

(19)



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(11)

EP 1 452 576 A2

(12)

EUROPEAN PATENT APPLICATION

published in accordance with Art. 158(3) EPC

(43) Date of publication:

01.09.2004 Bulletin 2004/36(51) Int Cl.7: **C10G 33/06**, C10G 7/00,**B01D 17/04**(21) Application number: **02757985.3**

(86) International application number:

PCT/AZ2002/000001(22) Date of filing: **26.08.2002**

(87) International publication number:

WO 2003/029385 (10.04.2003 Gazette 2003/15)

(84) Designated Contracting States:

**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
IE IT LI LU MC NL PT SE SK TR**

Designated Extension States:

AL LT LV MK RO SI(30) Priority: **07.12.2001 AZ 20010201****20.05.2002 EA 200200475**

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(74) Representative: **von Fünér, Nicolai, Dr. et al****v. Fünér Ebbinghaus Finck Hano****Patentanwälte****Mariahilfplatz 2&3****81541 München (DE)**(54) **METHOD FOR RECYCLING MIXED OIL WASTE AND DEVICE FOR CARRYING OUT SAID METHOD**

(57) A method of processing mixed petroleum-based wastes and an apparatus for its realization relates to methods and apparatuses of processing crude oil.

The invention allows to increase yield of commercial hydrocarbons due to efficiency of the pre-treatment of raw stock and determination of sparing thermal regimes, and also to decrease the power inputs and harmful influence on environment.

The method includes simultaneous dehydration, desalting mixed petroleum-based wastes and refining its from mechanical impurities and sulfur by vibratory-cavitation oscillations of a rotating vibrational device, two-stage heating of pulp of hydrocarbons, its circulation and recirculation.

For realization of the method, the apparatus has rotating vibrational devices (15), in-built in tanks for preparation of the raw stock (1), (2), connected with the means for heating the raw stock, made in the form of a plumb pipe-still kiln (4) with coil pipes and a torch in the form of perforated plate with cone-shaped holes. The kiln (4) is connected with a block of distillation in the form of vacuum distillation still (5), technologically connected with tank (2).

The invention can be used for production of burner oil, fuel oil and other kinds of fuel.

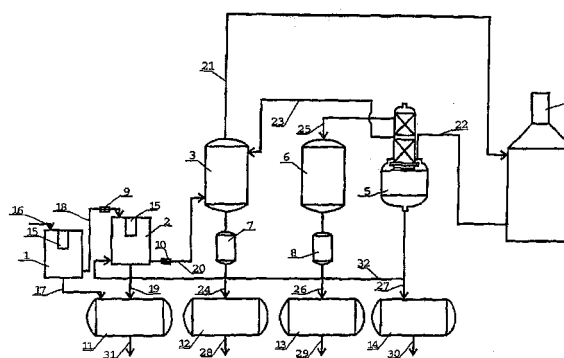


Fig. 1

EP 1 452 576 A2

Description

[0001] The invention relates to methods and apparatuses of processing oil stock, namely to the method of recycling mixed wastes of oil-processing and petroleum production, and to the apparatus for realization of the method, and can be used for production of burner oil, fuel oil and other kinds of fuel.

[0002] Method of recycling the high-molecular residues of oil-processing - the oil asphaltenes, by way of mixing thereof with technical sulfuric acid and bottoms of rectification stage of dimethyldioxane recycling, process for obtaining isoprene by decomposition of dimethyldioxane at heating is disclosed in patent RU 2064959.

[0003] The method of fractioning the petroleum, which comprises its staggered recuperative heating by outgoing and circulating currents, inter-stage electrical desalting, separation and washing the vapours, following heating and vapourising the petroleum residue, fractioning the vapours and liquid phase in column using reflux, condensation of the vapours and cooling the condensates with heat abstraction, mainly to petroleum, disengagement of cooled products, is disclosed in patent RU 2100403.

[0004] Vapour disengagement is implemented stepwise, where the first stage is carried out after recuperative heating the petroleum by the heat of condensation and cooling gasoline and kerosene fractions, and the following stages are carried out advantageously on the each stage of subsequent recuperative heating the petroleum, the vapours of each stage and vapours of overflow of the column are directed separately for the condensation, the condensation is carried out with fractionation.

[0005] The apparatus for fractioning the petroleum includes consecutively connected in the course of petroleum recuperative heaters, a electrodehydrator, the subsequent recuperative heaters, means for the vapour disengagement, that contains a steam washer with feeding the flushing water, means for heating and vapourising the petroleum residue, a fractionator, a stabilizer of gasoline, condensers of the outgoing currents, pumps, pipelines of feeding the petroleum and hydrocarbon gas, tubing for drawoff of the fractionation products, where at least one of the recuperative heaters is carried out in the form of fractionation condenser. The means for the vapour disengagement is carried out multi-stage, where the each stage contains the steam washer and includes vapour separator, fixed on the petroleum pipeline behind the fractionation condenser, and the recuperative heaters of petroleum behind the vapour separator, made advantageously in the form of evaporators, the steam washers and the top of the column is connected by steam pipes to the fractioning condenser, the means for heating and vapourising the petroleum residue includes the steam washer in the inter-stage separator and heater of hydrocarbon gas.

[0006] A method of breakdown of water-in-oil emulsions, which comprises charging of water drops and their subsequent withdrawal, in which the emulsion is previously passed through a system of the electroconductive elements, being located in an electrical field, and then through a system of potential electrodes, isolated by substance with electrical conductivity 10^{-9} - 10^{-10} (Ohm m)⁻¹, is described in RU 96109499/25.

[0007] The closest engineering solution to the invention is a method of processing the petroleum-based wastes and an apparatus for its implementation that are disclosed in RU 2161176. The method includes preliminary dehydration of crude oil, separation of water from a water-petrol mixture by settling with its further refinement, thermal cracking of the crude oil in a cracking-boiler with disengagement of the vapour products from a last cut, condensation of the vapour products, separation of the condensate into low and high-boiling fractions. The apparatus for implementation of the method of processing the petroleum-based wastes includes a block of thermal cracking, that carries out the heating and decomposition of the raw stock, consisting of the cracking-boiler, a dephlegmator, a condenser, a centrifuge, a block of filtration, a block of distillation, and also further includes a block of dehydration and topping of the crude oil, heat exchangers, separators, condensers, a block of water treating, consisting of a steam-stripping column and a filter.

[0008] Defaults of the known method and the apparatuses of processing the petroleum-based wastes are time length and insufficiency of pre-treatment of the raw stock that results in loss of hydrocarbons, decreasing a yield of commercial hydrocarbons, which further decreases due to decomposition, oxidation and coking of low molecular weight components of the raw stock because of the high thermal regimes that require significant power inputs. In turn the losses of hydrocarbons at the pre-treatment of the raw stock and presence of the products of decomposition at the high thermal regimes have negative influence on environment, polluting its with emissions and waste products.

[0009] It is as object of the invention to provide the method and the apparatus for processing the petroleum-based wastes that allow to increase the yield of commercial hydrocarbons due to increasing efficiency of the pre-treatment of the raw stock and determination of sparing thermal regimes, that exclude decomposition reactions, oxidation reactions and coking reactions of low molecular weight components of the raw stock, whereupon the power inputs and harmful influence on environment decrease.

[0010] The solution of the technical problem in the method of processing the mixed petroleum-based wastes, which comprises the dehydration of the crude oil, the heating and disengagement of the vapour products from the last cut, condensation of the vapour products, separation of the condensate into low and high-boiling fractions, is accomplished by that as the crude oil the mixed petroleum-based wastes are subjected to the processing, and the dehydration si-

multaneously with desalting are carried out by vibratory-cavitation oscillations of a rotating vibrational device, under action of which the raw stock is further refined from mechanical impurities and free sulfur, and after the two-stage heating, circulation and recirculation of the heated up pulp of hydrocarbons, the distillation of the low-boiling fractions is carry out, and the high-boiling fractions are separated by vacuum distillation giving the bottoms, and the distillate and light fraction of hydrocarbons are withdrawn from the column of vacuum distillation still giving, after separation, the burner oil and the light hydrocarbon fraction, correspondingly.

[0011] The mixed petroleum-based wastes, being subjected to the processing, have water content up to 25 %, and sulfur and mechanical impurities up to 10 %.

[0012] Thus, as mixed petroleum-based wastes, it is used the mixed residues of oil-processing and/or petroleum chemical plants, and/or spent hydrocarbon oils, and/or the oil stock, collected from traps of the refineries, from sea surface and other water spaces.

[0013] The dehydration, the desalting and the refining from the mechanical impurities and sulfur are carried out in two stages in tanks for preparation of the raw stock, and the circulation and the recirculation of the heated up pulp of hydrocarbons after the second stage of heating are executed up to determination of separation condition of hydrocarbons in the vacuum distillation still, the temperature of which is 270-300°C.

[0014] The distillation of the low-boiled fractions is carried out at temperature 35-180°C, preferably at temperature 70-150°C, at atmospheric pressure, and the vacuum distillation is carried out at temperature 180-320°C, preferably at temperature 210-300°C.

[0015] In addition; the vacuum distillate is withdrawn from the middle of the column of the vacuum distillation still.

[0016] The bottoms, obtained according to the method, is fuel oil with combustion heat 40560 kilojoule/kg, the obtained burner fuel has fire point 40°C, and the light hydrocarbon fraction has boiling point <180°C.

[0017] The current problem in the apparatus for realization of the method of processing mixed petroleum-based wastes, which comprises the block of dehydration of the crude oil, the block of distillation, the means for heating the raw stock, the heat exchanger, the condenser, the separators and the filters, is accomplished by that the block of the dehydration with combination of the functions of desalting and refining the crude oil is made as tanks of two-stage preparation of the raw stock with the built-in rotating vibrational devices, connected through the filters and a heat exchanger - recuperator with the means for heating the raw stock, made in the form of a plumb pipe-still kiln with coil pipes and the torch in the form of perforated plate with cone-shaped holes and connected with the block of distillation, that has an outlet for the end product in the form of the bottoms, and technologically connected with the tank of the second preparation stage of the raw stock and with the heat exchanger - recuperator and the condenser-cooler, having through the separators outlets of the end products: the burner fuel and the light hydrocarbon fraction, correspondingly.

[0018] In addition, the rotating vibrational devices are fixed in top of the tanks of the second preparation stage of the raw stock, the block of distillation represents the vacuum distillation still.

[0019] The end product, obtained on the apparatus in the form of bottoms, is fuel oil and has combustion heat 40560 kilojoule/kg.

[0020] Besides, the obtained burner fuel has fire point 40°C, and the light hydrocarbon fraction has boiling point <180°C.

[0021] The presence of the rotating vibrational device, that creates the oscillations in flow medium with determinate vibrational amplitude, passing into cavitation waves, therefore rate of movement of the microscopic globules of oil emulsion is increased, it is formed a possibility of collision and coagulation of globules, and also breaking of armouring shell on the surface of emulsive globules, generated by crystals of waxes, ceresines and inorganic compounds, and loss of water particles, provides quick and efficient dehydration, desalting and refining from sulfur and the mechanical impurities, of even strongly watered crude oil, and also increases of hydrocarbons density that results in enrichment of the yield of commercial hydrocarbons.

[0022] The two-stage preparation of the raw stock, the two-stage heating, the circulation and the recirculation of the heated up pulp of hydrocarbons allow to create the sparing temperature regimes that provides exclusion of the decomposition reactions, the oxidation reactions and the coking reactions of low molecular weight components of the raw stock, that in turn reduces laboriousness and accordingly power inputs, and also considerably reduces processing wastes and pollutions, making the said technology ecologically completely harmless.

[0023] The important factor concerning an ecology is also the crude oil used that represents wastes of oil-processing and/or petroleum chemical plants, and/or spent hydrocarbon oils, and/or the oil stock collected from traps of the refineries, from sea surface and other water area.

[0024] The lowering of power inputs is influenced also by a special design of the torch of the plumb pipe-still kiln, made in the form of perforated plate with numerous cone-shaped holes, in which these holes divide the torch flame into plenty of the smallest sprays with the increased output head of the combustible agent, and allow to heat evenly the flows of the raw stock that is provided by arrangement and a design of the kiln, and it, in turn, considerably saves a fuel rate.

[0025] The invention is illustrated by figures, where the general scheme of the apparatus for processing the mixed

petroleum-based wastes is shown in Fig. 1;

in Fig. 2 - the plumb pipe-still kiln in a sectional view;

in Fig. 3 - the torch, a top view;

in Fig. 4 - the torch, a view through A-A.

[0026] The apparatus for implementation of the method of processing the mixed petroleum-based wastes (Fig. 1) consists of the tanks 1, 2 for preparation of the raw stock, correspondingly, of the first and second stages, the heat exchanger - recuperator 3, the pipe-still kiln 4, the vacuum distillation still 5, the condenser - cooler 6, the separators 7 and 8, the filters 9 and 10, the tanks 11 for a plum of water, the tanks 12, 13, 14 for the end products of the burner fuel, the light hydrocarbons fraction and the bottoms, correspondingly.

[0027] The tanks 1 and 2 have the built-in rotating vibrational devices 15, fixed in a top of the tanks.

[0028] The apparatus is connected in a total flow sheet by lines 16 - 32.

[0029] The pipe-still kiln (Fig. 2), located vertically, contains coil pipes 33, 34, 35, forming radiant and conventional chambers, and the torch 36 in the form of perforated plate (Fig. 3) with cone-shaped holes in the cross section (Fig. 4).

[0030] The method of processing the mixed petroleum-based wastes on the apparatus implements as follows. The crude oil in the form of the waste products of the oil-processing, petroleum chemical plants, the spent hydrocarbon oils, the oil stock, collected from traps of the refineries, from sea surface and the artificial lakes, that represents a mixture of hydrocarbons with density $d_4^{20} = 0.86-0.88 \text{ g/cm}^3$, with initial boiling point 180°C and final boiling point 360°C , moisture content no more than 20-25 %, sulfur and mechanical impurities up to 10 %, is fed along the line 16 to the tank 1 for the first preparation stage of the raw stock, which is preheated up to temperature 60°C by means of, for example, water vapour, and settled during 7 hours. After settling, it is carried out the partial dehydration and desalting the settled raw stock by the vibratory-cavitational oscillations of the rotating vibrational device 15. The aqueous phase along the line 17 is transferred in the tank 11, and the organic phase along the line 18 through the filter 9 is fed to the tank 2 for the second preparation stage of the raw stock, which is subjected to further demulsification by the vibratory-cavitational oscillations of the rotating vibrational device 15. The aqueous phase formed along the line 19 is also transferred in the tank 11, from which it is withdrawn through a down-flow line 31.

[0031] The unrefined oil stock from tank 2 through the filter 8 is fed along the line 20 to a tube part of the heat exchanger - recuperator 3, where it is preheated up to 120°C , due to the heat of distillate, and along the line 21 fed to the pipe-still kiln 4. The crude oil is sequentially passed through the coil pipes 33, 34, 35 of the conventional and radiant chambers of the kiln 4, heating up to temperature $320-350^\circ\text{C}$, that is measured at the output of the kiln and adjusted by any known means, for example, by a thermocouple and a valve, correspondingly.

[0032] Heating in the pipe-still kiln 4 is carried out by feeding the combustible agent to the torch 36, for example, mixture of air and natural gas. Thus, the perforation of the torch and a conicity of the holes allow to speed up the reaching of the required temperature regime.

[0033] From the pipe-still kiln 4, the crude oil in vapour-liquid form is fed along the line 22 in a top of the vacuum distillation still 5, where the vapour-liquid mixture is separated into the distillate and the bottoms.

[0034] The distillate is withdrawn from the middle of the column of the vacuum distillation still at temperature from 180°C up to 360°C and a residual pressure 50 mmHg.

[0035] The vapours of distillate along the line 23 are transferred into annular space of the heat exchanger - recuperator 3, where the heat exchange with the crude oil takes place, and then along the line 24 the distillate through the separator 7, where being separated from the vapours of light distillates, is transferred into the tank 12, being under the vacuum 50 - 100 mmHg, for collecting of the desired fraction - the burner fuel, with boiling point $180^\circ - 320^\circ\text{C}$, density $0.835 - 0.84 \text{ g/m}^3$ and fire point 40°C .

[0036] The light fraction of hydrocarbons, with boiling point $<180^\circ\text{C}$, from the top of the column of the vacuum distillation still 5, is transferred along the line 25 into the cooler 6 for condensation, and through the separator 8 along the line 26 fed into the tank 13 for collecting of the light hydrocarbon fraction with the boiling point $<180^\circ\text{C}$.

[0037] The bottoms from below of the vacuum distillation still 5 (height of sampling 0,33H still) along the line 27 is fed in the tank 14 with possibility of registration of its temperature by any known means.

[0038] Physical-mechanical parameters of the bottoms are shown in Table.

Table

Parameter	Mazut F-5 according to GOST	Bottoms
Relative viscosity at 50°C mm^2/s , no more	36.2	35.0

Table (continued)

Parameter	Mazut F-5 according to GOST	Bottoms
Ash content, % no more	0.05	0.05
The content, % no more, of mechanical admixture water water-dissolv. acids and alkalis	0.10 0.3 absence	0.12 traces absence
Cokability, % no more	6.0	6.0
Temperature, °C, of flash in the closed crucible on gypsum, congelation, on gypsum	80 -5	85 -1
Combustion heat of mazut, kilojoule/kg (kcal/kg)	44454 (~10000)	40560 (9850)
Density at 20°C, kg/m ³ , no more	960	930

[0039] Referring to Table, the bottoms has the same quality parameters as mazut F-5, used as the fuel oil.

[0040] Total vacuum in the system is set up by known means, for example, by a pump such as BBH-12. In addition, the tanks 12, 13, 14, by turns, are disconnected from the vacuum system for unload of the end products through lines 28, 29, 30 into commercial tanks, whence they are directed to the consumer.

[0041] Until determination of temperature 270-300°C regime of separation of hydrocarbons in the vacuum distillation still 5, the pulp of hydrocarbons, being heated up in the kiln 4, circulates over the all system and along the line 32, through the tank 2 and along the line 20 under pressure, being set up by, for example, the pump, returns in the system. Feed control along lines 27 and 32 is carried out by any known means, for example, by valves.

[0042] Connection of vacuum to the system is carried out at the determination of temperature 200°-220°C regime in the vacuum distillation still 5.

[0043] The invention provides the decreasing of time of the settling and the demulsification of strongly watered mixed petroleum-based wastes, reduction of power inputs up to 1.5 - 2 % from the cost price of the end products, decreasing the processing waste and pollutions that makes the given technology ecologically completely harmless.

Claims

1. A method of processing mixed petroleum-based wastes, which comprises dehydration of crude oil, heating and disengagement of vapour products from the heavy cut, condensation of the vapour products, separation of the condensate into low and high-boiling fractions, **characterised in that** as the crude oil the mixed petroleum-based wastes are subjected to the processing, and the dehydration simultaneously with desalting are carried out by vibratory-cavitation oscillations of a rotating vibrational device, under action of which the raw stock is further refined from mechanical impurities and free sulfur, and after the two-stage heating, circulation and recirculation of the heated up pulp of hydrocarbons, the distillation of the low-boiling fractions is carry out, and the high-boiling fractions are separated by vacuum distillation giving the bottoms, and the distillate and light fraction of hydrocarbons are withdrawn from the column of vacuum distillation still giving, after separation, the burner oil and the light hydrocarbon fraction, correspondingly.
2. A method according to Claim 1, **characterised in that** the mixed petroleum-based wastes, being subjected to the processing, have water content up to 25 %.
3. A method according to Claims 1 or 2, **characterised in that** the mixed petroleum-based wastes, being subjected to the processing, have content of sulfur and mechanical impurities up to 10 %.
4. A method according to Claims 1-3, **characterised in that** as the mixed petroleum-based wastes, it is used the wastes of oil-processing and/or petrochemical plants, and/or spent hydrocarbon oils, and/or the oil stock, collected from traps of the refineries, from sea surface and other water areas.
5. A method according to Claims 1-4, **characterised in that** dehydration, desalting and refining from mechanical impurities and sulfur are carried out in two stages in tanks for preparation of raw stock.

6. A method according to Claims 1-5, **characterised in that** circulation and recirculation of the heated up pulp of hydrocarbons, after the second stage of heating, are executed up to determination of separation condition of hydrocarbons in vacuum distillation still.
- 5 7. A method according to Claims 1-6, **characterised in that** temperature of separation condition of hydrocarbons is 270-300°C.
8. A method according to Claims 1-7, **characterised in that** distillation of the low-boiled fractions is carried out at temperature 35-180°C.
- 10 9. A method according to Claims 1-8, **characterised in that** distillation of the low-boiled fractions is preferably carried out at temperature 70-150°C.
- 15 10. A method according to Claims 1-9, **characterised in that** distillation of the low-boiled fractions is carried out at atmospheric pressure.
11. A method according to Claims 1-10, **characterised in that** vacuum distillation is carried out at temperature 180-320°C.
- 20 12. A method according to Claims 1-11, **characterised in that** vacuum distillation is preferably carried out at temperature 210-300°C.
13. A method according to Claims 1-12, **characterised in that** vacuum distillate is withdrawn from the middle of column of vacuum distillation still.
- 25 14. A method according to Claims 1-13, **characterised in that** bottoms is fuel oil.
15. A method according to Claims 1-14, **characterised in that** obtained bottoms has combustion heat 40560 kilojoule/kg.
- 30 16. A method according to Claims 1-15, **characterised in that** obtained burner fuel has fire point 40°C.
17. A method according to Claims 1-16, **characterised in that** obtained light hydrocarbon fraction has boiling point <180°C.
- 35 18. An apparatus for realization of the method of processing mixed petroleum-based wastes, which comprises a block of dehydration of raw stock, a block of distillation, the means for heating the raw stock, a heat exchanger, a condenser, separators and filters, **characterised in that** the block of dehydration with combination of functions of desalting and refining the raw stock is made as tanks of two-stage preparation of the raw stock with the built-in rotating vibrational devices, connected through the filters and the heat exchanger - recuperator with the means for heating the raw stock, made in the form of a plumb pipe-still kiln with coil pipes and the torch in the form of perforated plate with cone-shaped holes and connected with the block of distillation, that has an outlet for the end product in the form of the bottoms, and technologically connected with the tank of the second preparation stage of the raw stock and with the heat exchanger - recuperator and the condenser-cooler, having through the separators outlets of the end products: the burner fuel and the light hydrocarbon fraction, correspondingly.
- 40 19. An apparatus according to Claim 18, **characterised in that** the rotating vibrational devices are fixed in top of the tanks of two-stage preparation of raw stock.
- 50 20. An apparatus according to Claims 18-19, **characterised in that** the block of distillation represents a vacuum distillation still.
21. An apparatus according to Claims 18-20, **characterised in that** end product in the form of bottoms is fuel oil.
- 55 22. An apparatus according to Claims 18-21, **characterised in that** bottoms has combustion heat 40560 kilojoule/kg.
23. An apparatus according to Claims 18-22, **characterised in that** burner fuel has fire point 40°C.

24. An apparatus according to Claims 18-22, ***characterised in that*** light hydrocarbon fraction has boiling point $<180^{\circ}\text{C}$.

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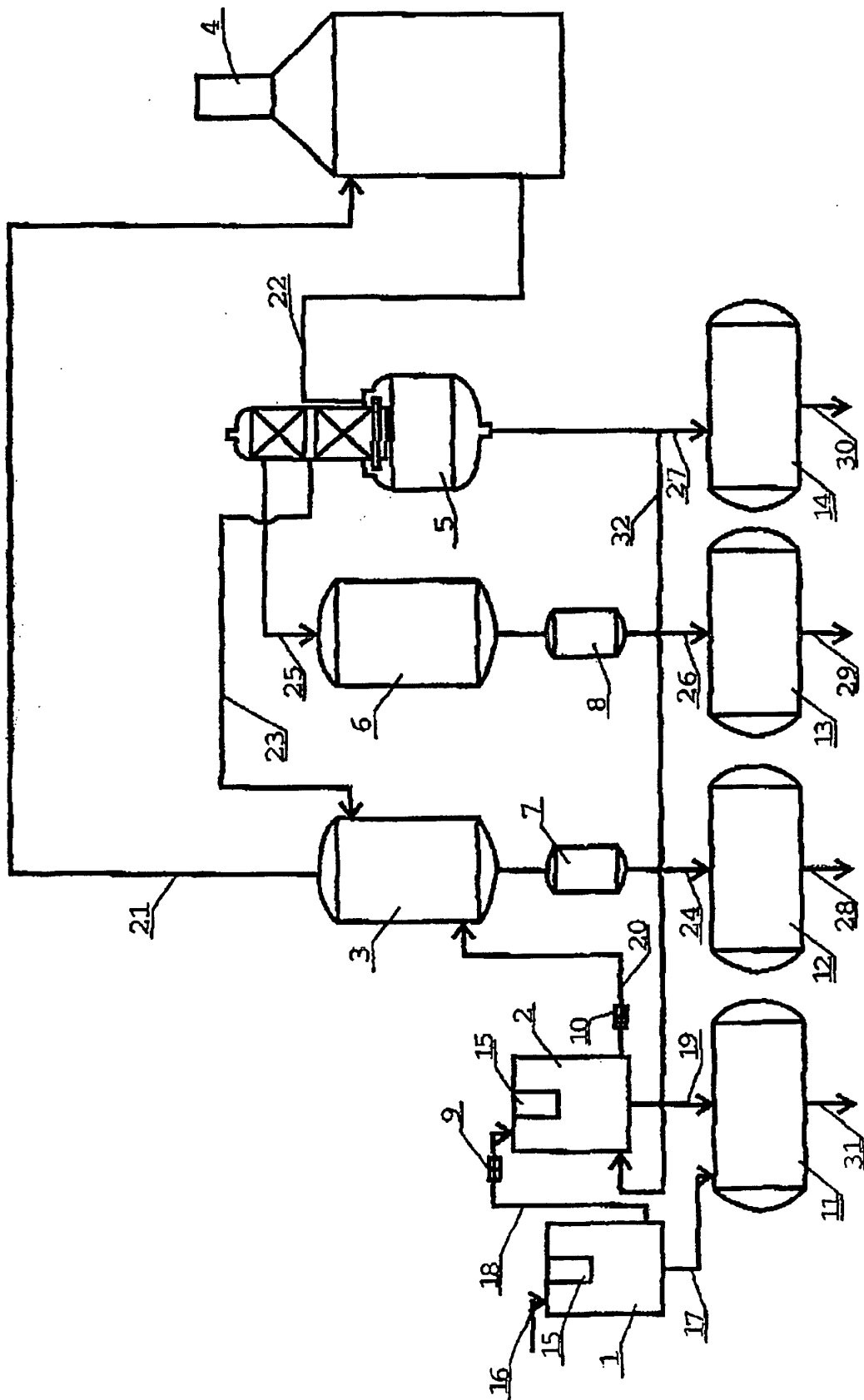


Fig. 1

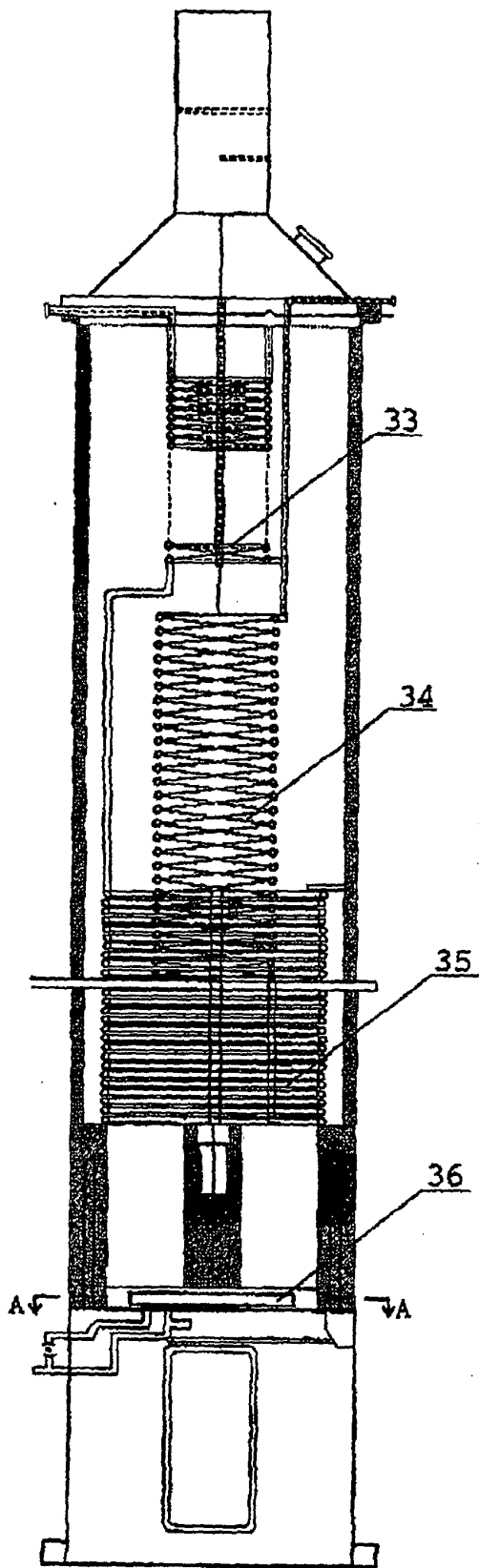


Fig. 2

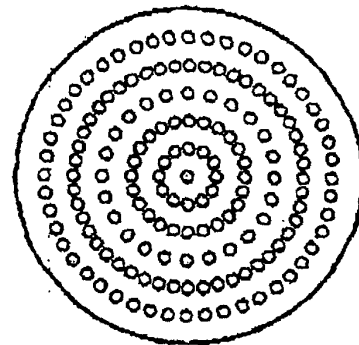


Fig. 3



Fig. 4