



(11)

EP 3 392 328 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
18.09.2019 Bulletin 2019/38

(51) Int Cl.:
C10M 175/00 (2006.01)

(21) Application number: **18166609.0**

(22) Date of filing: **10.04.2018**

(54) PROCESS FOR THE REGENERATION OF EXHAUST OILS

ALTÖLREGENERATIONSVERFAHREN

PROCÉDÉ DE RÉGÉNÉRATION D'HUILES USÉES

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**
Designated Validation States:
MA MD TN

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(30) Priority: **19.04.2017 IT 201700042853**

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(43) Date of publication of application:
24.10.2018 Bulletin 2018/43

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Description

[0001] The present invention refers to a process for the regeneration of exhaust oils, in which the silicon sources are removed.

[0002] Lubricating oils have been used for a very long time in almost all the fields of mechanics to facilitate the mutual sliding of engine parts or the like. A classic example is that of oil used in internal combustion engines to help the sliding of the pistons in the cylinders, without the mechanical parts getting stuck into one another.

[0003] Lubricating oils are often used in machinery having very fast relative sliding movements of their parts. Because of this, in addition to other aspects, lubricating oils frequently undergo temperature changes, which are in some cases remarkable. For this reason, oils undergo chemical reactions of various kinds and their nature is altered. As a consequence, reactions such as cleavage, dehydration, dehydrogenation, condensation, etc. take place. An example of such a reaction is the dehydrogenation-dehydration of oils, which leads to the formation of carbon in the form of carbon black. In some cases, the formation of asphaltenes and bitumens also occurs. Furthermore, oils can contact other substances, such as, for example, metallic and/or ceramic particles, thus remaining inside the oil itself. Moreover, it is not uncommon that spurious substances, such as various types of polymers, coming from the external, get mixed with oils, since their use and/or collection after use do not always take place in an appropriate manner and with precautions aimed at avoiding the introduction of foreign substances and of obtaining a quality waste, which can be easily regenerated.

[0004] The above-mentioned and other transformations determine the impairing of physical and chemical features of the oil, making it eventually harmful for the parts of the machines themselves to which it is applied, because the foreign substances inside the oil significantly increase friction. Therefore, it is appropriate to replace the oil with fresh oil after a certain period of use, so as to avoid performance reduction or, even, damage or breakage.

[0005] Exhaust oil normally contains a number of substances toxic for the humans and the environment, for which reason it cannot be simply discharged into the environment, but it must be appropriately treated so as to reduce its environmental impact. The regeneration of exhaust oils has thus emerged as a solution, allowing to reduce waste and the resulting environmental impact.

[0006] The first plants for re-refining exhaust oils date back to the 60s of the twentieth century, when environmental awareness began to develop and spread. Owing to the high costs to obtain freshly refined oils and because of the increase in consumption of these oils, the regeneration of exhaust oils has been gaining important market shares over time.

[0007] The establishment of mandatory consortia, responsible for the collection of exhaust oils, has also made

easily available the material to be treated - the actual raw material of these processes -, now widely accessible at a good price, although its quality is sometimes quite poor; in particular, there are types of waste exhibiting quality which can be quite different from each other. This type of market has significantly expanded over the years. About a third of exhaust oil is properly collected by the consortia and sent to regeneration or to other treatments to make it harmless, the rest being improperly dispersed in an uncontrolled manner into the environment and being a source of pollution or, in any case, lost in its service cycle, with a remarkable economic damage as well.

[0008] The typical yield of a regeneration process, starting from 100 kg of exhaust oil to be sent to the process, is now around 60 kg of regenerated oil (base for lubricants), 20-25 kg of fuel and 20-25 kg of bitumen.

[0009] Historically, the first processes were those with sulphuric acid or with liquid propane. In other words, oils are treated by adding sulphuric acid or propane, so as to eliminate a large part of impurities contained in exhaust oils. However, the process involving the use of acid has been virtually abandoned, due to the considerable pollution problems it entails.

[0010] The process with sulfuric acid causes, indeed, the build up of acid sludges, which retain inside them not negligible amounts of oil and which also contain polymeric compounds and heavy metals; these sludges are therefore difficult to dispose. Normally, such disposal takes place in landfills, preferably after a neutralisation, which, however, increases the volume to be disposed of the sludges themselves. The solution of sludge combustion has been tested, but turned out to be impractical.

[0011] Other processes, starting from the already mentioned one that makes use of propane, were thus developed.

[0012] The step of acid treatment is completely replaced by clarification with liquid propane. The chosen hydrocarbon is propane for being easily liquefiable and having a low density once liquefied. It therefore acts as fluidifying agent on oils to which it is added, so as to allow the separation of a high-density phase - containing high molecular weight polymers and heavy metals - from a second fraction, constituted by clarified and dehydrated oils. Propane is then removed and recycled by mixing it with the in-fed oils.

[0013] A hot filtration is then performed, allowing the recovery of a gaseous fraction. Discolouration and deodorisation of the content close the process.

[0014] However, this process allowing to achieve higher yields still has some disadvantages. First of all, handling propane can be dangerous for plant workers. Moreover, a part of the propane is trapped in the asphalt; this presence excludes the use of the obtained bitumen for the construction of roads, with considerable market limitation - in a strategic field - and consequent economic damage. As a result, the bitumen fraction in this process is simply a waste to be disposed and cannot be enhanced, as, instead, it would be desirable. Finally, the

process itself is much more expensive than the process with sulphuric acid.

[0015] In more recent years, a new type of process has been introduced, according to which exhaust oils are sent to the axial rotor of a distillation column and are sprayed by said rotor on the inner walls of the column, kept at a high temperature by a diathermic fluid flowing through some ducts. In contact with the heated walls, the vaporisable fraction evaporates, while the heavier fraction remains in the liquid phase. Fractions are then collected and further fractioned in a subsequent fractioning column, where they are divided into further cuts inside a subsequent fractioned distillation column. The yields of this process are high, but a pre-treatment is required to purify the exhaust oils.

[0016] EP 0 618 959, of the same Applicant, discloses a process for re-refining waste oils, in which said oils are contacted with a basic reagent and heated to remove contained water, polymers and heavy metals are separated and fractioned distillation is performed in a packed column, in order to obtain one or more base fractions for lubricant, followed by discolouration. The basic reagent is a strong base, water is removed together with a more volatile fraction in a preliminary step of flash distillation, while polymers and heavy metals are removed mostly by decanting. However, the packed distillation column tends to become clogged by solid residues, still contained in the oil to be fed inside the same. Furthermore, the partial vaporisation distillation column entails high operating costs.

[0017] Recently, the same Applicant filed the Italian patent application no. MI2015A 000626 for a process which, starting from that of EP 0 618 959, provides for a centrifugation step of the oil to be regenerated between the step of flash distillation and the step of distillation in the packed column. The pressure inside the packed distillation column is adjusted through a liquid-ring pump, obtaining a cleaner product and a reduced number of interventions to regenerate the distillation column.

[0018] WO2004/033 608 discloses a process and a device for the treatment of exhaust oils, which includes a preliminary separation by decanting of at least one fraction of the water and one fraction of solid particles (sediments), a preheating of the oily phase from the decanting step and centrifugal separation of the oil, preheated to a temperature below the boiling point of water, followed by the separation of water and other pollutants. The product obtained, however, is not reused to produce new lubricant bases, but is fed to a combustion step, along with other hydrocarbons, therefore with no enhancement of the same.

[0019] WO96/00 273 discloses a process of reclamation of exhaust oils, with a view to their reuse. According to this document, exhaust oil undergoes a centrifugation as it is to remove solids; the output oil is then contacted with diammonium phosphate and/or oxalic acid at a temperature between 60 and 85-90°C and is then subjected to a new centrifugation, to separate oil and water. There

are no distillation steps.

[0020] EP-A-3 098 291 discloses a process for the regeneration of waste oils, comprising a flash distillation step of the oil to be regenerated, a decanting step of the heavy fraction, a distillation step in a packed distillation column, allowing to produce an oil fraction to be sent to hydrotreating and a bitumen fraction. The bitumen fraction is ground, the liquid fraction obtained after grinding being separated and collected as bitumen and the remaining solid fraction being separated and recycled to said step of decanting of the heavy fraction.

[0021] All these and other regeneration processes, while leading to appreciable results in terms of base yields for lubricating oils and possibly to other poorer fractions, such as bitumen and the like, however often have the drawback of containing varying quantities of silicon, in the form of silica. Such silica is harmful to the oil, so that the standards commonly provide that the silica content in the oils must be below a threshold value. In fact, a high silicon content in a lubricating oil is often related to the increase in the level of wear metals in the exhaust oil, when it is then removed and collected for disposal (owed to the abrasion of the silicon on moving components). The presence of excessive quantities of silicon leads to a more frequent oil change and to damage or clogging of the filters, with their consequent occlusion. Furthermore, damage to moving parts can occur. Currently, the maximum allowed silicon content is 10 mg/l.

[0022] This problem is particularly felt for the lubricating bases that are obtained from the regeneration processes of exhaust oils and which provide a hydro-refining unit of the oils produced, before their use. In this case, the lubricating bases obtained contain around 50 mg/l of silica, i.e., they have a silicon content much higher than that allowed by the regulations and, thus, a removal of the silica becomes mandatory in order to put on the market the product obtained from the regeneration.

[0023] The underlying problem of the invention is to propose a process and a regeneration plant of exhaust oils which overcomes the above mentioned drawbacks and which allows to obtain as a main product, bases for lubricants with zero or low silicon content. According to a first aspect, this object is achieved through a process for the regeneration of exhaust oils, comprising a fractional distillation step and a hydro-refining step, characterised in that the hydrogen supplied during the hydro-refining step comes from the reforming of biogas, and in that the hydrogen recycled following after hydro-refining undergoes desiloxanation before being reintroduced into the hydro-refining reactor. According to a second aspect, the object is achieved through a plant for the regeneration of exhaust oils, comprising a column for fractional distillation and a hydro-refining reactor of the fractions leaving said fractional distillation column, wherein the outgoing product is separated into product and recycled matter, the latter consisting mainly of unreacted hydrogen, characterised in that said recycled matter is sent back to the hydro-refining reactor after having run through a desi-

loxanation unit and in that the hydrogen supplied during the hydro-refining step comes from the reforming of biogas. The dependent claims describe preferred features of the invention.

[0024] Further features and advantages of the invention will anyhow be more apparent from the following detailed description of a preferred embodiment, given by mere way of non-limiting example and illustrated in the accompanying drawings, wherein:

Fig. 1 is a block diagram illustrating, in general, a regeneration plant of exhaust oils within which the present invention can be applied; and

Fig. 2 is a block diagram illustrating an area of the plant of Fig. 1, according to a preferred embodiment of the present invention;

[0025] Fig. 1 shows, in an extremely general and schematic way, a plant for the regeneration of exhaust oils, of the type that can be used to put implement the process according to the present invention.

[0026] The plant comprises a feeding 1, from which the exhaust oils, as they come from the collection and possibly mixed with alkalis and pre-stirred, are fed. It is possible that the oils fed in 1 have already undergone some pre-treatments, of which, however, it is not considered necessary to further discuss here, because, although certainly useful for the quality of the product that can be obtained, such treatments, however, do not affect the present invention.

[0027] The feeding 1 is connected to a flash distillation column 2. The column 2 mainly serves to remove a large part of the pollutants contained in the oil to be regenerated, in particular water and contaminants dissolved therein or mixed therewith. The column 2 comprises two outlet ducts, 3 and 4. The duct 4 is connected to a fractional distillation column 5.

[0028] A member of flows come out from column 5. The duct 6 is an exhaust duct, mainly containing bitumen, while the ducts 7, 8 and 9 are connected to a hydro-refining reactor 10. The ducts 11, 12 and 13 come out of the column 10, which contain the bases for lubricants which constitute the desired product.

[0029] In Fig. 2 the hydro-refining reactor 10 is shown, for simplicity, fed by the duct 9 alone and with the outlet duct 13 alone; the arguments that will be referred below can also be applied to the ducts not shown, but still present in the system.

[0030] The duct 13 coming from the reactor 10 leads to a liquid-gas separator 14. The separator 14 has a drain 15 and a recycled 16.

[0031] According to the present invention, a desiloxanation unit 17 is inserted on the recycled 16. The recycle 16 continues until it converges into the feeding 9.

[0032] During the process for the regeneration of exhaust oils, the feeding 1 is sent to a flash distillation column 2, operating at a temperature just above the boiling temperature of the water, preferably at about 140°C. Low

pressure is maintained, generally around 250 torr. From column 2, water vapour flows through the duct 3, which is created by evaporation of the water contained in the oil to be regenerated, while the oil to be further regenerated flows through the duct 4, from which it is brought in known manner to a temperature higher than 300°C, thus being fed to the fractional distillation column 5. The bitumen by-product comes from the duct 5, which can be further treated in a manner known per se for its valorisation, while the product to be regenerated comes from the ducts 7, 8 and 9; the ducts 7, 8 and 9 themselves feed this product to be regenerated to the hydro-refining column 10, from which, through the ducts 11, 12 and 13, the bases for lubricants come out, which are the product of the process according to the invention. Possible microfiltration units can be provided downstream of the hydro-refining reactor 10, to further push the regeneration and obtain an even higher quality product.

[0033] In column 10, the hydro-refining takes place at a temperature between 260 and 360°C, at a pressure of about 100 bar and in the presence of a catalyst based on NiMoO₄.

[0034] Preferably, the hydrogen fed in the hydro-refining step comes from the reforming of biogas. In fact, the hydrogen obtained from this source allows to reduce the environmental impact linked to its production.

[0035] The products come from the reactor 10 through the ducts 11, 12 and 13. They are fed to the liquid-gas separator 14. The liquid flow 15 is sent for sale as a product, while the flow 16, containing mostly unreacted hydrogen, is sent to the desiloxanation unit 17. In said unit 17, known per se, the siloxane is removed from the gas flow, which, thus, remains purified. The removal of the siloxane can take place by means of activated carbons, anaerobic digestion, regenerative filtration, microemulsion, or by other techniques, mostly known per se.

[0036] In this way, the gas hydrogen which is thus recycled to the reactor 10, contains less siloxane than at the beginning. A siloxane and not another siliceous compound is removed, because it has been found that the silica found in the lubricating bases constituting the final product of these processes comes mainly from the transformation of siloxane into silica.

[0037] The arrangement of the desiloxanation unit 17 on the recycling of the unreacted hydrogen inside the duct 16 has advantages which are not imaginable per se in the light of the current state of the art. In fact, one could think of placing the aforementioned unit on the effluent of the product (15). In this way, the product would have a silicon content lower than the allowed limits, so that it can be easily sold without further treatments to remove silicon. However, the arrangement of the unit 17 on the duct 16 causes the hydrogen to be fed to the reactor 10 to contain a lower silicon concentration than is normally the case. In fact, it seems very likely that the silicon that is at the end of conventional regeneration processes contains silica obtained by transformation of siloxane and it seems that the siloxane is introduced into the regenera-

tion cycle by hydrogen, especially if it comes from reforming of biogas, which contains from 1500 to 4000 mg/l; normally, this type of hydrogen is used for its reduced environmental impact, but, as mentioned above, the siloxane content is higher than in the hydrogen obtained from other sources.

[0038] The fact that the unit 17 is arranged on the recycle duct avoids the hydrogen recycled to the reactor 10 from containing only negligible amounts of siloxane and its mixing with the fresh hydrogen thus allows to introduce into the reactor 10 a quantity lower than the normal siloxane, so as to allow a longer duration of the catalyst based on NiMoO_4 . Thus, compared to the traditional process, there is a more pure product (containing less silica), with a much longer duration of the life of the catalyst based on NiMoO_4 , with a consequent economic advantage that is not negligible, as, in addition to a lower purchase price and activation of the catalyst, there are less downtime of plant shutdown, with a not negligible increase in productivity. It is understood, however, that the invention is not to be considered as limited by the particular arrangement illustrated above, which represents only an exemplary embodiment of the same, but different variants are possible, all within the reach of a person skilled in the art, without departing from the scope of the invention itself, as defined by the following claims.

[0039] In particular, the plant has been described in very general terms and it is possible that there are other units, such as centrifuges, decanters, grinders, mixers and others.

LIST OF REFERENCE NUMERALS

[0040]

- 1 Exhaust oil feeding
- 2 Flash distillation column
- 3 Exhaust duct
- 4 Duct
- 5 Fractional distillation column
- 6 Exhaust duct
- 7 Duct
- 8 Duct
- 9 Duct
- 10 Hydro-refining reactor
- 11 Duct
- 12 Duct
- 13 Duct
- 14 Liquid-gas separator
- 15 Product delivery duct
- 16 Duct
- 17 Desiloxanation unit

Claims

1. Process for the regeneration of exhaust oils, comprising a fractional distillation step and a hydro-re-

fining step, **characterised in that** the hydrogen supplied during the hydro-refining step comes from the reforming of biogas, and **in that** the hydrogen recycled following after hydro-refining undergoes desiloxanation before being reintroduced into the hydro-refining reactor.

2. Process as in 1), **characterised in that** the removal of siloxane occurs by means of activated carbons, anaerobic digestion, regenerative filtration or microemulsion.
3. Process as in any one of the preceding claims, **characterised in that** a microfiltration step of the lubricating bases is provided downstream of the hydro-refining step.
4. Plant for the regeneration of exhaust oils, comprising a column (5) for fractional distillation and a hydro-refining reactor (10) of the fractions leaving said fractional distillation column (5), wherein the outgoing product is separated (14) into product (15) and recycle (16), the latter (16) consisting mainly of unreacted hydrogen, **characterised in that** said recycle (16) is sent back to the hydro-refining reactor (10) after having run through a desiloxanation unit (17) and **in that** the hydrogen supplied during the hydro-refining step comes from the reforming of biogas.
5. Plant as in 4), **characterised in that** it comprises a flash distillation column (2).
6. Plant as in 4) or in 5), **characterised in that** it furthermore comprises a microfiltration unit downstream of the hydro-refining reactor (10).

Patentansprüche

1. Verfahren für die Regeneration von Altölen, umfassend einen fraktionierten Destillationsschritt und einen Hydro-Verfeinerungsschritt, **dadurch gekennzeichnet, dass** der Wasserstoff, der während des Hydro-Verfeinerungsschritts geliefert wird, aus dem Reformieren von Biogas kommt, und dass der Wasserstoff, der folgend nach dem Hydro-Verfeinern recycelt wird, einer Desiloxanierung unterliegt, bevor er wieder in den Hydro-Verfeinerungsreaktor eingeführt wird.
2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** das Entfernen von Siloxan mittels Aktivkohle, anaerober Verarbeitung, regenerativer Filtration oder Mikroemulsion stattfindet.
3. Verfahren nach einem der vorangehenden Ansprüche, **dadurch gekennzeichnet, dass** ein Mikrofiltrationsschritt der schmierenden Basen stromab-

wärts des Hydro-Verfeinerungsschritts bereitgestellt wird.

4. Anlage für die Regeneration von Altölen, umfassend eine Säule (5) zur fraktionierten Destillation und einen Hydro-Verfeinerungsreaktor (10) der Fraktionen, die die fraktionierte Destillationssäule (5) verlassen, wobei das Ausgabeprodukt in Produkt (15) und Rezyklat (16) getrennt wird, wobei das letztere (16) hauptsächlich aus nicht umgesetztem Wasserstoff besteht, **dadurch gekennzeichnet, dass** das Rezyklat (16) zu dem Hydro-Verfeinerungsreaktor (10) nach Durchgang durch eine Desiloxanierungseinheit (17) zurückgeführt wird, und dass der Wasserstoff, der während des Hydro-Verfeinerungsschritts geliefert wird, aus dem Reformieren von Biogas kommt.
5. Anlage nach Anspruch 4, **dadurch gekennzeichnet, dass** sie eine Flash-Destillationssäule (2) umfasst.
6. Anlage nach Anspruch 4 oder Anspruch 5, **dadurch gekennzeichnet, dass** sie ferner eine Mikrofiltrationseinheit stromabwärts des Hydro-Verfeinerungsreaktors (10) umfasst.

être passé à travers une unité de désiloxanation (17) et **en ce que** l'hydrogène fourni durant l'étape d'hydroraffinage provient du reformage de biogaz.

- 5 5. Usine selon la revendication 4, **caractérisée en ce qu'elle** comprend une colonne de distillation éclair (2).
- 10 6. Usine selon la revendication 4 ou 5, **caractérisée en ce qu'elle** comprend en outre une unité de microfiltration en aval du réacteur d'hydroraffinage (10).
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Revendications

- 30 1. Procédé pour la régénération d'huiles usées, comprenant une étape de distillation fractionnée et une étape d'hydroraffinage, **caractérisé en ce que** l'hydrogène fourni durant l'étape d'hydroraffinage provient du reformage de biogaz, et **en ce que** l'hydrogène recyclé après hydroraffinage subit une désiloxanation avant d'être introduit dans le réacteur d'hydroraffinage.
- 35 2. Procédé selon la revendication 1, **caractérisé en ce que** l'élimination du siloxane a lieu au moyen de charbons activés, d'une digestion anaérobie, d'une filtration régénérative ou d'une microémulsion.
- 40 3. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce qu'une** étape de microfiltration des bases lubrifiantes est prévue en aval de l'étape d'hydroraffinage.
- 45 4. Usine pour la régénération d'huiles usées, comprenant une colonne (5) pour distillation fractionnée et un réacteur d'hydroraffinage (10) des fractions quittant ladite colonne de distillation fractionnée (5), dans laquelle le produit sortant est séparé (14) en produit (15) et en recyclage (16), ce dernier (16) consistant principalement en hydrogène n'ayant pas réagi, **caractérisée en ce que** ledit recyclage (16) est renvoyé au réacteur d'hydroraffinage (10) après
- 50
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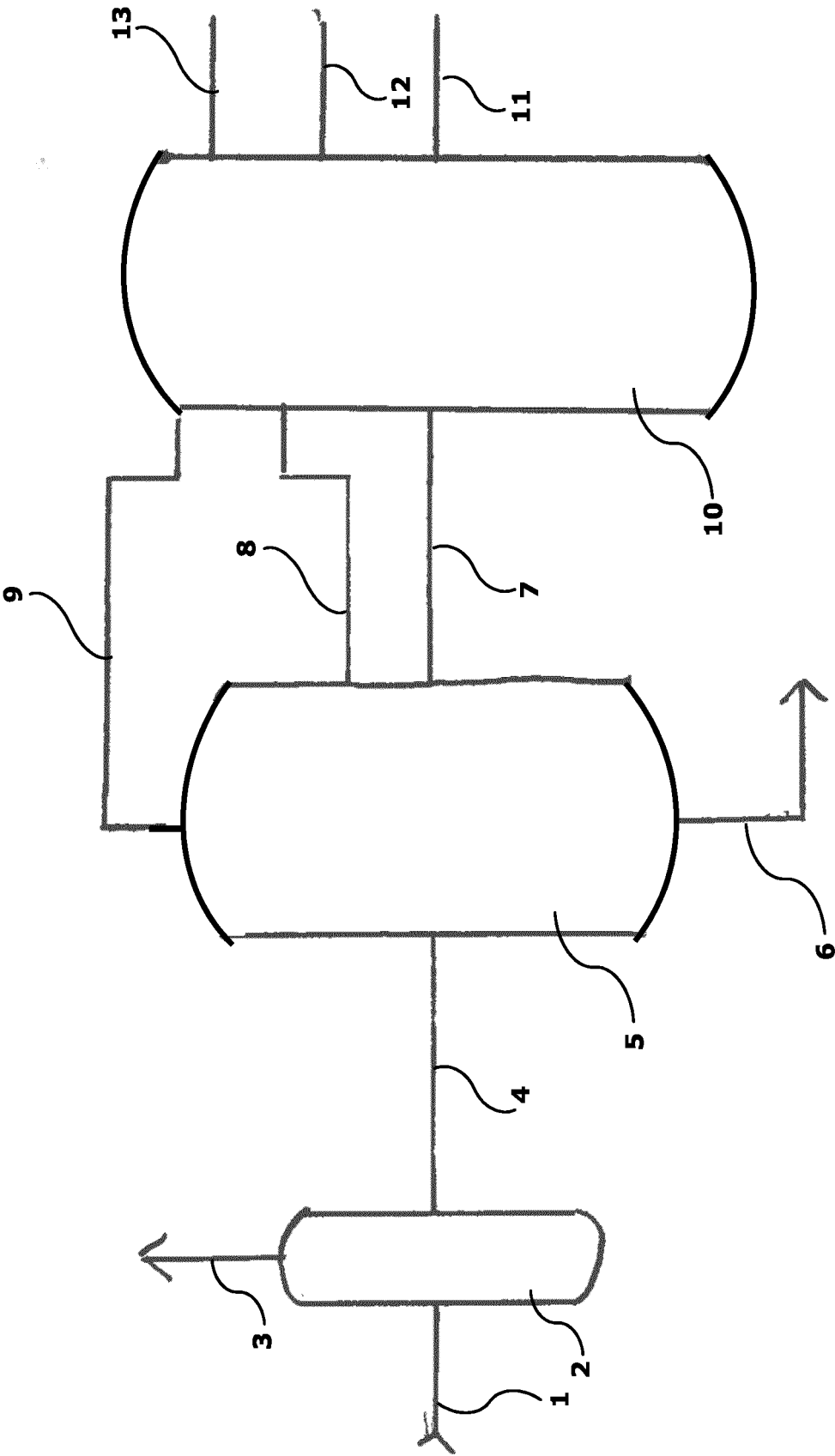


Fig. 1

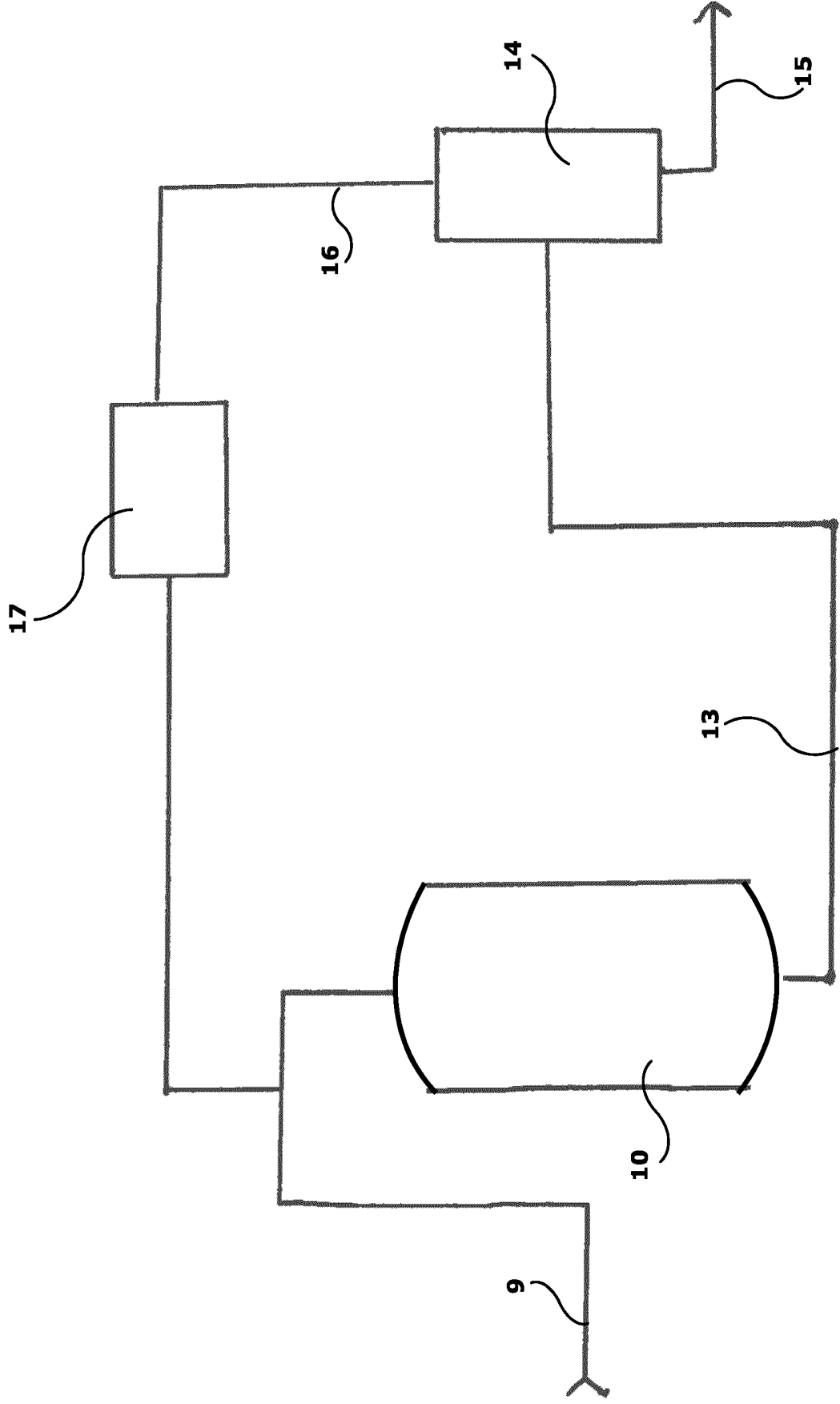


Fig. 2

REFERENCES CITED IN THE DESCRIPTION

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