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(54) Title: PROCESS AND EQUIPMENT FOR RECOVERY OF VALUABLE MATERIALS FROM TEREPHTHALIC ACID MANUFACTURE

(57) Abstract: A process for recovery of valuable materials from terephthalic acid manufacture. The process comprises the steps of diluting the reactor effluent from terephthalic acid manufacture with water in the weight ratio 1:1 to 1:12 and chilling the dilution of the effluent to 5 to 20 °C under stirring. The aqueous phase rich in the spent oxidation catalyst is separated from the solid phase rich in organic compounds and concentrated to recover the spent oxidation catalyst and water. Also equipment for recovery of valuable materials from the reactor effluent.



TITLE OF THE INVENTION

Process and equipment for recovery of valuable materials from terephthalic acid manufacture

FIELD OF THE INVENTION

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This invention relates to a process and equipment for recovery of valuable materials from terephthalic acid manufacture.

BACKGROUND OF THE INVENTION

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Terephthalic acid is manufactured by liquid-phase oxidation of *p*-xylene with air over cobalt-manganese-bromide catalyst system (cobalt acetate, manganese acetate, and hydrogen bromide) in acetic acid at 150 to 210 °C. The relative weight ratio of cobalt, manganese and bromine are important, and the typical values are manganese: cobalt ratio 3:1 and cobalt: bromine ratio 1:5. In the reactor and crystallizer of the terephthalic acid manufacturing plant, most of the terephthalic acid crystallizes out from the mother liquor and is separated by filtration. The mother liquor comprises mainly acetic acid and organic compounds like isophthalic acid, benzoic acid and terephthalic acid, and inorganic compounds like cobalt and manganese along with iron, nickel, chromium and sodium. It is a common practice to recycle a large portion of the recovered mother liquor to the oxidation reaction in order to recover the catalyst partially and promote the oxidation reaction while purging a small portion to a solvent recovery system so as to maintain the level of impurities and by-products in the reaction within tolerable limits. In the solvent recovery system, mother liquor purge is subjected to evaporation to remove considerable portion of acetic acid and water leaving behind a concentrate containing organic compounds together with heavy metal catalysts. The

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concentrate hereinreferred to as reactor effluent is disposed of by incineration usually in furnaces.

OBJECTS OF THE INVENTION

- 5 An object of the invention is to provide a process for recovery of valuable materials from the reactor effluent from terephthalic acid manufacture.

Another object of the invention is to provide an equipment for recovery of valuable materials from the reactor effluent from terephthalic acid manufacture.

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DETAILED DESCRIPTION OF THE INVENTION

- According to the invention there is provided a process for recovery of valuable materials from terephthalic acid manufacture, the process comprising the steps of diluting the reactor effluent from terephthalic acid manufacture with water in the weight ratio 1:1 to 1:12 and
15 chilling the dilution of the effluent to 5 to 20°C under stirring; separating the aqueous phase rich in the spent oxidation catalyst from the solid phase rich in organic compounds; and concentrating the aqueous phase to recover the spent oxidation catalyst and water.

- Preferably the dilution of the effluent with water is carried out in the weight ratio 1:10 and
20 the dilution of the effluent is chilled at 5-15°C. Preferably the separation of aqueous phase and solid phase is carried out by solid-liquid separation method. According to an embodiment of the invention, concentration of the aqueous phase is carried out by evaporation of the aqueous phase. According to another embodiment of the invention the concentration of the aqueous phase is carried out by precipitation by treatment with an alkali
25 to adjust the pH between 7 and 8 under stirring followed by separation of the precipitate by

filtration. Preferably the alkali is soda ash and preferably the precipitate is treated with acetic acid to convert the spent oxidation catalyst into acetate. According to another embodiment of the invention, the concentration of the aqueous phase is carried out by membrane separation method.

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According to the invention there is also provided an equipment for recovery of valuable materials from terephthalic acid manufacture, the equipment comprising a jacketed dilution cum chilling tank provided with a stirrer and connected to an inlet line for the reactor effluent from the terephthalic acid manufacture and to a dilution water inlet line, the jacket of the dilution cum chilling tank being connected to a chilling unit, a solid-liquid separator the inlet of which is connected to the outlet of the dilution cum chilling tank, a flasher drum provided with a reboiler and connected to the outlet of the solid liquid separator and a condenser the inlet of which is connected to the vapour outlet of the flasher drum.

15 According to the invention there is also provided an equipment for recovery of valuable materials from terephthalic acid manufacture, the equipment comprising a jacketed dilution cum chilling tank provided with a stirrer and connected to an inlet line for the reactor effluent from the terephthalic acid manufacture and to a dilution water inlet line, the jacket of the dilution cum chilling tank being connected to a chilling unit, a solid-liquid separator the inlet
20 of which is connected to the outlet of the dilution cum chilling tank, a precipitation tank provided with a stirrer and connected to the outlet of the solid liquid separator, the precipitation tank being further provided with an alkali dosing line and a CO₂ outlet line, a filter the inlet of which is connected to the outlet of the precipitation tank and a catalyst regeneration tank provided with a stirrer and connected to the outlet of the filter, the catalyst

regeneration tank being further provided with an acetic acid dosing line, CO₂ outlet line and a recovered catalyst outlet line.

According to the invention there is also provided an equipment for recovery of valuable materials from terephthalic acid manufacture, the equipment comprising a jacketed dilution cum chilling tank provided with a stirrer and connected to an inlet line for the reactor effluent from the terephthalic acid manufacture and to a dilution water inlet line, the jacket of the dilution cum chilling tank being connected to a chilling unit, a solid-liquid separator the inlet of which is connected to the outlet of the dilution cum chilling tank and a storage tank the inlet of which is connected to the outlet of the solid liquid separator and the outlet of which is connected to a membrane separator array means.

The following is a detailed description of the invention with reference to the accompanying drawings, in which;

Fig 1 is a flow diagram of the equipment for recovering valuable materials from the reactor effluent from terephthalic acid manufacture according to an embodiment of the invention;

Fig 2 is a flow diagram of the equipment for recovering valuable materials from the reactor effluent from terephthalic acid manufacture according to another embodiment of the invention; and

Fig 3 is a flow diagram of the equipment for recovering valuable materials from the reactor effluent from terephthalic acid manufacture according to another embodiment of the invention.

The equipment 1A as illustrated in Fig 1 of the accompanying drawings comprises a jacketed dilution cum chilling tank 2 provided with a stirrer 3. The jacket of the tank is marked 4. 5 is a chilling unit for recirculating a coolant (not shown) in the jacket of the tank 2 via recirculation lines marked 6 and 7. The tank 2 is connected to a reactor effluent inlet line 8 and a dilution water inlet line 9. 10 is a solid liquid separator the inlet of which is connected to the outlet of the tank 2 via line 11. Sediment outlet line of the solid liquid separator is marked 12. 13 is a flasher drum, the recovered catalyst discharge line of which is marked 14. 15 is a reboiler provided with the flasher drum. 16 is a condenser the inlet of which is connected to the vapour outlet of the flasher drum via line 17. The outlet of the condenser is connected to a recovered water line 18 which in turn is connected to the dilution water inlet line 9. Coolant inlet and outlet of the condenser are marked 19 and 20 respectively. Reactor effluent (not shown) at about 80 to 90°C from terephthalic acid manufacturing plant (not shown) is fed into the tank 2 via effluent inlet line 8. Dilution water (not shown) is fed into the tank 2 via dilution water inlet line 9. Dilution of the effluent is carried out with water in the tank 2 in the weight ratio 1:1 to 1:12 preferably 1:10 under agitation with the stirrer 3. The effluent dilution in the tank 2 is chilled at 5-20°C, preferably 5-15°C by circulating coolant (not shown) from the chilling unit in the jacket of the tank 2. Due to dilution and chilling the organic compounds present in the effluent solidify. The aqueous phase rich in spent oxidation catalyst is separated from the solid phase rich in organic compounds in the solid liquid separator. The solid phase is discharged through the sediment outlet line 12. The aqueous phase is flashed in the flasher drum. The reboiler reboils the aqueous phase and feeds into the flasher drum. The concentrate rich in the spent oxidation catalyst is collected via the recovered catalyst discharge line 14. The vapour phase mainly containing water is fed

into the condenser 16 via line 17 and is condensed in the condenser. The water recovered in the condenser is fed into the tank 2 via the recovered water line 18.

The equipment 1B as illustrated in Fig 2 of the accompanying drawings comprises a precipitation tank 21 provided with a stirrer 22. 23 is an alkali dosing line provided with the precipitation tank. 24 is the CO₂ gas outlet of the precipitation tank. The precipitation tank is connected to the outlet of the solid liquid separator via line 25. 26 is a filter connected to the outlet of the precipitation tank via line 26a. 27 is the filtrate outlet line of the filter. 28 is a catalyst regeneration tank the inlet of which is connected to the outlet of the filter via line 27a. The regeneration tank 28 is provided with a stirrer 29. 30 is an acetic acid dosing line provided with the regeneration tank. 31 is the CO₂ gas outlet of the regeneration tank. 32 is the recovered catalyst outlet line of the regeneration tank. The aqueous phase from the solid liquid separator is treated in the precipitation tank 21 with an alkali preferably soda ash under agitation to precipitate the organic catalyst. The precipitation is carried out at a pH of 7-8. The slurry comprising the spent catalyst is filtered in the filter and the solid phase is fed into the regeneration tank. The filtrate namely the recovered water is drained out via the filtrate outlet line 27. The catalyst is converted into the acetate in the regeneration tank by treatment with acetic acid under agitation and collected via the outlet line 32.

The equipment 1C as illustrated in Fig 3 of the accompanying drawings comprises a storage tank 33 the inlet of which is connected to the outlet of the solid liquid separator 10 via line 34. A plurality of membrane separators are marked 35, 36, 37 and 38. The inlet of membrane separator 35 is connected to the outlet of storage tank 33 via line 39. Reject line 40 of membrane separator 35 is connected to a wash tank 41 which in turn is connected to the inlet of membrane separator 36 via line 42. 43 is a reject storage tank connected to the reject

line 44 of membrane separator 36 and further connected to the inlet of membrane separator 37 via line 45. 46 is a recovered catalyst storage tank connected to membrane separator 37 via line 47a. Recovered catalyst outlet line of the storage tank 46 is marked 47b. The outlet lines marked 48, 49 and 50 of membrane separators 35, 36 and 37, respectively are connected to the inlet of membrane separator 38 via line 51. 52 is an alkali dosing line connected across line 51 close to the inlet of membrane separator 38. 53 is a recovered water line connected to the outlet of membrane separator 38 and to dilution water inlet line 9. 54 is a cross line connected to line 53 and to wash tank 41. 55 is the waste water outlet line of the membrane separator 38. Aqueous phase from the solid liquid separator 10 is stored in tank 33. The aqueous phase undergoes reverse osmosis in membrane separator 35. The solid phase containing the spent catalyst is washed in wash tank 41 and subjected to further osmosis in membrane separator 36. The reject from membrane separator 36 is stored in storage tank 43 and fed into membrane separator 37. The reject is further subjected to reverse osmosis in membrane separator 37. The recovered catalyst is collected and stored in tank 46 and recovered via outlet line 47b. The permeates from membrane separators 35, 36 and 37 is further subjected to reverse osmosis in membrane separator 38. The feed going into the membrane separator 38 is dosed with an alkali preferably caustic soda so as to solidify the organic compounds, if any. The alkali treatment is carried out to adjust the pH between 7 and 8. The waste water is discharged via waste water outlet line 55 and the recovered water is partly fed into inlet line 9 and partly fed into wash tank 41.

According to the invention valuable materials in the reactor effluent namely spent oxidation catalyst and water are thus recovered and reused instead of being disposed of by incineration.

The following experimental examples are illustrative of the invention but not limitative of the scope thereof.

Example 1

- 5 (a) In a typical equipment of Fig 1 of the accompanying drawings, reactor effluent (50 litres) at 90°C was diluted with water in the weight ratios of 1:1, 1:2, 1:5, 1:8, 1:10 and 1: 12 under agitation and chilled to 10°C. The percentages of recovery of organic materials like cobalt and manganese were 9, 21, 53, 77, 91, 92 and 10, 25, 62, 85, 94, 99, respectively.
- 10 (b) To maintain the level of impurities of organic materials and by-products in the reactor within tolerable limits, a few experiments were carried by varying the chilling temperature of the reactor effluent to 5°C, 10°C, and 15°C. The overall percentage recovery of the organic materials was found to be 80, 84 and 87, respectively.
- (c) The recovered solution of 1:10 dilution and chilling temperature of 10°C was
15 concentrated by evaporation to recover 80 to 85% of water.

Example 2

- In a typical equipment of Fig 2 of the accompanying drawings, reactor effluent (50 litres) at 90°C was diluted with water in the weight ratio of 1:10 under agitation and chilled to 10°C.
- 20 Precipitation of the organic catalyst was carried out with soda ash addition till pH of the solution became 7 to 8. Further acetic acid addition was carried out to convert the carbonates into acetates. The percentages recovery of cobalt and manganese were found to be 95 and 94, respectively.

Example 3

In a typical equipment of Fig 3 of the accompanying drawings, reactor effluent (50 litres) at 90°C was diluted in the weight ratio of 1:10 under agitation and chilled to 10°C. The percentages of recovery of cobalt and manganese were found to be 98 and 99, respectively.

- 5 Water was also recovered by precipitating the remaining organics from the permeate of the first three membrane separators by adding caustic till the pH of the permeate became 7 to 8 and then passing the solution through the fourth membrane separator. The percentage recovery of water was found to be in the range of 35 to 40.

CLAIMS :

1. A process for recovery of valuable materials from terephthalic acid manufacture, the process comprising the steps of diluting the reactor effluent from terephthalic acid manufacture with water in the weight ratio 1:1 to 1:12 and chilling the dilution of the effluent to 5 to 20°C under stirring; separating the aqueous phase rich in the spent oxidation catalyst from the solid phase rich in organic compounds; and concentrating the aqueous phase to recover the spent oxidation catalyst and water.
2. The process as claimed in claim 1, wherein the dilution of the effluent with water is carried out in the weight ratio 1:10.
3. The process as claimed in claim 1 or 2, wherein the dilution of the effluent is chilled at 5 to 15°C.
4. The process as claimed in anyone of claims 1 to 3, wherein the separation of aqueous phase and solid phase is carried out by solid-liquid separation method.
5. The process as claimed in anyone of claims 1 to 4, wherein the concentration of the aqueous phase is carried out by evaporation of the aqueous phase.
6. The process as claimed in anyone of claims 1 to 4, wherein the concentration of the aqueous phase is carried out by precipitation by treatment with an alkali to adjust the pH between 7.8 under stirring followed by separation of the precipitate by filtration.

7. The process as claimed in claim 6, wherein the alkali is soda ash.

8. The process as claimed in claim 6 or 7, wherein the precipitate is treated with acetic acid to convert the spent oxidation catalyst into acetate.

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9. The process as claimed in anyone of claims 1 to 4, wherein the concentration of the aqueous phase is carried out by membrane separation method.

10. An equipment for recovery of valuable materials from terephthalic acid manufacture, the equipment comprising a jacketed dilution cum chilling tank provided with a stirrer and connected to an inlet line for the reactor effluent from the terephthalic acid manufacture and to a dilution water inlet line, the jacket of the dilution cum chilling tank being connected to a chilling unit, a solid-liquid separator the inlet of which is connected to the outlet of the dilution cum chilling tank, a flasher drum provided with a reboiler and connected to the outlet of the solid liquid separator and a condenser the inlet of which is connected to the vapour outlet of the flasher drum.

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11. An equipment for recovery of valuable materials from terephthalic acid manufacture, the equipment comprising a jacketed dilution cum chilling tank provided with a stirrer and connected to an inlet line for the reactor effluent from the terephthalic acid manufacture and to a dilution water inlet line, the jacket of the dilution cum chilling tank being connected to a chilling unit, a solid-liquid separator the inlet of which is connected to the outlet of the dilution cum chilling tank, a precipitation tank provided with a stirrer and connected to the outlet of the solid liquid separator, the precipitation tank being further provided with an alkali dosing line and a CO₂ outlet line, a filter the inlet of which is connected to the outlet of the

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precipitation tank and a catalyst regeneration tank provided with a stirrer and connected to the outlet of the filter, the catalyst regeneration tank being further provided with an acetic acid dosing line, CO₂ outlet line and a recovered catalyst outlet line.

- 5 12. An equipment for recovery of valuable materials from terephthalic acid manufacture, the equipment comprising a jacketed dilution cum chilling tank provided with a stirrer and connected to an inlet line for the reactor effluent from the terephthalic acid manufacture and to a dilution water inlet line, the jacket of the dilution cum chilling tank being connected to a chilling unit, a solid-liquid separator the inlet of which is connected to the outlet of the
10 dilution cum chilling tank and a storage tank the inlet of which is connected to the outlet of the solid liquid separator and the outlet of which is connected to a membrane separator array means.

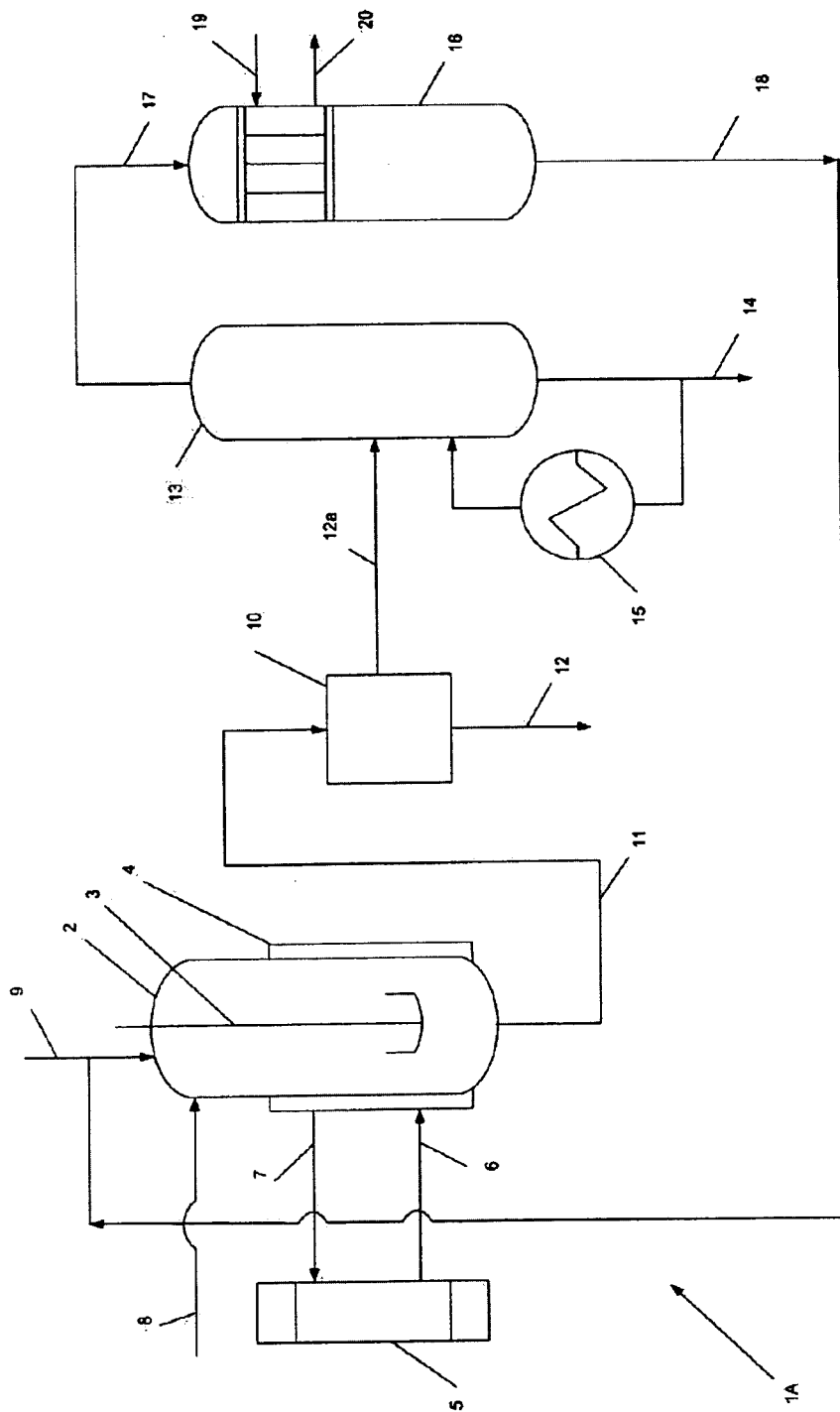


Fig. 1

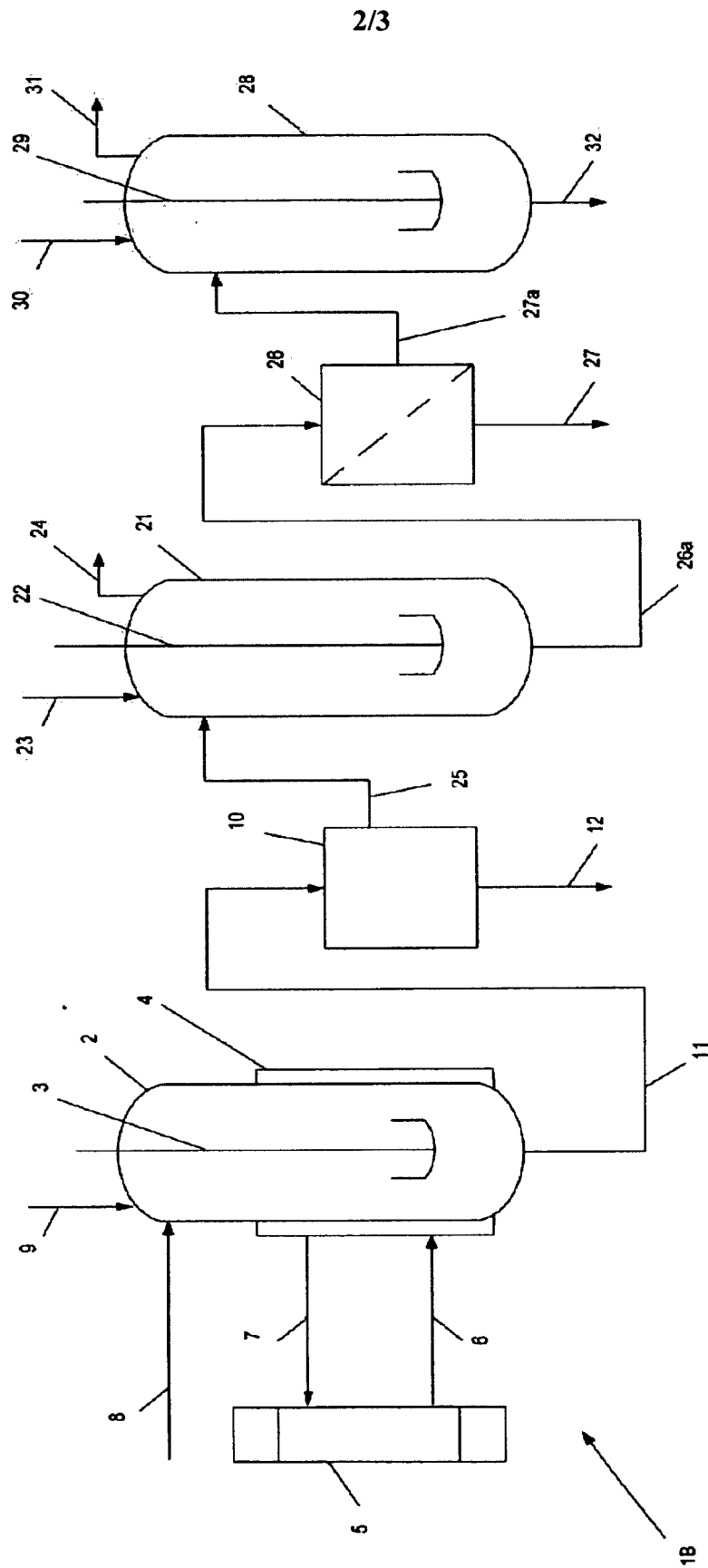


Fig. 2

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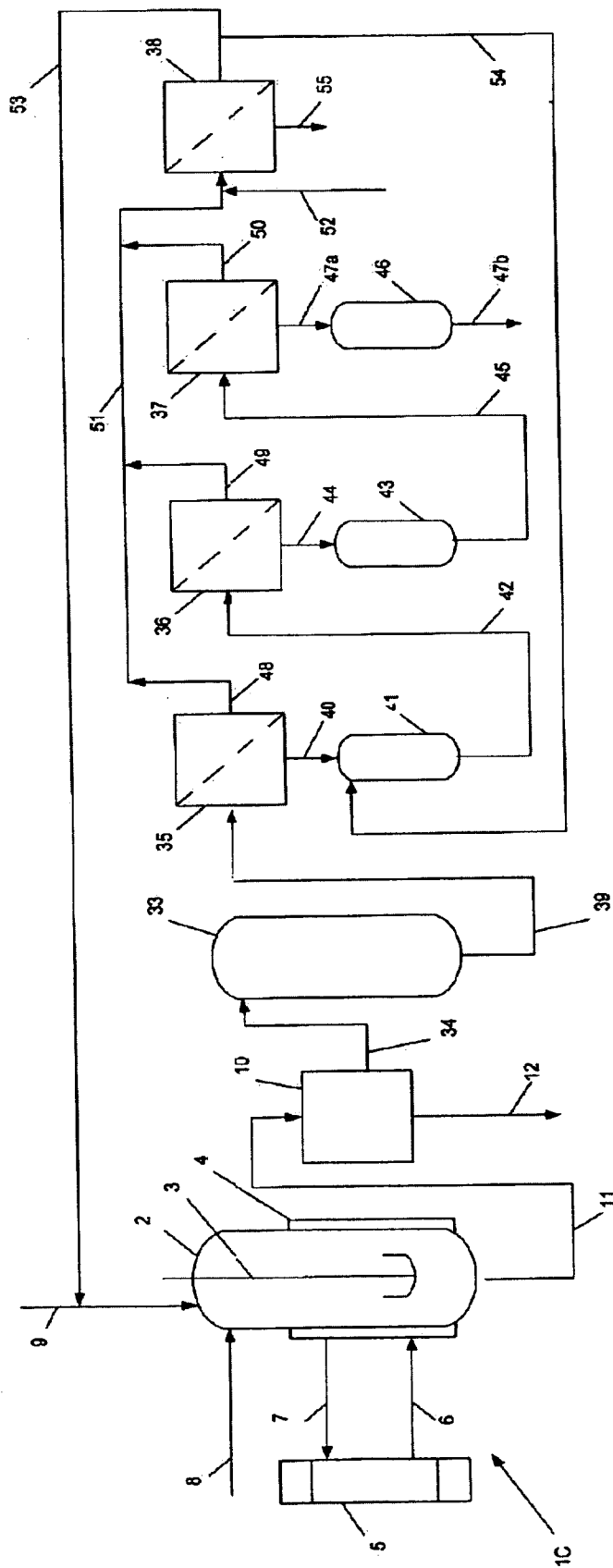


Fig. 3