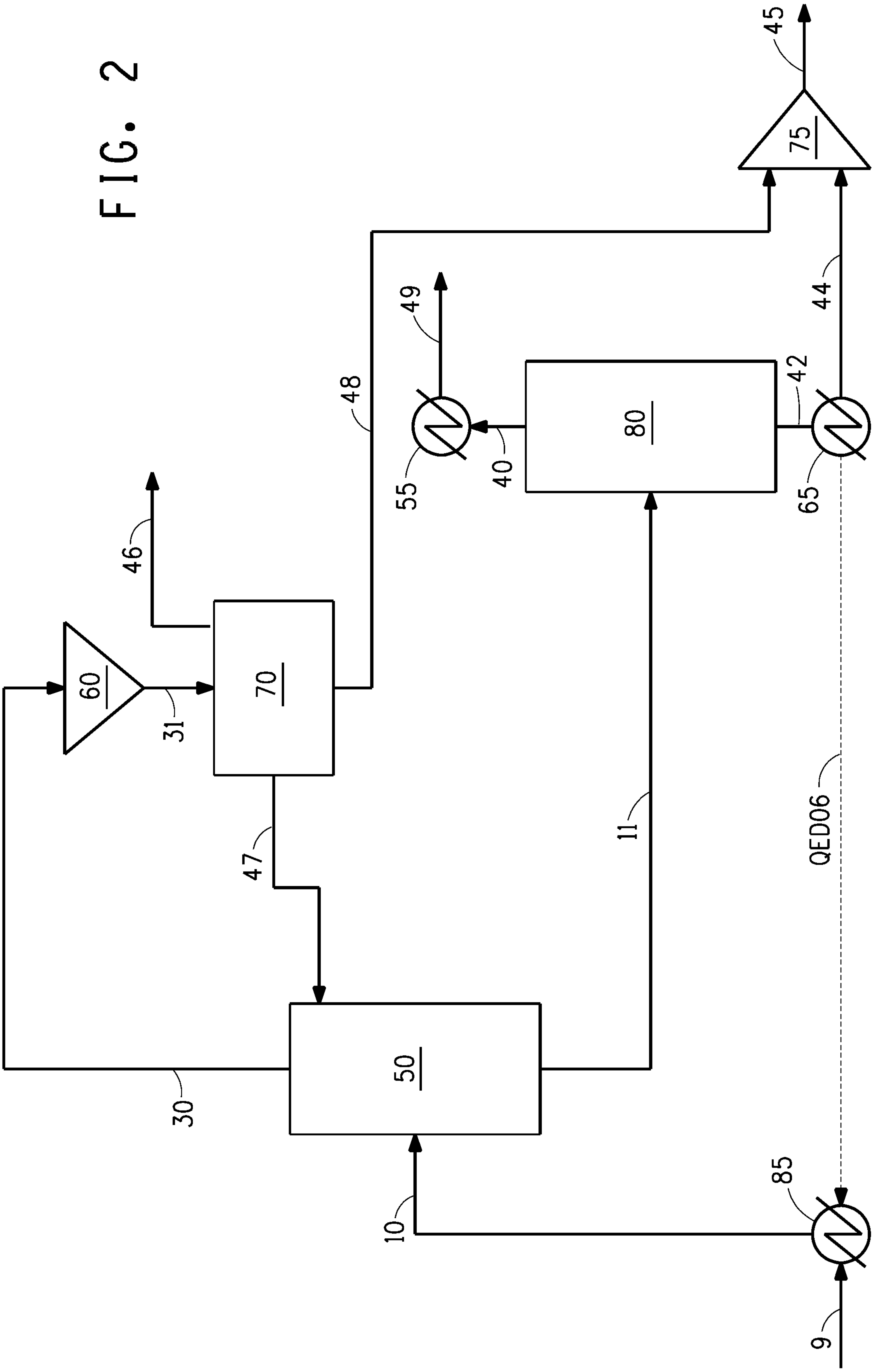
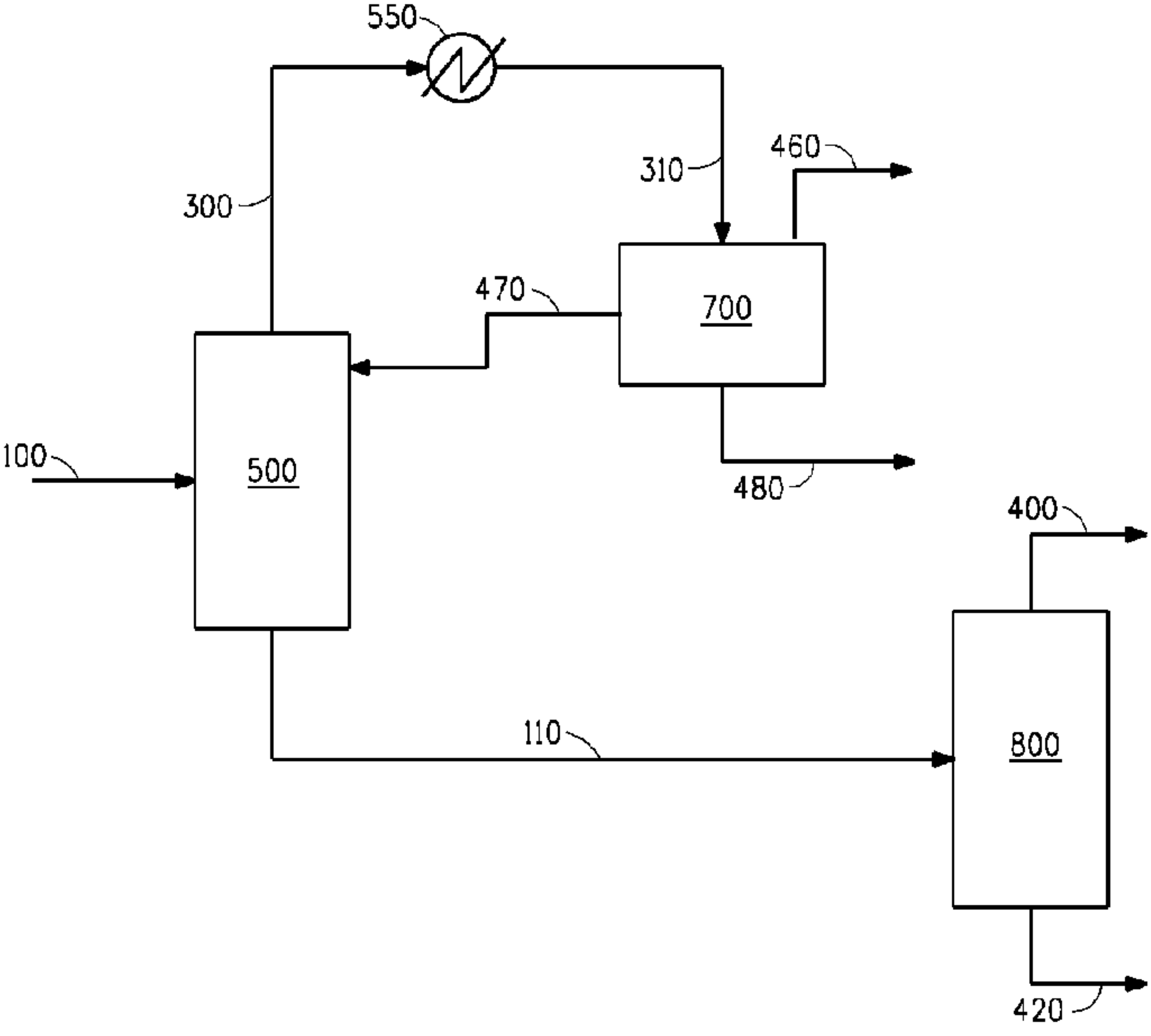


FIG. 1

FIG. 2

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