

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
4 June 2009 (04.06.2009)

PCT

(10) International Publication Number
WO 2009/068110 A1

(51) International Patent Classification:
C07C 29/84 (2006.01)

(21) International Application Number:
PCT/EP2007/063068

(22) International Filing Date:
30 November 2007 (30.11.2007)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicant (for all designated States except US):
METABOLIC EXPLORER [FR/FR]; Biopole Clermont-Limagne, F-63360 Saint Beuzire (FR).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **OLLIVIER, Frédéric** [FR/FR]; 17 rue de Créqui, F-69006 Lyon (FR).
ROUSSEAU, Pascal [FR/FR]; 21 rue Dussaussoy, F-69006 Lyon (FR).

(74) Agent: **CABINET REGIMBEAU - WARCOIN, AHNER, TEXIER, LE FORESTIER, CALLON DE LAMARCK, COLLIN, TETAZ**; 139 rue Vendôme, F-69477 Lyon Cedex 06 (FR).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:

— of inventorship (Rule 4.17(iv))

Published:

— with international search report



WO 2009/068110 A1

(54) Title: METHOD FOR PURIFYING AN ALCOHOL FROM A FERMENTATION BROTH

(57) Abstract: Method for purifying an alcohol, notably 1,3-propanediol, from a fermentation broth.

METHOD FOR PURIFYING AN ALCOHOL FROM A FERMENTATION BROTH

The present invention relates to the purification of an alcohol from a fermentation broth.

5 The production of alcohol by microbial fermentation has many advantages. For example, the production of butanol, 1,3-propanediol and 1,2-propanediol by fermentation are well known. The raw material in the fermentation medium can be glycerol. The synthesis of 1,3-propanediol by fermentation of glycerol by *clostridium* has been described in particular. The synthesis of 1,3-propanediol by fermentation of glycerol provides a
10 significant reduction in production costs compared to chemical synthesis using petroleum products.

The production of alcohols by fermentation is often accompanied by the production of organic acids and/or ketones. Thus, the production of 1,3-propanediol by microbial fermentation can be accompanied by the co-production of other products including
15 acetone or acids in the form acetic and/or butyric acids or acetate and/or butyrate salt.

The alcohol produced by fermentation must then be purified from the fermentation broth. The fermentation broth can contain by-products that are also advantageous to purify (acetone, butyrate or acetate, for example) in addition to, typically, water, organic impurities, mineral salts and organic salts.

20 In the specific case of 1,3-propanediol, organic impurities responsible for 1,3-propanediol's color and odor are often observed. These impurities have not been identified but it is possible that they occur due to 1,3-propanediol degradation. Such degradation must thus be avoided during 1,3-propanediol production and purification.

A problem encountered during the purification of alcohol from fermentation broth
25 is the elimination of salts. These salts are typically sodium chlorides and calcium chlorides but also ammonium and phosphate salts. The concentration of these salts in the fermentation broth controls their precipitation during alcohol purification.

Many methods for purifying 1,3-propanediol from fermentation broth have been described, notably EP 1,218,327, US 7,056,439, EP 1,103,618 and WO2004/101479.

30 With regard to salts, most notably it has been proposed to eliminate salts upstream from the purification method by various techniques such as the use of ion-exchange resins (WO2004101479), electrodialysis (Gong et al., 2006; Gong et al., 2004) and precipitation-filtration (US 6,361,983).

However, these techniques do not always provide satisfactory results.

The present invention proposes a novel method for purifying an alcohol, notably 1,3-propanediol, from a fermentation broth.

Advantageously, the methods according to the present invention avoid the precipitation of salts during the purification of alcohol from the fermentation broth. In the
5 inventive methods, the addition of glycerol solubilizes salts in order to retain them in the liquid phase until the end of the purification process.

Advantageously, the methods according to the present invention prevent the appearance of the impurities responsible for 1,3-propanediol color and odor.

10 According to another advantage of the present invention, the methods of the present invention provide improved yield.

Description of the invention

15 The invention relates to methods for purifying an alcohol from a fermentation broth comprising at least the following steps:

- filtering the fermentation broth in order to obtain an aqueous solution containing the alcohol,
- adding glycerol to the aqueous solution,
- 20 - recovering the alcohol.

In one embodiment of the invention, the purification method comprises at least the following steps:

- filtering the fermentation broth in order to obtain an aqueous solution containing the alcohol,
- 25 - eliminating water from the aqueous solution,
- adding glycerol to the aqueous solution,
- recovering the alcohol.

In one embodiment of the invention, the purification method comprises at least the following steps:

- 30 - filtering the fermentation broth in order to obtain an aqueous solution containing the alcohol,
- eliminating water from the aqueous solution,
- adding glycerol to the aqueous solution,

- eliminating by distillation products with a vapor pressure greater than that of the alcohol to be purified,
- eliminating by distillation products with a vapor pressure less than that of the alcohol to be purified,
- 5 - recovering the alcohol.

In a specific embodiment of the invention, the purification method also comprises a step of adjusting the pH of the aqueous solution to $\text{pH} < 7$.

In another specific embodiment of the invention, the purification method also comprises a step of extracting with a hydrophobic solvent to eliminate organic acids.

10 In another embodiment of the invention, the purification method also comprises a step of eliminating anions in the aqueous solution.

Preferably, water is eliminated by evaporation in the inventive methods.

Preferentially, glycerol is added in proportions ranging from 5% to 100% by weight of the aqueous solution.

15 The invention thus relates to the use of glycerol to purify an alcohol from a fermentation broth.

In a preferred embodiment of the invention, the alcohol to be purified from the culture broth is 1,3-propanediol.

Advantageously, after recovering the alcohol, glycerol is recovered.

20 Glycerol may be recovered by standard methods well known to the skilled person. Glycerol may for example be recovered by distillation.

According to a first embodiment, the method for purifying an alcohol from a culture broth comprises at least the following steps:

- 25 - filtering the fermentation broth in order to obtain an aqueous solution containing the alcohol,
- evaporating water in the aqueous solution,
- adding glycerol to the aqueous solution,
- eliminating by distillation products with a vapor pressure greater than that of
- 30 the alcohol to be purified,
- eliminating by distillation products with a vapor pressure less than that of the alcohol to be purified,
- recovering the alcohol.

In another embodiment of the invention, the purification method comprises at least the following steps:

- filtering the fermentation broth in order to obtain an aqueous solution containing the alcohol,
- 5 – evaporating water in the aqueous solution,
- adjusting the pH of the aqueous solution to $\text{pH} < 7$, preferably < 3 ,
- adding glycerol to the aqueous solution,
- eliminating by distillation products with a vapor pressure greater than that of the alcohol to be purified,
- 10 – eliminating by distillation products with a vapor pressure less than that of the alcohol to be purified,
- recovering the alcohol.

In another embodiment of the invention, the purification method comprises at least the following steps:

- 15 – filtering the fermentation broth in order to obtain an aqueous solution containing the alcohol,
- evaporating water in the aqueous solution,
- adjusting the pH of the aqueous solution to $\text{pH} < 7$, preferably < 3 ,
- extracting with a hydrophobic solvent to eliminate organic acids,
- 20 – adding glycerol to the aqueous solution,
- eliminating by distillation products with a vapor pressure greater than that of the alcohol to be purified,
- eliminating by distillation products with a vapor pressure less than that of the alcohol to be purified,
- 25 – recovering the alcohol.

In another embodiment of the invention, the purification method comprises at least the following steps:

- filtering the fermentation broth in order to obtain an aqueous solution containing the alcohol,
- 30 – eliminating anions in the aqueous solution, preferably by a strong ion-exchange resin,
- evaporating water in the aqueous solution,
- adding glycerol to the aqueous solution,

- eliminating by distillation products with a vapor pressure greater than that of the alcohol to be purified,
- eliminating by distillation products with a vapor pressure less than that of the alcohol to be purified,
- 5 - recovering the alcohol.

In another embodiment of the invention, the purification method comprises at least the following steps:

- quenching fermentation by adding a base
- filtering the fermentation broth in order to obtain an aqueous solution
10 containing the alcohol,
- evaporating water in the aqueous solution,
- adding glycerol to the aqueous solution,
- eliminating by distillation products with a vapor pressure greater than that of the alcohol to be purified,
- 15 - eliminating by distillation products with a vapor pressure less than that of the alcohol to be purified,
- recovering the alcohol.

In another embodiment of the invention, the purification method comprises at least the following steps:

- 20 - filtering the fermentation broth in order to obtain an aqueous solution containing the alcohol,
- evaporating water in the aqueous solution,
- adding glycerol to the aqueous solution,
- bleaching,
- 25 - eliminating by distillation products with a vapor pressure greater than that of the alcohol to be purified,
- eliminating by distillation products with a vapor pressure less than that of the alcohol to be purified,
- recovering the alcohol.

30

The invention thus relates to the purification of an alcohol from a fermentation broth. "Alcohol" means a molecule with at least one alcohol function. Preferably, the alcohol to be purified is a diol or a heavy alcohol. Preferentially, the alcohol is selected

from among butanol, 1,3-propanediol and 1,2-propanediol. More preferentially, the invention relates to the purification of 1,3-propanediol from a fermentation broth.

Advantageously, the raw material used in the production of alcohol by fermentation is glycerol.

5 Thus, the invention most notably relates to the purification of 1,3-propanediol from a fermentation broth. 1,3-propanediol can, for example, be produced by the fermentation of glycerol. Such fermentation leads to the co-production of sodium and ammonium butyrate or acetate and/or acetone. The fermentation broth obtained after fermentation contains, for example, water, 1,3-propanediol, glycerol, butyrate and acetate mineral salts
10 and organic salts. The noble products to recover are 1,3-propanediol and acetone (or acids in the form of acetic and/or butyric acid or acetate and/or butyrate salts). Acetone can be recovered according to known techniques such as, for example, by stripping the solution with carbon dioxide.

In the methods according to the present invention, the fermentation reaction can
15 optionally be quenched by adding a base to the fermentation broth. A base is added, for example, in the form of soda, potash or ammonia with the purpose of arresting bacterial activity. The pH achieved is between 7.5 and 14.

Next, the first step of the alcohol purification method consists of filtering the fermentation broth to eliminate insoluble elements, most notably large molecules, biomass,
20 proteins and all suspended particles. Preferably, all molecules heavier than 200 Da are eliminated. "Filtering" preferentially means a membrane separation method. Advantageously, filtration consists successively of microfiltration, ultrafiltration and nanofiltration.

The purification method also comprises a step of adding glycerol to the aqueous
25 solution. The added glycerol helps solubilize the salts present in the solution. Preferably, glycerol is added in proportions ranging from 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90% to 100% by weight of the aqueous solution. Glycerol, in particular biodiesel-based glycerol, can contain sodium chloride as well as other anions. Thus it may be advantageous to pre-treat the glycerol beforehand, with a strong anion-exchange resin, for
30 example, in order to eliminate anions.

After adding glycerol to the aqueous solution, the alcohol is then purified and recovered. The alcohol can be purified according to any known alcohol-purification

technique, in particular by distillation. Advantageously, topping and stripping are performed.

Optionally, the method according to the present invention also comprises a step of eliminating water and thus of concentrating the aqueous solution. Water can be eliminated
5 by various techniques known to persons skilled in the art. In a preferred embodiment of the purification method according to the invention, water is eliminated by evaporation. Preferably, evaporation is carried out under reduced pressure (40–150 mbar). Organic acids (acid acetic, butyric acid, lactic acid) can also be partially eliminated during this evaporation process.

10 In a specific embodiment of the invention, the purification method comprises a step of bleaching after adding glycerol. “Bleaching” means evaporating a 50%, 60%, 70%, 80%, 90% to 99% fraction of the mixture. The objective is to maintain the heavy products and salts at the bottom and to work on the pre-purified mixture recovered at the top.

The purification of alcohol from the aqueous solution can be carried out by
15 distillation. Elimination by the distillation of products with a vapor pressure greater than that of the alcohol to be purified and products with a vapor pressure less than that of the alcohol to be purified is carried out according to conventional techniques known to persons skilled in the art. Preferably, the distillation steps take place at a pressure below 60 mbar. During topping, products with a vapor pressure greater than that of the alcohol to be
20 purified are most notably water and organic acids. During stripping, products with a vapor pressure less than that of the alcohol to be purified are most notably glycerol and salts.

An optional step of the inventive purification method is adjusting pH to $\text{pH} < 7$. Preferably, the pH of the aqueous solution is adjusted to $\text{pH} < 4$, more preferentially to $\text{pH} < 3$. This adjustment is achieved, for example, by adding H_2SO_4 or HNO_3 . Preferably,
25 sulfuric acid is used.

In one embodiment of the inventive method, purification of the alcohol comprises an extraction step using a hydrophobic solvent. Any suitable hydrophobic solvent can be used to purify the alcohol. Preferably, the hydrophobic solvent is selected among the following solvents: ethyl acetate, butyl acetate, methyl isobutyl ketone, n-butanol, toluene,
30 benzene, n-hexane, isopentyl acetate, diisobutyl ketone, 5-nonanone, 2-ethyl-hexanal, 1-octanal, 2-methyl-hexanal, 1-heptanal, 3-heptanone, 2-nonanone, 2-octanone, 2-heptanone and n-heptyl acetate. Liquid-liquid extraction with a hydrophobic solvent makes it possible to extract the organic acids contained in the aqueous solution obtained

after filtration or in the culture broth. In this case, subsequent elimination by distilling products with a vapor pressure greater than that of the alcohol leads primarily to eliminating water.

The step of extracting organic acids with a hydrophobic solvent can be carried out
5 at various points of the inventive alcohol purification method.

Preferably, extracting with a hydrophobic solvent takes place after the step of adjusting the aqueous solution's pH. Indeed, acidification of the solution converts acetates into acids before extraction with the hydrophobic solvent.

In addition, persons skilled in the art will understand that the order of the steps of
10 the inventive purification method can be modified. In particular, the order of the steps of eliminating water, adding glycerol, bleaching and adjusting pH can be modified. Thus, these operations can be performed in the following orders:

- adjust pH, eliminate water, add glycerol;
- adjust pH, add glycerol, eliminate water;
- 15 - add glycerol, adjust pH, eliminate water.

In one embodiment of the invention, the method comprises a step of eliminating anions. Any suitable technique for eliminating anions can be used in the inventive methods. Eliminating anions using a strong anion-exchange resin can be cited in particular. Preferentially, this step is carried out before or after the water elimination step.

In an advantageous embodiment of the inventive method, after recovering the
20 alcohol, glycerol is recovered. The glycerol can be regenerated and then recycled in the purification process or the fermentation process. The glycerol can be recovered according to any suitable method and then recycled in the purification method. Preferably, the glycerol is recovered by distillation. The glycerol can for example be regenerated by short
25 path distillation.

Figures

Figure 1: Method for purifying 1,3-propanediol by adding glycerol.

30 (1) Microfiltration, (2) Ultrafiltration, (3) Nanofiltration, (4) Water evaporation, (5) Glycerol addition, (6) Topping, (7) Stripping.

Figure 2: Method for purifying organic acids and 1,3-propanediol by distillation, after acidification of the medium, and adding glycerol.

(1) Microfiltration, (2) Ultrafiltration, (3) Nanofiltration, (4) Water evaporation, (5) Acid addition, (6) Glycerol addition, (7) Topping, (8) Stripping.

5

Figure 3: Method for purifying organic acids by liquid-liquid extraction and 1,3-propanediol by distillation, after acidification of the medium and adding glycerol.

(1) Microfiltration, (2) Ultrafiltration, (3) Nanofiltration, (4) Water evaporation, (5) Acid addition, (6) Liquid-liquid extraction, (7) Glycerol addition, (8) Topping, (9) Stripping.

10

Figure 4: Method for purifying 1,3-propanediol by distillation and elimination of anions by a strong anion-exchange resin, then adding glycerol optionally treated on an ion-exchange resin.

(1) Microfiltration, (2) Ultrafiltration, (3) Nanofiltration, (4) Water evaporation, (5) Glycerol addition, (6) Strong ion-exchange resin, (7) Topping, (8) Stripping.

15

Figure 5: Method for purifying 1,3-propanediol by distillation after adding glycerol optionally treated on an ion-exchange resin.

(1) Microfiltration, (2) Ultrafiltration, (3) Nanofiltration, (4) Water evaporation, (5) Treatment of glycerol on an ion-exchange resin, (6) Glycerol addition, (7) Topping, (8) Stripping.

20

Figure 6: Method for quenching fermentation by adding a base and purifying 1,3-propanediol by distillation after adding glycerol optionally treated on an ion-exchange resin.

(1) Quenching fermentation by adding a base, (2) Microfiltration, (3) Ultrafiltration, (4) Nanofiltration, (5) Water evaporation, (6) Glycerol addition, (7) Topping, (8) Stripping.

25

Figure 7: Method for purifying 1,3-propanediol by adding glycerol and bleaching of the fermentation must.

(1) Microfiltration, (2) Ultrafiltration, (3) Nanofiltration, (4) Water evaporation, (5) Glycerol addition, (6) Bleaching (evaporation), (7) Topping, (8) Stripping.

30

ExamplesExample 1:

Example 1 relates to the basic invention:

- 5 - 100 ml of fermentation broth containing water, 1,3–propanediol, acid acetic, butyric acid, mineral salts and organic salts (ammonium, sodium acetate) are filtered by microfiltration, ultrafiltration and nanofiltration.
- The resulting mixture is heated under 30 mbar to evaporate water.
- Glycerol is added to the medium.
- 10 - The resulting mixture is distilled on a 20–theoretical–stage column under 5 mbar of pressure. Volatile products are eliminated (primarily water and acid acetic).
- The resulting mixture is distilled on a 20–theoretical–stage column under 1 mbar of pressure.
- 15 - The 1,3–propanediol obtained is greater than 99% pure. Chlorides are undetectable.

Example 2:

- 20 - 100 ml of fermentation broth containing water, 1,3–propanediol, acid acetic, butyric acid, mineral salts and organic salts (ammonium, sodium acetate) are filtered by microfiltration, ultrafiltration and nanofiltration.
- The resulting mixture is heated under 30 mbar to evaporate the water.
- 50 g of glycerol are passed through a strong anion–exchange resin to eliminate anions, primarily chlorides. Glycerol is added to the fermentation mixture.
- 25 - The resulting mixture is distilled on a 20–theoretical–stage column under 5 mbar of pressure. Volatile products are eliminated (primarily water and acid acetic).
- The resulting mixture is distilled on a 20–theoretical–stage column under 1 mbar of pressure.
- 30 - The 1,3–propanediol obtained is greater than 99% pure. Chlorides are undetectable.

CLAIMS

1. A method for purifying an alcohol from a fermentation broth, comprising at least the following steps:
 - 5 – filtering the fermentation broth in order to obtain an aqueous solution containing the alcohol,
 - adding glycerol to the aqueous solution,
 - purifying and recovering the alcohol.

- 10 2. A purification method according to claim 1, comprising at least the following steps:
 - filtering the fermentation broth in order to obtain an aqueous solution containing the alcohol,
 - eliminating water from the aqueous solution,
 - adding glycerol to the aqueous solution,
 - 15 – purifying and recovering the alcohol.

3. A purification method according to one of the preceding claims, comprising at least the following steps:
 - filtering the fermentation broth in order to obtain an aqueous solution containing
20 the alcohol,
 - eliminating water from the aqueous solution,
 - adding glycerol to the aqueous solution,
 - eliminating by distillation products with a vapor pressure greater than that of the alcohol to be purified,
 - 25 – eliminating by distillation products with a vapor pressure less than that of the alcohol to be purified,
 - recovering the alcohol.

4. A purification method according to one of the preceding claims, also comprising a
30 step of adjusting the pH of the aqueous solution to $\text{pH} < 3$.

5. A purification method according to one of the preceding claims, also comprising a step of extracting with a hydrophobic solvent to eliminate organic acids.

6. A purification method according to one of the preceding claims, also comprising a step of eliminating anions in the aqueous solution.
- 5 7. A method according to one of the preceding claims, wherein water is eliminated by evaporation.
8. A method according to one of the preceding claims, wherein glycerol is added in proportions ranging from 5% to 100% by weight of the aqueous solution.
- 10 9. A method according to one of the preceding claims, wherein the alcohol to be purified from the culture broth is 1,3-propanediol.
- 15 10. A method according to one of the preceding claims, wherein after alcohol is recovered, glycerol is recovered.
11. A method according to one of the preceding claims, wherein the added glycerol is pre-treated with a strong anion-exchange resin to eliminate anions from the crude glycerol.
- 20 12. The use of glycerol to purify an alcohol from a fermentation broth.

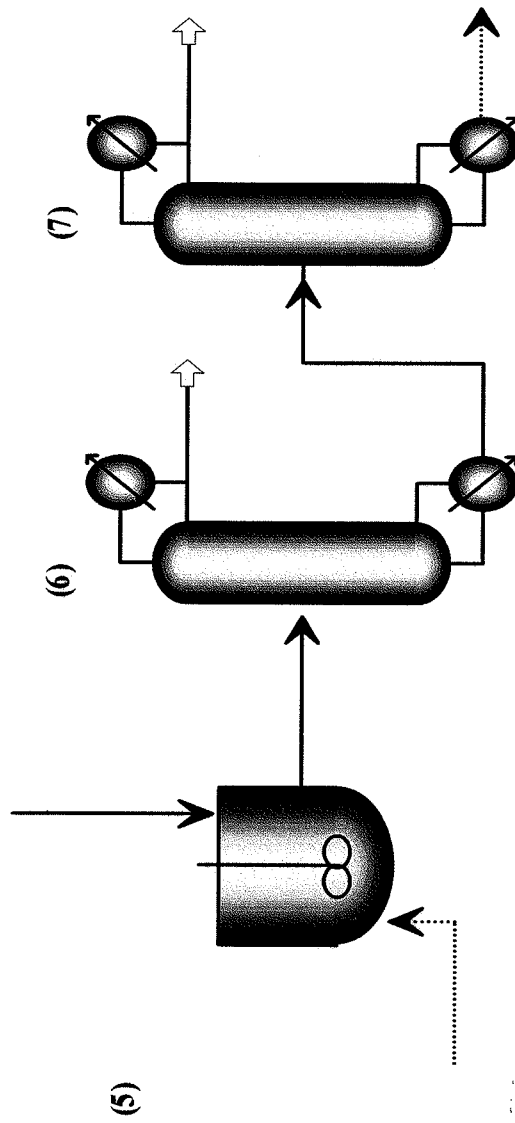
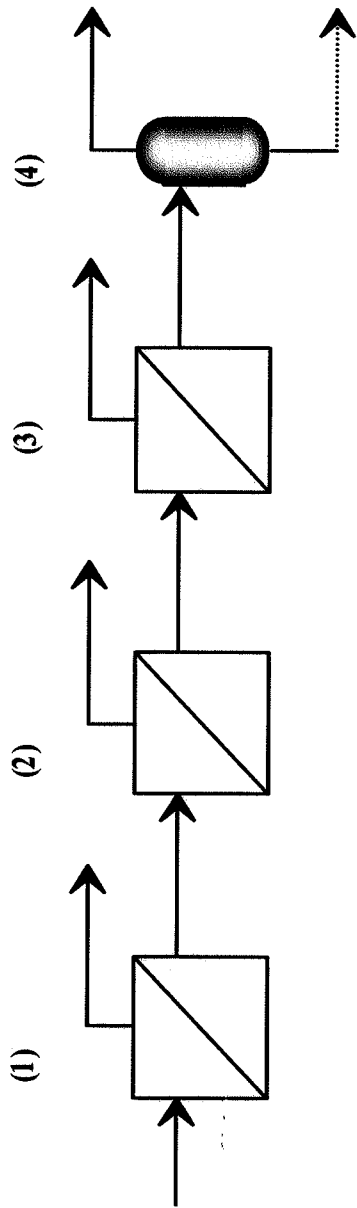


FIG. 1

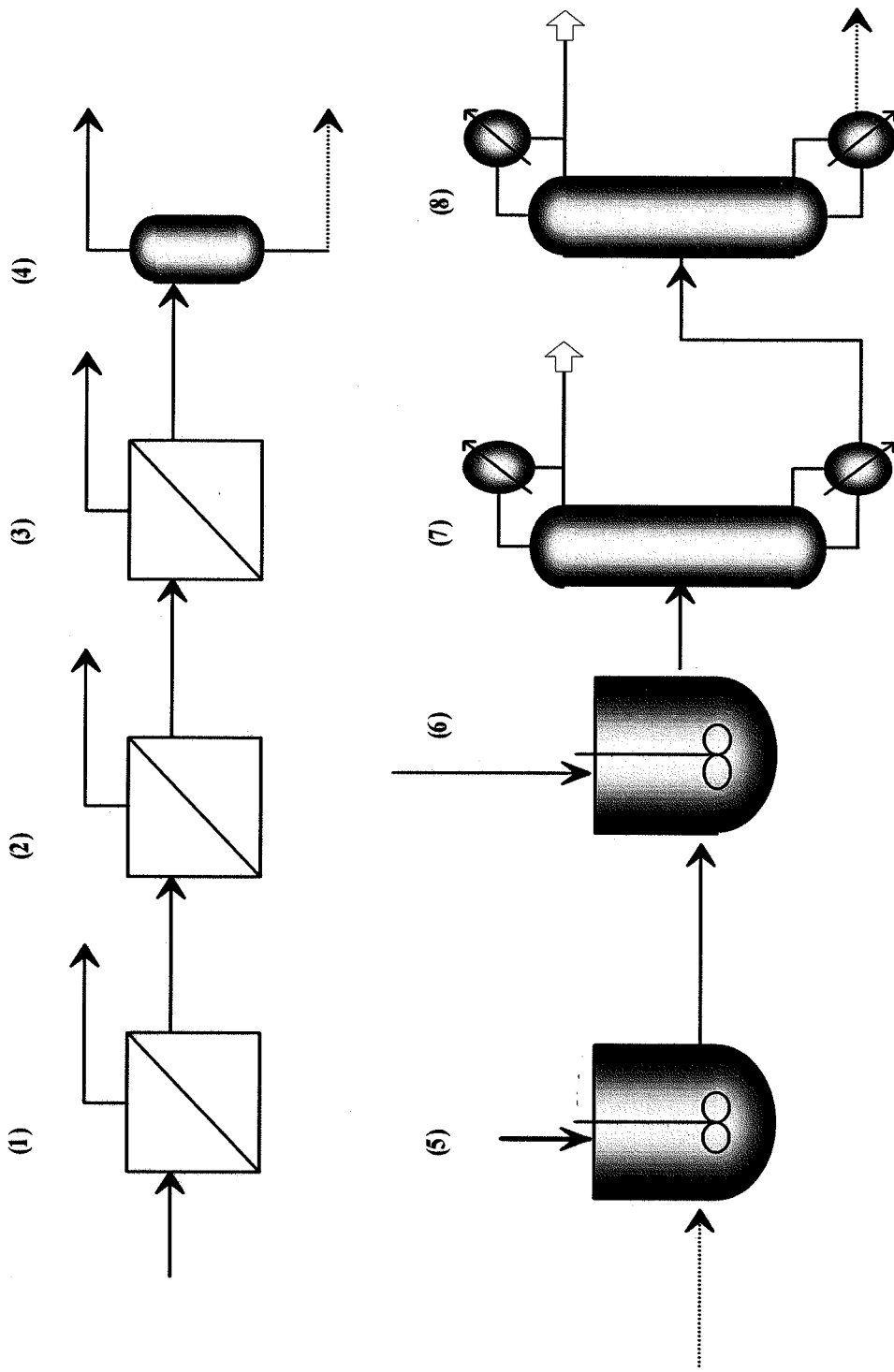


FIG. 2

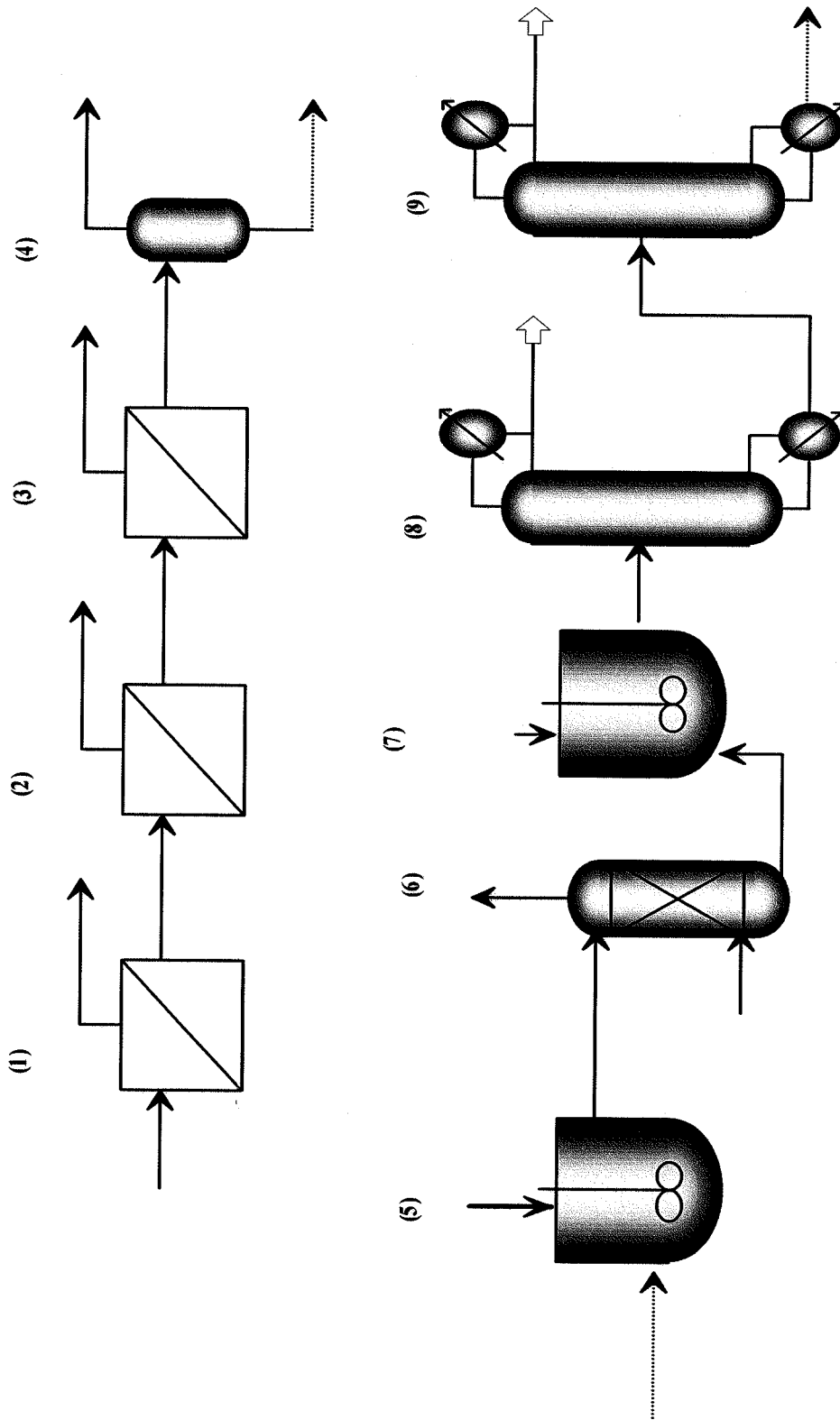


FIG. 3

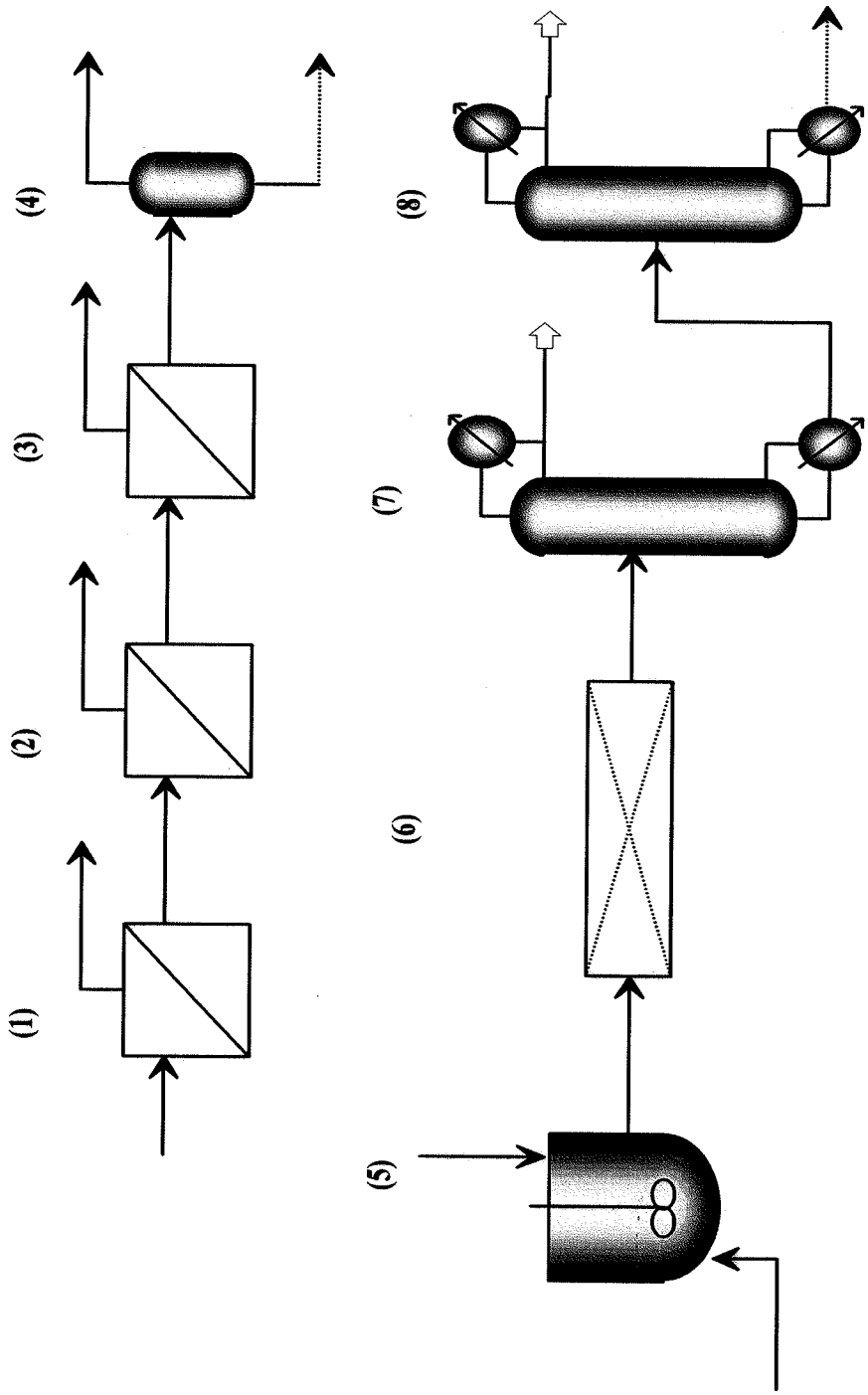


FIG. 4

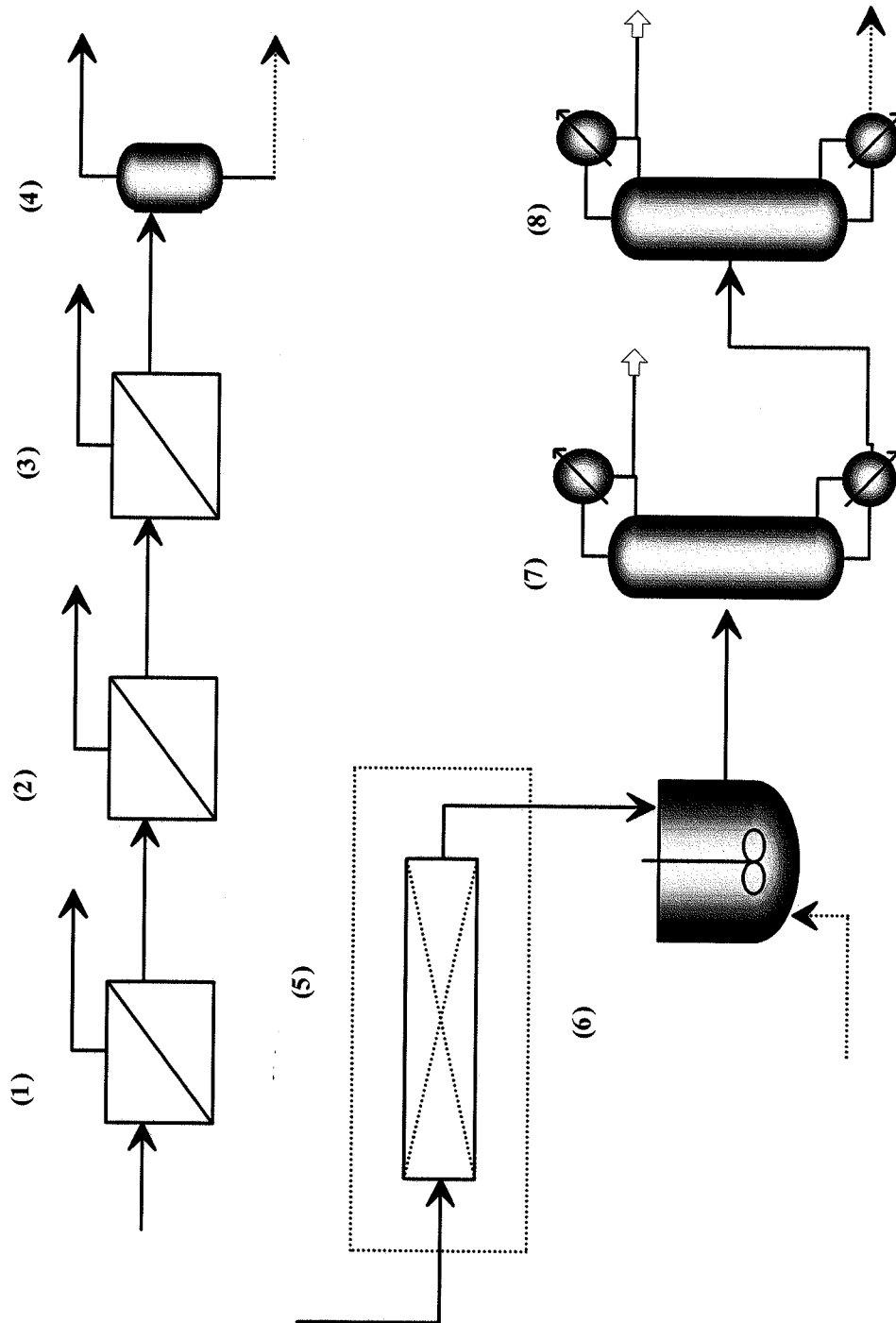


FIG. 5

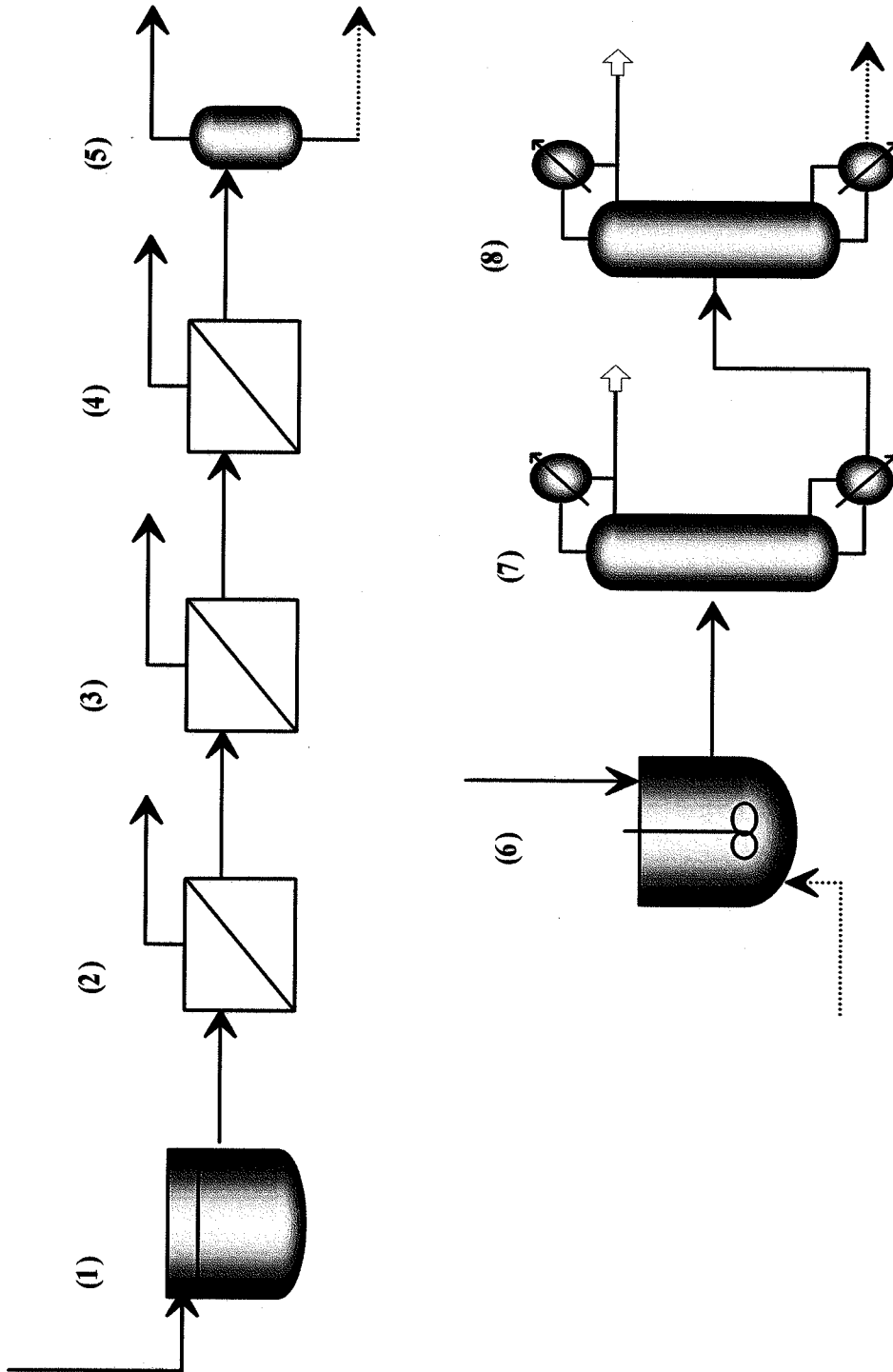


FIG. 6

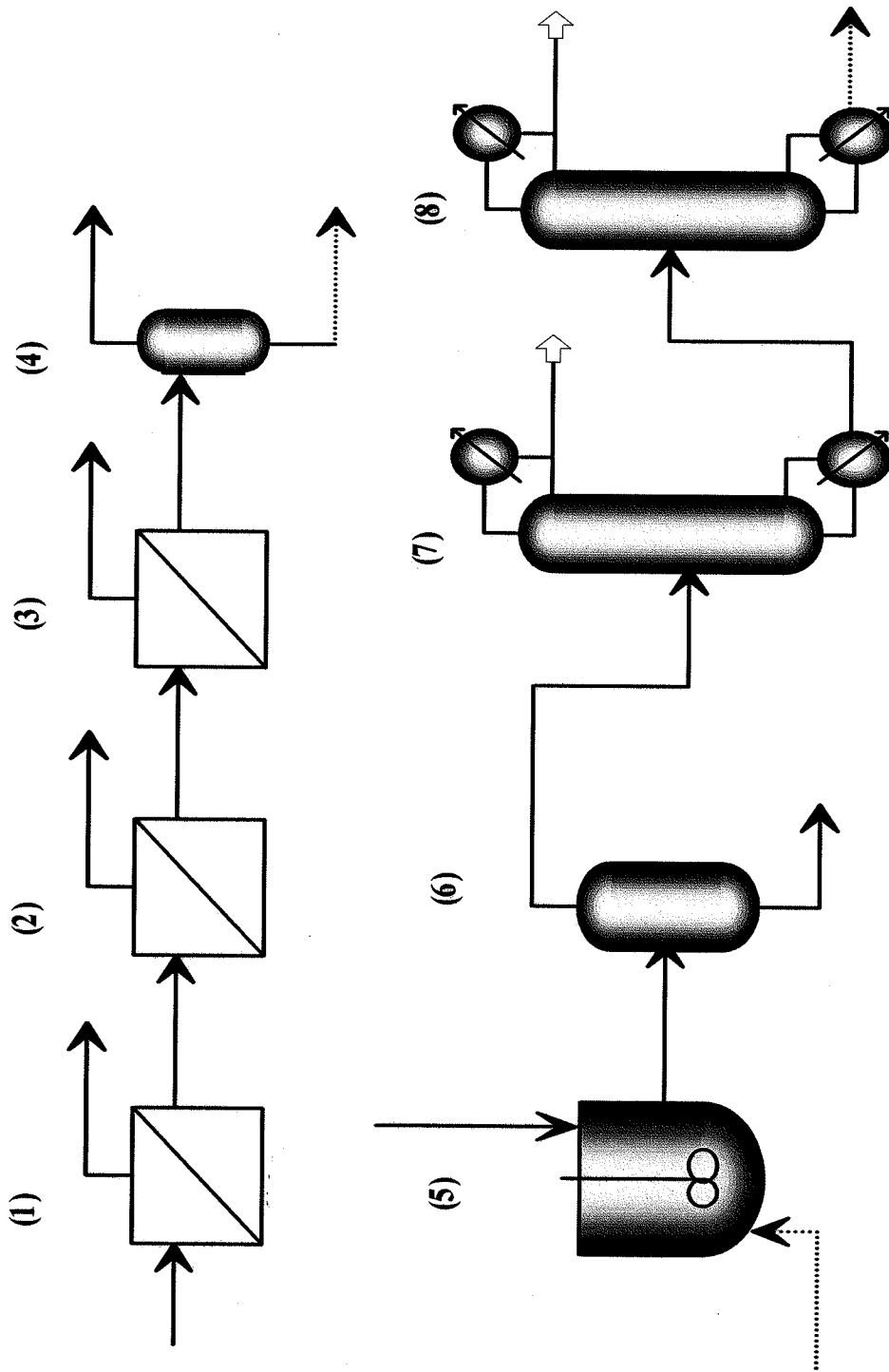


FIG. 7

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/063068

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C29/84

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)

B01D C07C 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)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2004/101479 A (DU PONT [US]; STALEY MFG CO A E [US]; ADKESSON DENNIS MICHAEL [US]; AL) 25 November 2004 (2004-11-25) page 1 page 4 claims	1-12
Y	US 4 584 063 A (BERG LLOYD [US] ET AL) 22 April 1986 (1986-04-22) column 3, lines 16-18 column 4, lines 3-5 claims; examples; tables	1-12

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

9 September 2008

Date of mailing of the international search report

19/09/2008

Name and mailing address of the ISA/

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NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
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Böhm, Ingo

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2007/063068

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 361 983 B1 (AMES TYLER T [US]) 26 March 2002 (2002-03-26) column 1, lines 9-12 column 2, lines 45-54 column 3, lines 22-25, 60-67 claims; examples	1, 12
A	WO 2006/025697 A (CJ CORP [KR]; PARK YOUNG-HOON [KR]; CHO KWANG-MYUNG [KR]; KANG SEONG-U) 9 March 2006 (2006-03-09) paragraphs [0008], [0009], [0012] claims; examples	1
A	GONZALEZ-PAJUELO ET AL: "Metabolic engineering of Clostridium acetobutylicum for the industrial production of 1,3-propanediol from glycerol" METABOLIC ENGINEERING, ACADEMIC PRESS, US, vol. 7, no. 5-6, 1 September 2005 (2005-09-01), pages 329-336, XP005207140 ISSN: 1096-7176 the whole document	1
A	EP 1 218 327 A (DU PONT [US]) 3 July 2002 (2002-07-03) cited in the application paragraphs [0001], [0014] claims	1, 12
A	US 2004/222153 A1 (BANIEL AVRAHAM M [IL] ET AL) 11 November 2004 (2004-11-11) paragraph [0005] - paragraph [0009]	1, 12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2007/063068

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2004101479	A	25-11-2004	BR PI0410685 A 20-06-2006
			CA 2522928 A1 25-11-2004
			CN 1816629 A 09-08-2006
			EP 1625224 A2 15-02-2006
			JP 2007502325 T 08-02-2007
			KR 20060052677 A 19-05-2006
US 4584063	A	22-04-1986	NONE
US 6361983	B1	26-03-2002	NONE
WO 2006025697	A	09-03-2006	BR PI0514743 A 24-06-2008
			CN 101010272 A 01-08-2007
			KR 20060020864 A 07-03-2006
			US 2008097130 A1 24-04-2008
EP 1218327	A	03-07-2002	AT 284855 T 15-01-2005
			AU 781408 B2 19-05-2005
			AU 7750400 A 10-05-2001
			CA 2384774 A1 12-04-2001
			CN 1377333 A 30-10-2002
			DE 60016770 D1 20-01-2005
			DE 60016770 T2 15-12-2005
			ES 2233457 T3 16-06-2005
			HK 1045149 A1 03-06-2005
			WO 0125178 A1 12-04-2001
			US 2004222153
BR PI0410680 A 20-06-2006			
CA 2524452 A1 25-11-2004			
CN 1812825 A 02-08-2006			
EP 1620362 A2 01-02-2006			
JP 2006528688 T 21-12-2006			
KR 20060021838 A 08-03-2006			
MX PA05011894 A 17-02-2006			
NZ 543388 A 31-07-2008			
RU 2323200 C2 27-04-2008			
US 2006124545 A1 15-06-2006			
WO 2004101437 A2 25-11-2004			