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Holtzapple et al.

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(54) **METHODS AND SYSTEMS FOR BIOMASS CONVERSION TO CARBOXYLIC ACIDS AND ALCOHOLS**

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(60) Provisional application No. 60/580,291, filed on Jun. 16, 2004.

(51) **Int. Cl.**

C12P 7/40	(2006.01)
C12P 7/64	(2006.01)

(52) **U.S. Cl.** **435/136**; 435/134; 435/135; 435/161

(58) **Field of Classification Search** 435/134, 435/135, 136
See application file for complete search history.

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(57) **ABSTRACT**

The disclosure includes a method, process and apparatus for the conversion of biomass to carboxylic acids and/or primary alcohols. The system may include a pretreatment/fermentation subsystem operable to produce a fermentation broth containing carboxylic acid salts from biomass, such as lignocellulosic biomass. The system may also include a dewatering subsystem operable to remove excess water from the fermentation broth to produce a concentrated product. The system may also includes an acid springing subsystem operable to produce a mixed carboxylic acid product. The system may also include a hydrogenation subsystem operable to produce an alcohol mixture, such as a mixture containing primary alcohols. Methods of operating this system or other systems to obtain a carboxylic acid or alcohol mixture are also provided.

10 Claims, 5 Drawing Sheets

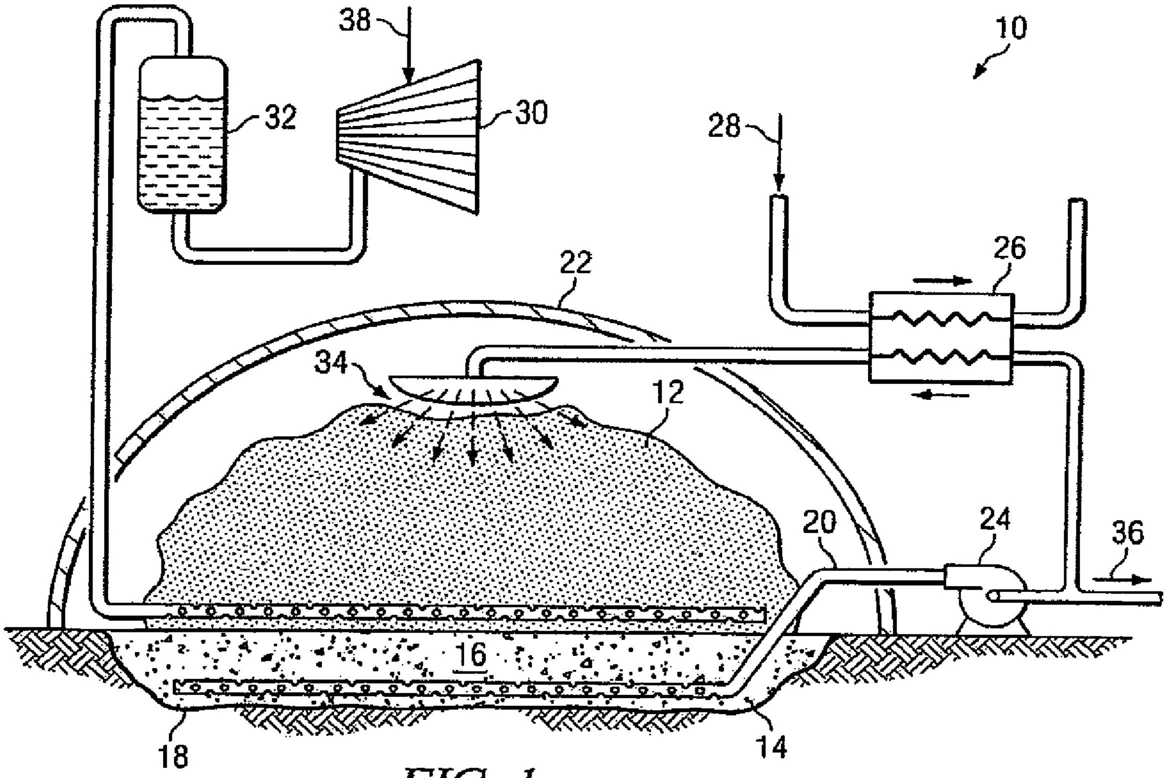

FIG. 1

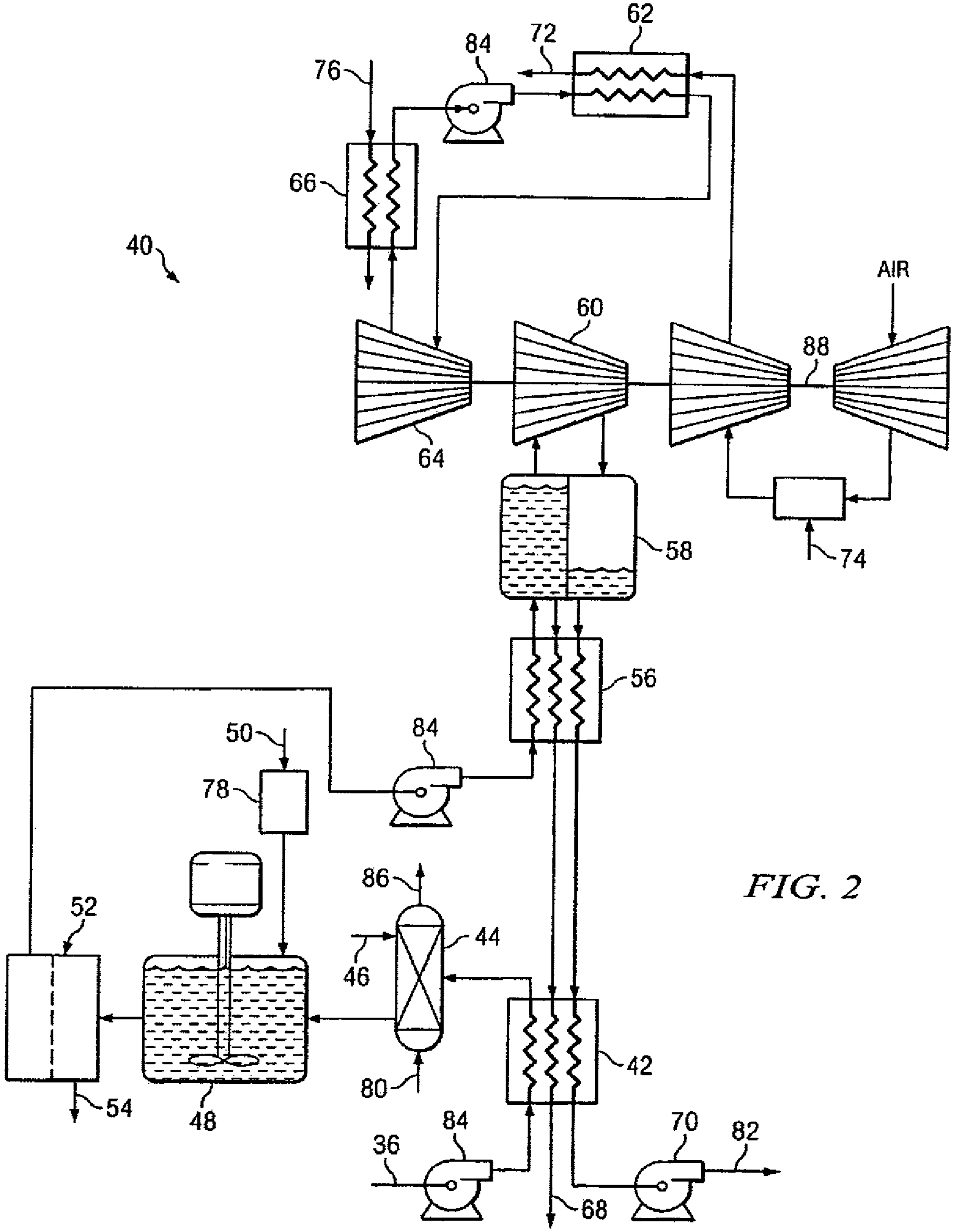
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FIG. 2

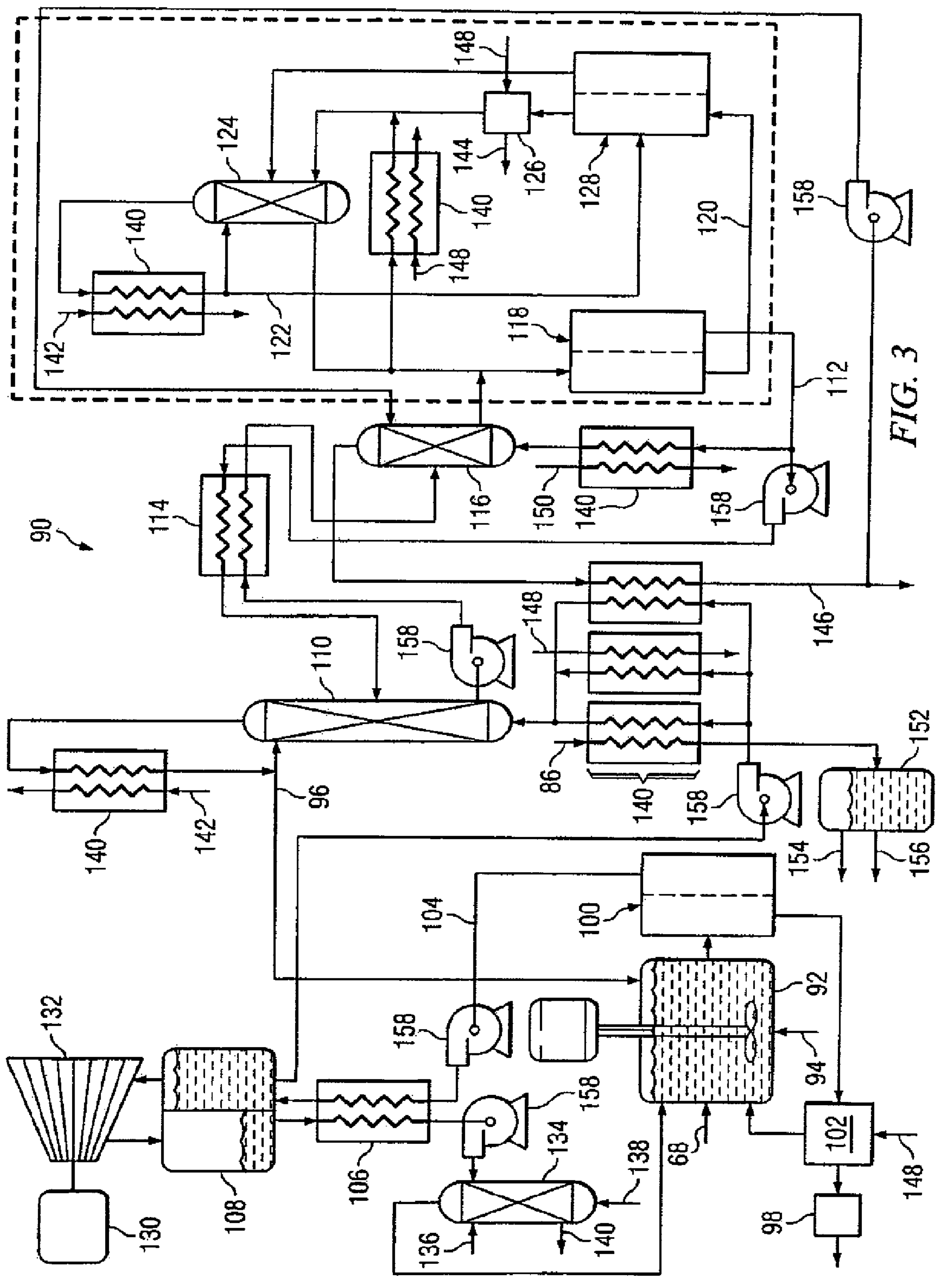
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FIG. 3

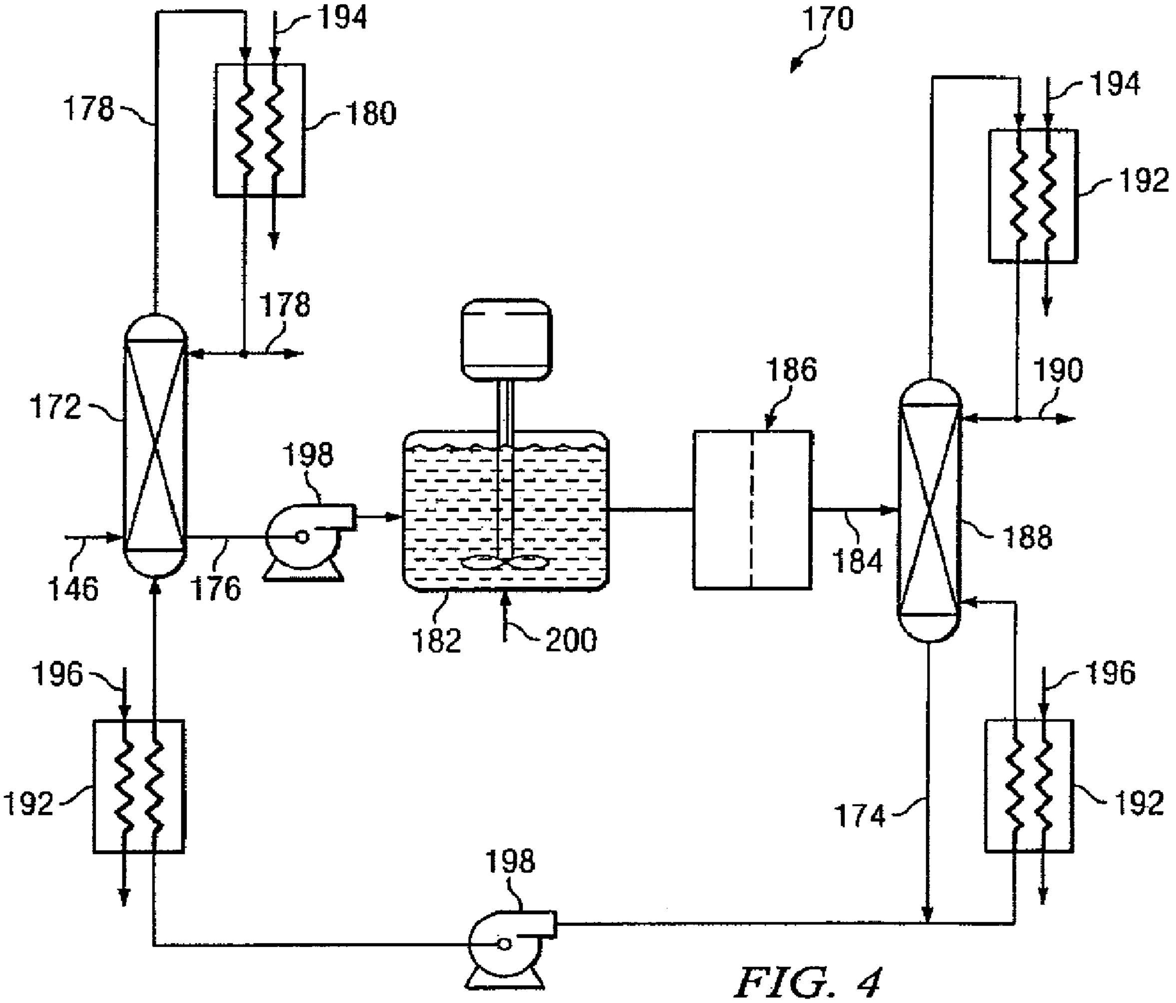
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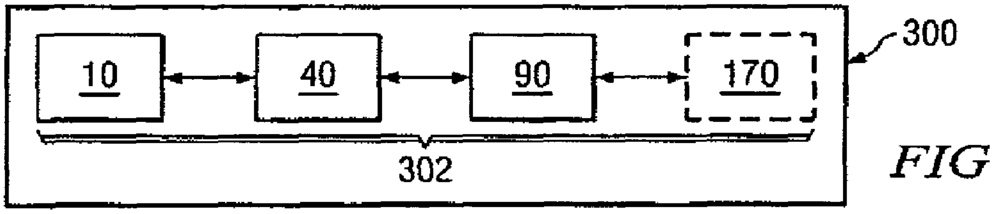
FIG. 4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302
300

FIG. 5

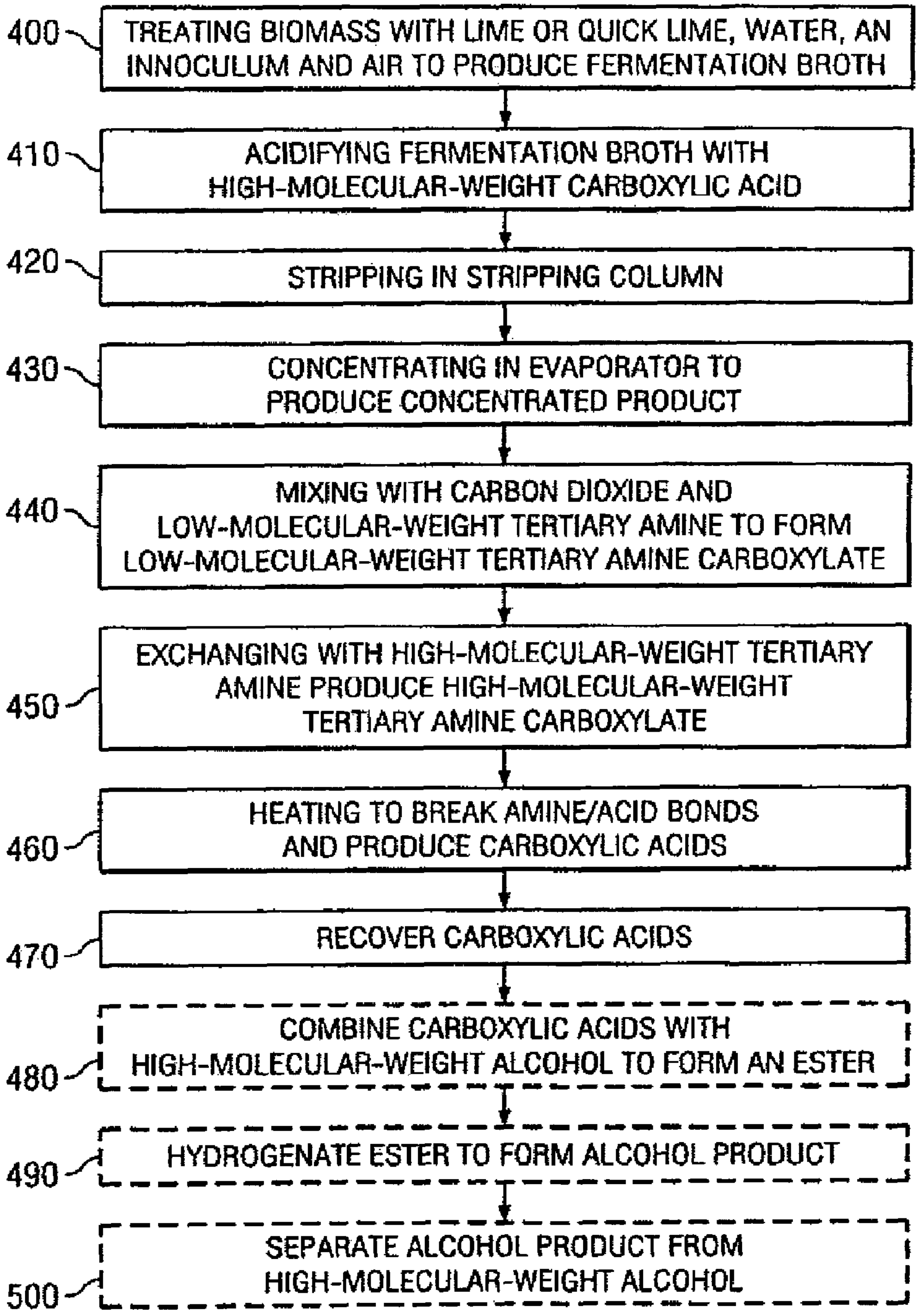
400
TREATING BIOMASS WITH LIME OR QUICK LIME, WATER, AN INNOCULUM AND AIR TO PRODUCE FERMENTATION BROTH
410
ACIDIFYING FERMENTATION BROTH WITH HIGH-MOLECULAR-WEIGHT CARBOXYLIC ACID
420
STRIPPING IN STRIPPING COLUMN
430
CONCENTRATING IN EVAPORATOR TO PRODUCE CONCENTRATED PRODUCT
440
MIXING WITH CARBON DIOXIDE AND LOW-MOLECULAR-WEIGHT TERTIARY AMINE TO FORM LOW-MOLECULAR-WEIGHT TERTIARY AMINE CARBOXYLATE
450
EXCHANGING WITH HIGH-MOLECULAR-WEIGHT TERTIARY AMINE PRODUCE HIGH-MOLECULAR-WEIGHT TERTIARY AMINE CARBOXYLATE
460
HEATING TO BREAK AMINE/ACID BONDS AND PRODUCE CARBOXYLIC ACIDS
470
RECOVER CARBOXYLIC ACIDS
480
COMBINE CARBOXYLIC ACIDS WITH HIGH-MOLECULAR-WEIGHT ALCOHOL TO FORM AN ESTER
490
HYDROGENATE ESTER TO FORM ALCOHOL PRODUCT
500
SEPARATE ALCOHOL PRODUCT FROM HIGH-MOLECULAR-WEIGHT ALCOHOL

FIG. 6

METHODS AND SYSTEMS FOR BIOMASS CONVERSION TO CARBOXYLIC ACIDS AND ALCOHOLS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation of U.S. patent application Ser. No. 11/153,978, filed Jun. 16, 2005, now U.S. Pat. No. 7,820,417 which claims the benefit under 35 U.S.C. §119(e) of U.S. Provisional Patent Application No. 60/580,291 filed Jun. 16, 2004, the disclosures of which are hereby incorporated herein by reference.

FIELD OF THE INVENTION

The present invention relates to methods of converting biomass to useful substances, such as carboxylic acids and primary alcohols, through an integrated pretreatment, fermentation, dewatering and treatment process. More specifically it may relate to a method applied to lignocellulosic biomass.

BACKGROUND

A great deal of biomass, particularly lignocellulosic biomass, remains unused or inefficiently used during agricultural and industrial processes. Disposal of this biomass is often difficult or costly. Therefore, methods of using this biomass to produce useful chemicals are quite valuable.

Organic acids are important chemicals of commerce. Historically, organic acids were produced from animal fat or vegetable oil sources or from petroleum sources in substantially nonaqueous systems. More recently, organic acids have been identified as among the most attractive products for manufacture from biomass by fermentation. Alcohols are also important industrial chemicals that may be produced by fermentation of biomass. However, extraction of organic acids and alcohols from the overall fermentation product is not easy and is often inefficient in the use of energy, water and reactant chemicals.

SUMMARY

The present invention includes a method, process and apparatus for the conversion of biomass to carboxylic acids and/or primary alcohols.

According to one embodiment, the invention includes a system for the conversion of biomass. The system includes a pretreatment/fermentation subsystem operable to pretreat biomass with lime or quick lime and air to produce treated biomass and ferment the treated biomass with an inoculum to produce a fermentation broth containing carboxylic acid salts. The system also includes a dewatering subsystem operable to remove excess water from the fermentation broth to produce a concentrated product. Finally, the system includes an acid springing subsystem operable to combine the concentrated product with a low-molecular-weight tertiary amine or ammonia to produce a low-molecular-weight tertiary amine or ammonia carboxylate product from the carboxylic acid salts, replace the low-molecular-weight tertiary amine or ammonia in the low-molecular-weight tertiary amine or ammonia carboxylate product with a high-molecular-weight tertiary amine to form a high-molecular-weight tertiary amine carboxylate product, and thermally break the amine-carboxylate bonds in the high-molecular-weight tertiary amine carboxylate product to produce a mixed carboxylic acid product.

In a more specific embodiment the system may also include a hydrogenation subsystem operable to combine the mixed carboxylic acid produce with a high-molecular-weight alcohol to form an ester, convert the ester to an alcohol mixture using a hydrogenation catalyst, and separate the alcohol mixture from the high-molecular-weight alcohol.

According to another embodiment, the invention includes a method of obtaining a fermentation product. The method may include: treating a pile of biomass with lime or quick lime, water, an innoculum and air to produce a fermentation broth; acidifying the fermentation broth with a high-molecular-weight carboxyllic acid to produce acidified fermentation broth; stripping the fermentation broth in a stripping column to produce stripped fermentation broth; concentrating the stripped fermentation broth in an evaporator to produce concentrated product; mixing the concentrated product with a low-molecular-weight tertiary amine or ammonia and carbon dioxide to produce a low-molecular-weight tertiary amine or ammonia carboxylate; exchanging the low-molecular-weight tertiary amine or ammonia carboxylate with a high-molecular-weight tertiary amine to produce a high-molecular-weight tertiary amine carboxylate; heating the high-molecular-weight tertiary amine carboxylate to a temperature sufficient to break acid/amine bonds to produce a free carboxylic acid product; and recovering the free carboxylic acid product.

In a more specific embodiment, the method may also include: combining the carboxylic acid produce with a high-molecular-weight alcohol to from an ester; hydrogenating the ester to form an alcohol product; separating the high-molecular-weight alcohol from the alcohol product; and recovering the alcohol product.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention may be better understood through reference to the following detailed description, taken in conjunction with the drawings, in which:

FIG. **1** illustrates a pretreatment and fermentation system, according to an embodiment of the present invention;

FIG. **2** illustrates a dewatering system, according to an embodiment of the present invention;

FIG. **3** illustrates an acid springing system, according to an embodiment of the present invention;

FIG. **4** illustrates a hydrogenation system, according to an embodiment of the present invention;

FIG. **5** illustrates a biomass converting system, according to an embodiment of the present invention; and

FIG. **6** illustrates a flow diagram of a method for producing carboxylic acids and alcohols, according to an embodiment of the invention.

DETAILED DESCRIPTION

The present invention relates to systems, methods, and devices for the conversion of biomass, particularly lignocellulosic biomass, to carboxylic acids and alcohols, particularly primary alcohols.

Referring now to FIG. **1**, pretreatment and filtration system **10** may be provided in which biomass pile **12** may be blended with lime or quick lime (calcium carbonate or calcium oxide) and carbon dioxide (not shown) and piled on top of pit **14** filled with gravel **16**. Pit **14** may also be lined with liner **18**. Biomass pile **12** may include any sort of biomass. In selected embodiments it may include lignocellulosic biomass, such as processed sugarcane or sorghum stalks or corn stover. Perforated drain pipe **20** may be embedded in gravel **16**. Biomass pile **12** may be covered by cover **22** to keep out rain and debris, particularly if system **10** is outside. Pump **24** may circulate water **34** from pit **14** to the top of biomass pile **12**. As water **34** circulates through pile **12**, it may flow through heat exchanger **26**, which may regulate the temperature. Cooling water or heat source **28** may also circulate through heat exchanger **26**.

During approximately the first month after biomass pile **12** is assembled, air **38** may be blown through pile **12** using blower **30**. To remove carbon dioxide from the air, it may be bubbled through lime water slurry **32**. Oxygen-rich air **28** may also be supplied. The combined effect of lime plus air **28** in pile **12** removes lignin from the biomass, rendering it more digestible. Further, the lime removes acetyl groups from hemicellulose, which also helps digestibility. Once the lime is exhausted, the pH drops to near neutral, at which point a mixed-culture inoculum may be added.

The inoculum may be derived from any source, but in many embodiments it may be derived from soil. Organisms derived from organic-rich soil in marine environments appear to be particularly well-suited for use with embodiments of the present invention. Such organisms are able to be productive in high-salt environments. For example, the innoculum may include a salt-tolerant microorganism.

After inoculation, the organisms digest the biomass and convert it to carboxylic acids. These acids react with the calcium carbonate or calcium oxiode in pile **12**, producing calcium carboxylate salts or other calcium salts that are dissolved in the water that circulates through the pile. This aqueous solution, called fermentation broth **36** may be harvested and sent for further processing.

Referring now to FIG. **2**, fermentation broth **36** may be dewatered in dewatering system **40**. Fermentation broth **26** may be pumped through heat exchanger **42**, which preheats the broth. Preheated fermentation broth **36** may then be acidified with high-molecular-weight carboxylic acid **46** (e.g. caproic, valeric, hepotanoic acids). Acidified fermentation broth **36** may be sent to stripping column **44** where steam **80** strips out dissolved carbon dioxide, a noncondensible gas that may interferes with evaporator **58** and cause calcium carbonate scaling on heat exchanger **56**. Preferably, stripper **44** may operate at 1 atm, or higher, which allows exiting steam **86** to be used for heat elsewhere in the process. Further, if heat exchanger **42** becomes fouled by dissolved calcium carbonate, the pressure in stripper **44** may be reduced, which lowers the temperature of steam exiting heat exchanger **42** and may reduce fouling. However, if stripper **44** is operated at a reduced pressure, a vacuum pump (not shown) may be needed to remove the noncondensible gases from fermentation broth **36**.

Steam-stripped, acidified fermentation broth **36** may then be sent to mixer **48** where the pH may be raised to between approximately 11 and 12 through the addition of lime **50** from reservoir **78**, which causes scum **54** to precipitate. Scum **54** may then be removed in solids separator **52**. This degassed, descummed fermentation broth **36** may be further heated in heat exchanger **56**, after which it may enter evaporator **58**. Compressor **60** may evaporate water from the low-pressure chamber of evaporator **58**. The heat of condensation released in the high-pressure chamber of evaporator **58** may provide the heat of evaporation needed in the low-pressure chamber. The energy needed to drive the evaporation process may be provided by an engine.

In the embodiment shown in FIG. **2**, a combined cycle engine may be used, which increases energy efficiency. Gas turbine **88** may provide shaft power to compressor **60**. Gas turbine may use fuel **74**. Exhaust gas **72** from gas turbine **88** may be directed to boiler **62**, which may produce high-pressure steam that may drives steam turbine **64**. Heat exchanger **66** may condense the low-pressure steam exiting steam turbine **64**. Cooling water **76** may be used to facilitate this cooling. Distilled water **82** from the high-pressure section of evaporator **58** may be cooled in heat exchangers **56** and **42**, and may be returned to pretreatment/fermentation system **10**. Concentrated product **68** may be cooled in heat exchangers **56** and **42**, and sent to acid springing system **90**. Liquid turbine **70** may recapture some work from the high-pressure liquids that exit evaporator **58**.

Pumps **84** may be included at various points in the system to facilitate fluid flow.

Referring now to FIG. **3**, concentrated product **68** may next be sent to acid springing system **90**. In mixer **92**, concentrated product **68** from dewatering system **40** may be mixed with carbon dioxide **94** and low-molecular-weight tertiary amine **96**, such as triethyl amine. The carboxylate reacts with low-molecular-weight tertiary amine **96** to form a soluble salt. The calcium reacts with carbon dioxide **94** to form insoluble calcium carbonate **98**, which may be recovered using solids separator **100**. Calcium carbonate **98** may then be washed with distilled water to remove adhering product and steam stripped in vessel **102** to ensure that all low-molecular-weight tertiary amine **96** is removed from calcium carbonate **98**. Calcium carbonate **98** may then be sent to pretreatment/fermentation system **10** to act as a buffer or to a lime kiln (not shown) to be converted to lime.

Aqueous solution **104** contains dissolved low-molecular-weight tertiary amine carboxylate. It may then be preheated in heat exchanger **106** and sent to evaporator **108**, where most of the water may be removed using the same vapor-compression technology used in dewatering system **40**. Specifically, turbine **130** may provide energy to compressor **132**. Waste fluid exiting evaporator **108** may be sent to column **134** where it may be combined with lime **136** and steam **138** to provide additional product stream to mixer **92** and water **140** to pretreatment/fermentation system **10**.

The concentrated low-molecular-weight tertiary amine carboxylate solution **104** may then be sent to column **110** where high-molecular-weight tertiary amine **112**, such as trioctyl amine or triethanol amine, may be added. Low-molecular-weight tertiary amine **96** may be replaced and exit the top of column **110**, while high-molecular-weight tertiary amine carboxylate solution **104** may exit the bottom of column **110**.

The high-molecular-weight tertiary amine carboxylate solution **104** may then be preheated in heat exchanger **114** and sent to column **116**. In column **116**, the temperature may be high enough to break chemical bonds, allowing the more volatile carboxylic acids **146** to exit the top of column **116**. The less volatile high-molecular-weight tertiary amine **112** may exit the bottom of the column and may be recycled to column **110**.

Any salts **120** that are in high-molecular-weight tertiary amine **112** may be removed using a solids separator **118**. Recovered salts **120** may be washed with volatile solvent **122**, such as triethyl amine, to remove high-molecular-weight tertiary amine **112** in separator **118**. Solvent **122** may be separated from the recovered high-molecular-weight tertiary amine in distillation column **124**. Salts **120** may then be steam stripped in stripper **126** to remove volatile solvent **122** and form solids **144**.

System **90** may contain various heat exchangers **140** that may be used to recycle process heat. Various fluids may pass through these heat exchangers, such as cooling waters **142**, steam **148**, and fuel **150**. In one heat exchanger **140**, steam **86** from dewatering system **40** may be used as a heat source then collected in condensor **152** where carbon dioxide **154** may be separated from water **156**, which may be returned to fermentation/pretreatment system **10**.

Pumps **158** may also be included at various points in the system to facilitate fluid flow.

Referring now to FIG. **4**, mixed carboxylic acids **146** from acid springing system **90** may be sent to hydrogenation system **170**. Mixed acids **146** may be placed in column **172** and combined with high-molecular-weight alcohol **174** such as heptanol. Carboxylic acids **146** react with alcohol **174** to form ester **176** and water **178**. Water **178** may be separated in column **172** and sent to heat exchanger **180** then returned to column **172** or used elsewhere in systems **10**, **40**, **90** or **170**. Ester **176** may be sent to hydrogenation reactor **182** which contains a suitable hydrogenation catalyst, such as a Raney nickel. In reactor **182**, hydrogen **200** is added and ester **176** is converted to alcohol. Solids may be separated from alcohol **184** using solids separator **186**. Alcohol mixture **184** may be sent column **188** which may recover high-molecular-weight alcohol **174** from the bottom and alcohol product **190** from the top. Alcohol product **190** may be a primary alcohol.

System **170** may contain various heat exchangers **192** that may be used to recycle process heat. Various fluids may pass through these heat exchangers, such as cooling waters **194** and steam **196**. Pumps **198** may also be included at various points in the system to facilitate fluid flow.

Alternative systems to recover carboxylic acids without production of alcohol are known in the art any may be used in place of the hydrogenation system of FIG. **4**.

Referring now to FIG. **5**, system **300** may include as subsystems **302** pretreatment/fermentation system **10**, dewatering system **40**, acid sprining system **90** and optionally also hydrogenation system **170**. System **300** may reuse process heat, water, lime, carbon dioxide and other materials among different subsystems **302**.

In an alternative embodiment not explicitly shown, ammonia may be used in place of low-molecular-weight tertiary amine **96** in acid sprining system **90**. Further, if the ammonia is supplied earlier, the a reaction between calcium carboxylate, carbon dioxide and ammonia may occur prior to entry into dewatering system **40**. In this embodiment, an aqueous solution of ammonia carboxylate may be evaporated in dewatering system **40** rather than calcium carboxylate. This may help prevent scaling in heat exchangers or system **40** because ammonium salts have a lesser tendency to scale than calcium salts. Ammonia is also cheap and lost ammonia may be diverted to pretreatment/fermentation system **10** where it may serve as a nitrogen source. However, ammonia may react with carboxylic acids to form amides, which may not be a desired byproduct.

Embodiments of the invention may include all processes involved in the operation of the above-described systems. Referring now to FIG. **6**, the invention may include an integrated method for producing carboxylic acids and alcohols. The method may include treating pile of biomass **12** with lime or quick lime, water **34**, an innoculum and air in step **400** to produce fermentation broth **36**. In step **410**, fermentation broth **36** may be acidified with high-molecular-weight carboxylic acid **46** then, in step **420**, stripped in stripping column **44**. In step **430**, the product may be concentrated in evaporator **58** to produce concentrated product **68**. Concentrated product **68** may be mixed with carbon dioxide **94** and low-molecular-weight tertiary amine **96** in step **440** to form a low-molecular-weight tertiary amine carboxylate. This carboxylate may be exchanged with high-molecular-weight tertiary amine **112** in column **110** in step **450** to produce a high-molecular-weight tertiary amine carboxylate. The high-molecular-weight tertiary amine carboxlate may be heated in column **116** to a temperature high enough to break the acid to amine bonds in step **460**. This produces carboxylic acids **146** which may be recovered in step **470**. In some embodiments, carboxylic acids **146** may be combined with high-molecular-weight alcohol **174** to form ester **176** in step **480**. In step **490**, ester **176** may be hydrogenated in chamber **182** to form alcohol product **190**. In step **500**, high-molecular-weight alcohol **174** and alcohol product **190** may be separated in column **188**. Alcohol product **190** may be a primary alcohol.

In an alternative embodiment, ammonia may be used in place of low-molecular-weight tertiary amine **96**. Ammonia may be added immediately after step **400**.

Various methods, systems and apparati useful in the present invention may also be described in U.S. Pat. No. 6,043,392, issued Mar. 28, 2000, U.S. Pat. No. 5,986,133, issued Nov. 16, 1999, U.S. Pat. No. 6,478,965, issued Nov. 12, 2002, U.S. Pat. No. 6,395,926, issued May 28, 2002, U.S. Pat. No. 5,962,307, issued Oct. 5, 1999, and WO 04/041995, published May 21, 2004, and their U.S. and foreign counterpart applications and patents. All of the above patents and applications are incorporated by reference herein.

What is claimed is:

1. A method comprising:

treating biomass with an inoculum to produce a fermentation broth;

mixing the fermentation broth with ammonia and carbon dioxide or with ammonium bicarbonate to produce a mixture comprising ammonium carboxylate; and

reacting said mixture with an alcohol to form an ester and to release ammonia.

2. The method of claim **1** wherein said inoculum comprises a salt-tolerant microorganism.

3. The method of claim **1** wherein the biomass comprises lignocellulosic biomass.

4. The method of claim **1** further comprising pretreating the biomass with lime or quick lime prior to treating the biomass with the inoculum.

5. The method of claim **4** further comprising:

removing carbon dioxide from air to produce treated air; and

adding said treated air to the biomass while pretreating the biomass.

6. The method of claim **1** further comprising dewatering the mixture comprising ammonium carboxylate prior to reacting the mixture.

7. The method of claim **1** further comprising recycling the released ammonia from the reaction step to the mixing step.

8. The method of claim **1**, wherein said alcohol comprises a high molecular weight alcohol.

9. The method of claim **1** further comprising:

acidifying the fermentation broth with a carboxylic acid to produce acidified fermentation broth; and

stripping the acidified fermentation broth prior to mixing the fermentation broth with ammonia and carbon dioxide or with ammonium bicarbonate.

10. The method of claim **9** wherein stripping said acidified fermentation broth comprises removing carbon dioxide dissolved therein.

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