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(54) Process for decreasing acidity of a crude oil

Verfahren zur Verminderung des Sauregehalts von Rohöl

Procédé de réduction de l'acidité d'huile brute

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Description

[0001] The present invention relates to a process for decreasing the acidity of a crude oil.

[0002] Whole crudes and crude fractions with high petroleum acid content such as those containing naphthenic acids are corrosive to the equipment used to extract, transport and process the crude.

[0003] Efforts to minimize naphthenic acid corrosion have included a number of approaches. U.S. Patent 5,182,013 refers to such recognized approaches as blending of higher naphthenic acid content oil with low naphthenic acid content oil. Additionally, a variety of attempts have been made to address the problem by using corrosion inhibitors for the metal surfaces of equipment exposed to the acids, or by neutralizing and removing the acids from the oil. For example, Kalichevsky and Kobe in *Petroleum Refining with Chemicals (1956),* Chapter 4, disclose various alkali treatments of crudes and crude fractions. U.S. Patent 4,199,440 which teaches the use of difficult-to-break caustic-in-oil emulsions discloses treatment of a liquid hydrocarbon with a dilute aqueous alkaline solution, specifically dilute aqueous NaOH or KOH. U.S. Patent 4,300,995 discloses the treatment of carbonous material particularly coal and its products, heavy oils, vacuum gas oil, petroleum resids having acidic functionalities with a dilute quaternary base such as tetramethylammonium hydroxide in a liquid (alcohol or water). IR data of the untreated crude show a peak at 3300-3600 cm^{-1} corresponding to a phenolic hydroxide (Example 6). The C^{13} NMR spectrum of O-methylated crude shows a signal at 55 ppm corresponding to a methyl phenoxide (Examples 3 and 4). This patent was aimed at improving yields and physical characteristics of the products and did not address the question of acidity reduction. Kalichevsky and Kobe as well as U.S. Patent 4,199,440 note, however, that a problem arises because certain aqueous base solutions form stable caustic-in-oil emulsions, necessitating use of only dilute aqueous base solutions.

[0004] While these processes have achieved varying degrees of success there is a continuing need to develop more efficient methods for treating acidic crudes.

SUMMARY OF THE INVENTION

[0005] A process for decreasing the acidity of an acidic crude oil comprising: contacting an acidic crude oil with an effective amount of an aqueous base at conditions of pH and temperature sufficient to form an unstable emulsion of the acidic crude oil in the aqueous base and breaking the emulsion to form a phase containing treated crude oil having a decreased acidity and aqueous phase containing residual base and neutralized acids.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] Figure 1 describes the unstable oil in water emulsion treatment of the present invention as a standalone process.

[0007] Figure 2 describes the unstable oil in water emulsion treatment for removal of naphthenic acid from a crude oil at the well head integrated with a representative currently available process.

DETAILED DESCRIPTION OF THE INVENTION

[0008] Some crude oils contain organic acids that contribute to corrosion or fouling of refinery equipment and that are difficult to separate from the processed oil. The organic acids generally fall within the category of naphthenic and other organic acids. Naphthenic acid is a generic term used to identify a mixture of organic acids present in petroleum stocks. Naphthenic acids may be present either alone or in combination with other organic acids, such as phenols. Naphthenic acids alone or in combination with other organic acids can cause corrosion at temperatures ranging from about 65°C (150°F) to 420°C (790°F).

[0009] The crudes that may be used are any naphthenic acid-containing whole crude oils that are liquid or liquefiable at the temperatures at which the present invention is carried out. As used herein the term whole crudes means unrefined, non-distilled crudes. The acidic crudes are preferably whole crudes. However, acidic fractions of whole crudes such as vacuum gas oil also may be treated. An additional benefit of the treatment process is the absence or substantial absence of stable emulsion formation. Stable emulsion formation is undesirable and a particular problem that is encountered during treatment of acidic crudes with aqueous bases. The formation of a stable crude oil-aqueous base emulsion tends to interfere with the efficient separation of the crude oil and aqueous phases and thus with recovery of the treated crude oil. Thus, in addition to their corrosivity such acids must be removed from the crude oil due to their tendency to encourage stable emulsion formation during processing, especially desalting processes.

[0010] Unexpectedly, and contrary to prior art teachings, Applicants have discovered that acidic crudes, e. g., those containing naphthenic acids, may be treated by mixing the crude with an effective amount of an aqueous base at conditions of pH and temperature sufficient to form an unstable emulsion of the crude oil in the aqueous base ("oil-in-aqueous base") and coalescing (destabilizing) the emulsion to produce a first phase containing a treated or final crude oil having a reduced or essential absence of acidity and a second phase containing at least the remaining unreacted aqueous base. Neutralized acids, such as the corresponding naphthenate are present in the second phase or at the interface between the first and second phases. When the starting acidic crude is a calcium-containing crude, the process produces a treated crude having a decreased acidity and calcium content. Typically, the calcium is present as an insoluble, calcium-containing phase that is disposed between the first and second phases when the emulsion is broken. Optionally, the aqueous phase containing excess base may be recovered and reused in either a batch or continuous process to contact additional untreated crude, typically until the pH of the recovered aqueous phase reaches a pH of 8.0. Thus, desirably the aqueous phase is not completely neutralized and excess base is present in the recovered aqueous base.

[0011] The aqueous base is suitably an aqueous Group IA or IIA hydroxide, preferably NaOH or KOH solution, more preferably NaOH, having a pH of at least 8, preferably 8 to 12.

[0012] An unstable emulsion is formed by adding the acidic crude oil with only mild agitation to the aqueous base in a sufficient ratio to produce a dispersion of oil in a continuous aqueous base phase. The crude oil should be added to the aqueous base rather than the aqueous base being added to the crude oil, in order to minimize formation of a stable aqueous base-in-oil emulsion. A ratio of 1:3 to 1:15, preferably 1:3 to 1:4 of oil to aqueous base is used based on the weight of oil and water. A stable emulsion will form if the ratio of oil to aqueous base is 1:1 or less. The weight percent of base in water ranges from 0.5 to 3.0%. Droplet size of from 10-50 microns preferably 20-50 microns is typically needed. Contacting of the crude oil and aqueous phase should be carried out for a period of time sufficient to disperse the oil in the aqueous phase preferably to cause at least 50% by weight, more preferably at least 80%, most preferably 90% of the oil in the aqueous phase.

[0013] Contacting is carried out until the pH of the basic aqueous phase decreases to about 8. Until such time the aqueous phase may be recycled for use to treat additional starting acidic crude oil.

[0014] The contacting of the crude oil and aqueous base solution to form the unstable emulsion is carried out at temperature typically from about 10°C to 40°C. At temperatures of greater than 40°C the probability of forming a stable emulsion increases.

[0015] Contacting times depend on the nature of the crude to be treated, its acid content, and the amount and type of aqueous base added, but typically may be carried out for from about 2 minutes to about 2 hours. Similarly, time needed to coalesce or destabilize the emulsion will vary but typically 1-2 minutes is a minimum. Oil type, particle size and distribution of oil droplets affects coalescence/destabilization rates. Gravity or an electrostatic field may be applied to facilitate demulsification. Destabilizing or demulsifying additives or agents are not required, but may be used to enhance the rate of emulsion breaking.

[0016] Additionally, there may be added to the basic aqueous phase prior to contacting with the starting acidic crude oil a sufficient amount of non-ionic surfactant, preferably of a straight chain ethoxylated alcohol having a chain length of from 12 to 18 carbon atoms and from 10 to 50 ethoxy groups typically in an amount of less than 0.001 wt% based on weight of crude oil to enhance formation of the unstable emulsion.

[0017] The emulsion may be broken by any suitable method, preferably by gravity coalescence to generate a treated crude having a reduced acidity and an aqueous phase containing napthenate salts.

[0018] The bases and surfactants suitable for use in the process may be purchased commercially or synthesized using known procedures.

[0019] The concentration of acid in the crude oil is typically expressed as an acid neutralization number or acid number, which is the number of milligrams of KOH required to neutralize the acidity of one gram of oil. It may be determined according to ASTM D-664. Any acidic crude may be treated according to the present invention, for example, crudes having an acid neutralization number of from 0.5 to 10 mg KOH/g oil. Typically, the decrease in acid content may be determined by a decrease in the neutralization number or in the intensity of the carboxyl band in the infrared spectrum at about 1708 cm^{-1}. Whole crude oils with acid numbers of about 1.0 and lower are considered to be of moderate to low corrosivity. Crudes with acid numbers greater than 1.5 are considered corrosive. Acidic crudes having free carboxyl groups may be effectively treated using the process of the present invention.

[0020] Whole crude oils are very complex mixtures containing a wide range of contaminants and in which a large number of competing reactions may occur. Unexpectedly, in the current process not only is the acidity of the crude reduced but a reduction in calcium content is also effected.

[0021] The process of the present invention has utility in processes in which inhibiting or controlling liquid phase corrosion, e.g., of metal surfaces, is desired. More generally, the present invention may be used in applications in which a reduction in the acidity of an acidic whole crude would be beneficial.

[0022] By way of example the process is especially beneficial for treatment to decrease acidity and calcium content of acidic crude oils at the wellhead. Such crudes typically contain impurities such as naturally occurring or coproduced water and gases. In Figure 1 a full well stream containing whole acidic crude oil, water and gases is passed via line 1 to a separator 3, and separated into a gas stream, which is removed via line 2, a water stream containing trace amounts of oil which is removed via line 4 and combined with base, typically aqueous, from line 6 prior to entering contactor 7, and an oil stream containing trace amounts of water which is passed via line 5 to contactor 7. The upper water and base stream from line 4 and 6 and lower oil stream from line 5 are contacted in contactor 7 to form an unstable oil in aqueous base emulsion. Treated oil containing residual water is drawn off overhead from contactor 7 via line 5a and passed to separator 8 to separate the treated oil from residual aqueous base. The lower phase of aqueous base containing residual treated oil is drawn off below via line 4a and passed to separator 9 from which aqueous base is recovered and passed out via line 10 and may be recycled to line 6 or disposed of, and residual treated oil is passed via line 9a to stabilizer tower 12. From separator 8 treated oil is removed via line 8b to stabilizer tower 12 while aqueous base is removed via line 8a to separator 9. From stabilizer tower 12 gases and volatiles are removed through line 13 and treated oil via line 11.

[0023] In Figure 2 the process is shown integrated into a currently available process, thus 3, 8, 9 and 12 and the lines connecting them represent a process that exists typically at the wellhead for the separation of the full well stream of line 1 into gas stream via line 2, treated oil stream via line 11, and aqueous base via line 10. The streams leaving the separator 3 are gas via line 2, water containing traces of oil via line 4, and oil stream containing traces of water via line 5. The water containing trace amounts of oil passes via line 4 to a separator 9 which removes trace oil. The water is then injected into the well. The oil stream 5 passes to a separator 8 which removes traces of water. Finally the oil is passed via line 8b to a stabilizer tower 12 where residual gas and volatiles are removed overhead via line 13 and treated oil via line 11. The new contactor is represented by the block 7 and the lines connecting it to a typical current process. The feeds to contactor 7 are water via line 4 and the oil via line 5. Prior to entering contactor 7, base added via line 6 to the water line 4 as described with respect to Figure 1 above. In contactor 7, the aqueous base from lines 4 and 6 and oil from line 5 are mixed so as to form the unstable oil-in-caustic emulsion as described with respect to Figure 1, and after a sufficient mixing time, the phases are allowed to separate. The separated aqueous base-containing residual oil phase is passed via line 4a to separator 9, and the separated oil phase to separator 8. Valves V1 and V2 are provided to allow operation of the crude oil treatment process either in whole or in part with, or without the portions of the process associated with forming the unstable emulsion and separating the resulting products (contactor 7 and lines connected thereto) described in Figure 1. The reference numerals in Figure 2 correspond to the same numerals in Figure 1.

[0024] The present invention may be demonstrated with reference to the following non-limiting examples.

Example 1

[0025] 25g of Bolobo 2/4 (Chad crude oil) was added to 80 ml of 1.5 wt% NaOH solution in a separatory funnel. The oil/water mixture was shaken gently on a wrist shaker for 20 minutes. It was determined by droplet size measurements using a Coulter Multisizer 11 instrument that greater than 90% of the crude oil was dispersed as an oil-in-water emulsion. After contacting for 20 minutes, the shaker was stopped and the emulsion allowed to stand. In 10 minutes the emulsion destabilized and a yellowish lower aqueous phase separated out. The aqueous phase pH of 8.0 and the treated oil were separated. The aqueous phase was reused by repeating the above experiment (Example 2) with addition of a fresh batch of 20g of Bolobo 2/4 crude. Two treated crude oil samples were generated from the experiment:

[0026] Sample #1 in which the acidic crude was treated with fresh aqueous NaOH.

[0027] Sample #2 in which a second batch of acidic crude was treated with reused aqueous phase.

[0028] Both treated crude samples were centrifuged to remove traces of aqueous phase and then analyzed by the ASTM D-664 method. A 100% neutralization of the acid was observed. The corresponding aqueous phases from Samples #1 and #2 were neutralized with concentrated HCl to pH = and the petroleum acids were precipitated. The precipitated acids were extracted with methylene chloride and analyzed by infrared spectroscopy. A characteristic IR absorption at 1703 cm^{-1} was observed confirming the extraction of naphthenic acid into the aqueous phase.

Example 2

[0029] The procedure of Example 1 was repeated using ammonium hydroxide instead of sodium hydroxide. No reduction in acidity or extraction of acid into the aqueous phase was observed.

Example 3

[0030] The procedure of Example 1 was repeated using tetrabutyl ammonium hydroxide instead of sodium hydroxide. A stable unbreakable emulsion resulted. The treated crude could not be separated from the aqueous phase.

Example 4

[0031] A Chad crude (Kome 6/1) that was high in calcium (916 ppm) and in acidity was subjected to the procedure of Example 1. In addition to reduction in acidity, the calcium in the treated crude was reduced from 800 ppm to 32 ppm (96% reduction in calcium). A calcium-containing layer formed between the treated crude and aqueous phase when the unstable emulsion broke.

Claims

1. A process for decreasing the acidity of an acidic crude oil, comprising:

   (a) forming an unstable emulsion of the acidic crude oil in an aqueous base by mixing the crude with an effective amount of the aqueous base at condition of pH and temperature sufficient to form the unstable emulsion;

(b) breaking the unstable emulsion to produce a first phase containing treated crude oil having a decreased acidity and a second aqueous phase containing residual base and neutralized acids.

2. The process of claim 1, wherein the acidic crude oil is a calcium-containing acidic crude oil.

3. The process of claim 2, wherein the breaking of the emulsion produces a third phase, disposed between and separable from the first and second phases, containing calcium compounds.

4. The process of claim 2 or claim 3, for decreasing the acidity and calcium content of a calcium-containing acidic crude oil with water impurities, comprising:

(a) separating the crude oil into a first stream containing primarily water and trace amounts of the crude oil and a second stream containing primarily crude oil and trace amounts of water;

(b) combining the first stream with aqueous base;

(c) countercurrently contacting the first stream with aqueous base of (b) and second stream of (a) to produce an unstable oil in aqueous base emulsion;

(d) recovering a lower phase containing primarily aqueous base and residual treated oil and an upper phase containing primarily treated oil and residual aqueous base;

(e) separating the upper phase from step (d) into a treated oil stream containing residual water and an aqueous base stream containing residual treated oil;

(f) passing the lower phase of step (d) and the aqueous base stream of step (e) to a separator to recover an aqueous base stream and treated oil stream;

(g) passing the treated oil stream from step (e) and the treated oil stream from step (f) to a stabilizer tower;

(h) degassing and recovering the treated oil stream.

5. The process of any preceding claim, wherein the acidic crude oil in the aqueous emulsion has a droplet size of 10 to 50 microns.

6. The process of any preceding claim, wherein the acidic crude oil contains naphthenic acids.

7. The process of any preceding claim, wherein the base is present in an amount of from about 0. 5 to 3 wt% in water when the crude oil is added.

8. The process of any preceding claim, wherein a weight ratio of acidic crude oil to aqueous base of 1:3 to 1:15 is employed in producing the unstable emulsion.

9. The process of any preceding claim, wherein the base is selected from Group IA and IIA hydroxides, preferably NaOH or KOH.

10. The process of any preceding claim, wherein the aqueous base further contains a non-ionic ethoxylated alcohol surfactant having from 10 to 50 ethoxy groups and a chain length of 12 to 18 carbon atoms.

Patentansprüche

1. Verfahren zur Verringerung der Acidität eines sauren Rohöls, bei dem:

(a) eine instabile Emulsion des sauren Rohöls in einer wässrigen Base gebildet wird, indem das Rohöl mit einer wirksamen Menge der wässrigen Base bei pH- und Temperaturbedingungen gemischt wird, die geeignet sind, eine instabile Emulsion zu ergeben,

(b) die instabile Emulsion gebrochen wird, um eine erste Phase, die behandeltes Rohöl mit einer verringerten Acidität enthält, und eine zweite wässrige Phase herzustellen, die restliche Base und neutralisierte Säuren enthält.

2. Verfahren nach Anspruch 1, bei dem das saure Rohöl ein Calcium enthaltendes saures Rohöl ist.

3. Verfahren nach Anspruch 2, bei dem das Brechen der Emulsion eine dritte, Calciumverbindungen enthaltende Phase erzeugt, die sich zwischen der ersten und zweiten Phase befindet und von diesen abtrennbar ist.

4. Verfahren nach Anspruch 2 oder 3 zur Verringerung der Acidität und des Calciumgehalts eines Calcium enthaltenden sauren Rohöls mit Wasserverunreinigungen, bei dem

(a) das Rohöl in einen ersten Strom, der hauptsächlich Wasser und Spurenmengen des Rohöls enthält, und einen zweiten Strom, der hauptsächlich Rohöl und Spurenmengen an Wasser enthält, getrennt wird;

(b) der erste Strom mit wässriger Base kombiniert wird;

(c) der erste Strom mit wässriger Base aus (b) und der zweite Strom aus (a) im Gegenstrom kontaktiert werden, um eine instabile Öl-in-wässriger-Base-Emulsion zu ergeben;

(d) eine untere Phase, die hauptsächlich wässrige Base und restliches behandeltes Öl enthält, und eine obere Phase, die hauptsächlich behandeltes Öl und restliche wässrige Base enthält, gewonnen werden,

(e) die obere Phase aus Stufe (d) in einen behandelten Ölstrom, der restliches Wasser enthält, und einen wässrigen Basenstrom, der restliches behandeltes Öl enthält, aufgetrennt wird;

(f) die untere Phase aus Stufe (d) und der wässrige Basenstrom aus Stufe (e) in einen Separator geleitet werden, um einen wässrigen Basestrom und einen behandelten Ölstrom zu gewinnen;

(g) der behandelte Ölstrom aus Stufe (e) und der behandelte Ölstrom aus Stufe (f) in einen Stabilisatorturm geleitet werden; und

(h) der behandelte Ölstrom entgast und gewonnen wird.

5. Verfahren nach einem vorhergehenden Anspruch, bei dem das saure Rohöl in der wässrigen Emulsion eine Tröpfchengröße von 10 bis 50 μm hat.

6. Verfahren nach einem der vorhergehenden Ansprüche, bei dem das saure Rohöl naphthenische Säuren enthält.

7. Verfahren nach einem der vorhergehenden Ansprüche, bei dem die Base in einer Menge von etwa 0,5 bis 3 Gew.-% in Wasser vorliegt, wenn das Rohöl zugegeben wird.

8. Verfahren nach einem der vorhergehenden Ansprüche, bei dem ein Gewichtsverhältnis von saurem Rohöl zu wässriger Base von 1 : 3 bis 1 : 15 zur Herstellung der instabilen Emulsion verwendet wird.

9. Verfahren nach einem der vorhergehenden Ansprüche, bei dem die Base ausgewählt ist aus Gruppe IA und IIA Hydroxiden, bevorzugt NaOH oder KOH.

10. Verfahren nach einem der vorhergehenden Ansprüche, bei dem die wässrige Base außerdem ein nichtionisches ethoxyliertes Alkoholtensid mit 10 bis 50 Ethoxygruppen und einer Kettenlänge von 12 bis 18 Kohlenstoffatomen enthält.

Revendications

1. Procédé de réduction de l'acidité d'un pétrole brut acide comprenant :

(a) la formation d'une émulsion instable du pétrole brut acide dans une base aqueuse en mélangeant le brut avec une quantité efficace de la base aqueuse dans des conditions de pH et de température suffisantes pour former l'émulsion instable,
(b) la décomposition de l'émulsion instable pour produire une première phase contenant du pétrole brut traité ayant une acidité réduite et une deuxième phase aqueuse contenant la base résiduelle et des acides neutralisés.

2. Procédé selon la revendication 1, dans lequel le pétrole brut acide est un pétrole brut acide contenant du calcium.

3. Procédé selon la revendication 2, dans lequel la décomposition de l'émulsion produit une troisième phase, disposée entre la première et la deuxième phase, contenant des composés de calcium.

4. Procédé selon la revendication 2 ou 3, pour la réduction de l'acidité et de la teneur en calcium d'un pétrole brut acide contenant du calcium avec des impuretés aqueuses, comprenant :

(a) la séparation du pétrole brut en un premier courant contenant principalement de l'eau et des traces du pétrole brut et en un second courant contenant principalement du pétrole brut et des traces d'eau,
(b) la combinaison du premier courant avec la base aqueuse,
(c) la mise en contact à contre-courant du premier courant avec la base aqueuse de (b) et le second courant de (a) pour produire une huile instable dans une émulsion de base aqueuse,
(d) la récupération d'une phase inférieure contenant principalement une base aqueuse et une huile traitée résiduelle et une phase supérieure contenant principalement de l'huile traitée et une base aqueuse résiduelle,
(e) la séparation de la phase supérieure de

l'étape (d) en un courant d'huile traité contenant de l'eau résiduelle et en un courant de base aqueuse contenant de l'huile traitée résiduelle,
(f) le passage de la phase inférieure de l'étape (d) et du courant de base aqueuse de l'étape (e) vers un séparateur pour récupérer un courant de base aqueuse et un courant d'huile traitée,
(g) le passage du courant d'huile traitée de l'étape (e) et du courant d'huile traitée de l'étape (f) vers une tour de stabilisation, et
(h) le dégazage et la récupération du courant d'huile traitée.

5. Procédé selon l'une quelconque des revendications précédentes, dans lequel le pétrole brut acide de l'émulsion aqueuse a une taille de gouttelettes de 10 à 50 micromètres.

6. Procédé selon l'une quelconque des revendications précédentes, dans lequel le pétrole brut acide contient des acides naphténiques.

7. Procédé selon l'une quelconque des revendications précédentes, dans lequel la base est présente en quantité d'environ 0,5% à 3% en poids dans l'eau lorsque le pétrole brut est ajouté.

8. Procédé selon l'une quelconque des revendications précédentes, dans lequel un rapport pondéral du pétrole brut acide à la base aqueuse de 1:3 à 1:15 est utilisé pour produire l'émulsion instable.

9. Procédé selon l'une quelconque des revendications précédentes, dans lequel la base est choisie dans les hydroxydes des groupes IA et IIA, de préférence NaOH ou KOH.

10. Procédé selon l'une quelconque des revendications précédentes, dans lequel la base aqueuse contient en outre un agent tensioactif d'alcool éthoxylé non ionique ayant 10 à 50 groupes éthoxy et une longueur de chaîne de 12 à 18 atomes de carbone.

FIGURE 1

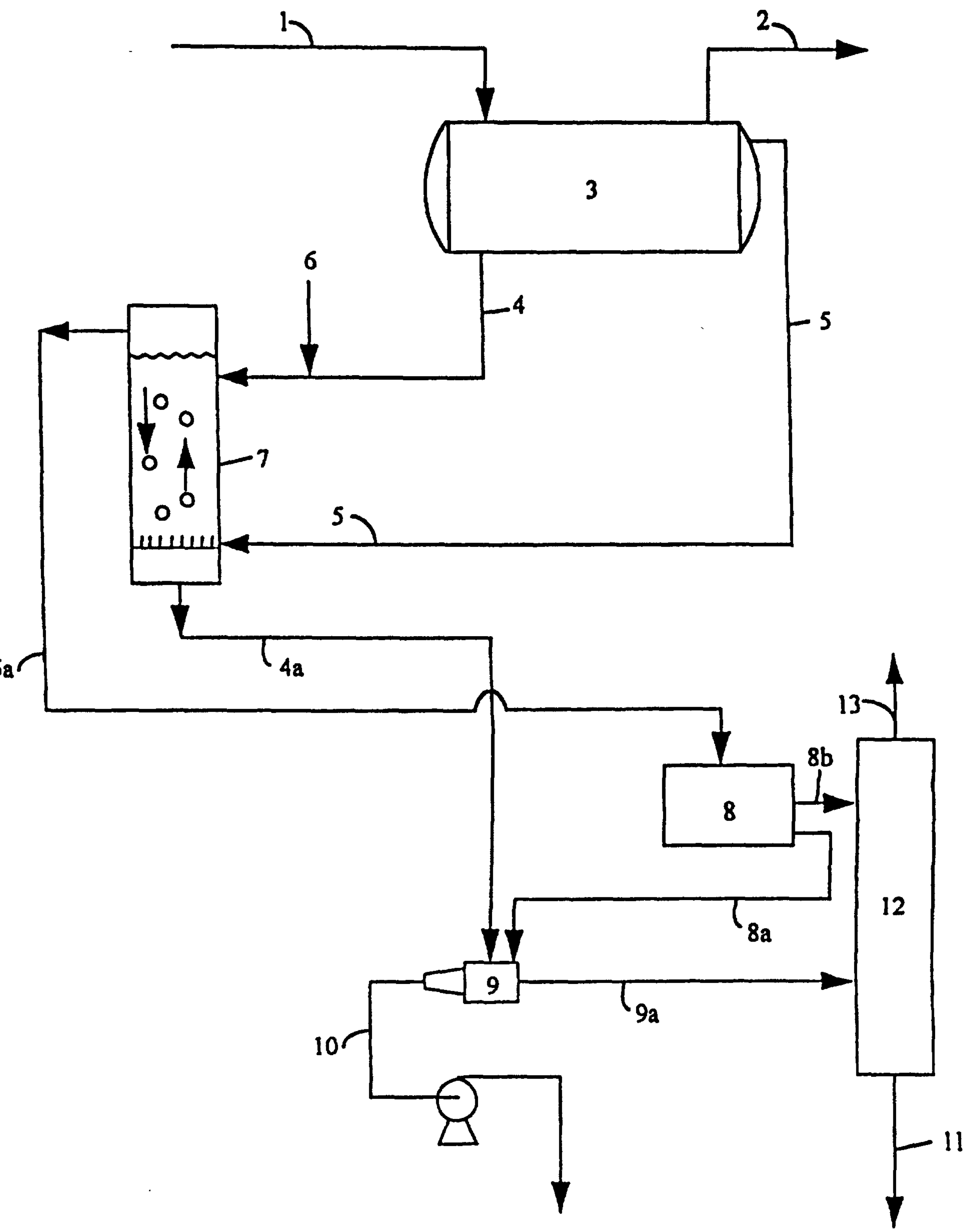

FIGURE 2