

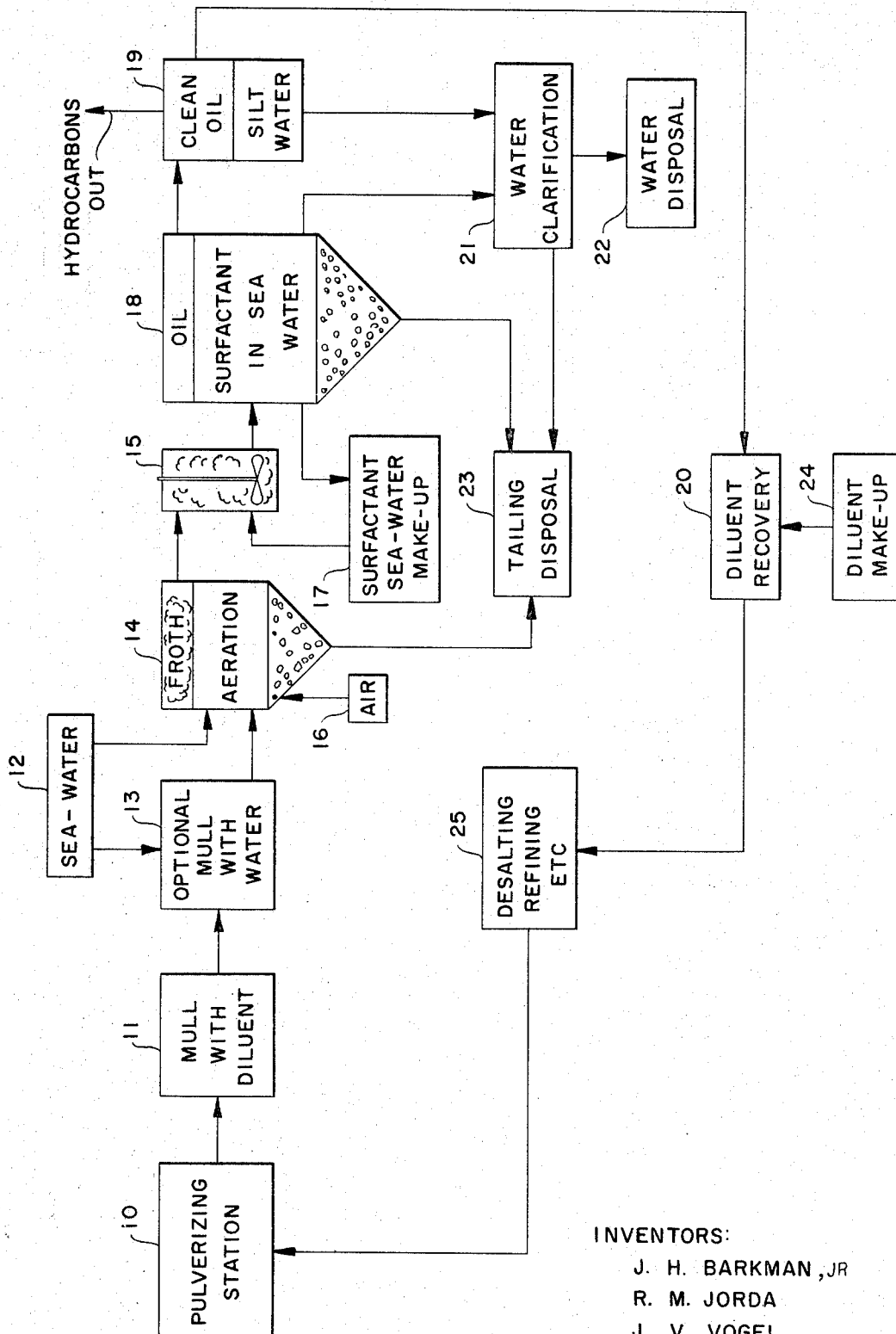
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RECOVERY OF OIL FROM BITUMINOUS SANDS

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RECOVERY OF OIL FROM BITUMINOUS SANDS
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ABSTRACT OF THE DISCLOSURE

A process for recovering oil from a tar sand wherein pulverized tar sand is mixed with a liquid hydrocarbon diluent. The diluted tar sand is then mixed with a first volume of hot brine at a controlled pH. The materials which float in the first volume of hot brine are isolated and mixed with a second volume of hot brine containing a surfactant. The second volume of hot brine is also at a controlled pH. Finally, any hydrocarbon materials that are substantially free of solids and aqueous liquids and float in the second volume of brine are isolated.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to a process for the separation or breaking of crude oil from bituminous sands, shales or other oil-bearing materials; and more particularly, to the separation or breaking of oil from tar sand.

Description of the prior art

Large deposits of bituminous sand are found in various localities throughout the world. The term "bituminous sand" is used herein to include those materials commonly referred to as oil sands, tar sands, and the like. One of the most extensive deposits of bituminous sands occurs, for instance, in the Athabasca district of Province of Alberta, Canada, and extends for many thousands of square miles in thicknesses ranging up to more than 200 feet.

Various methods have been proposed previously for separating crude oil from bituminous sands such as the Alberta tar sands, but none of these methods has met with any substantial success. Since the crude oil obtainable from this type of bituminous sand is a relatively viscous material having high tar content and relatively low commercial value in comparison with other crude oils, a successful commercial process must involve relatively little expense in the separation of the crude oil from the bituminous sands. Operating costs of previously conceived methods for separating the oil from bituminous sands have been sufficiently high so as to discourage commercial exploitation.

The most successful of the previously known methods for separating oil from tar sands such as the Alberta tar sands have involved the mixing of the bituminous sands with water followed by separation of sand from the mixture. In these processes, it has been found that complete separation of the crude oil from the water has presented considerable difficulty due to the formation of oil-water emulsions resulting in the discarding of significant quantities of crude oil which could not be successfully separated from the water.

Also, such prior art techniques involving tar sand extraction by aqueous systems, such as the hot water or the cold water process (discussed in a U.S. Pat. No. 2,825,677 to Coulson), and those discussed in various other patents for example U.S. Pat. Nos. 1,615,121 and 2,924,565, have generally stressed the need for using alkaline salts, such as sodium carbonate or sodium silicate, or high pH (of the order of 8 or more). All of these are incompatible

with ordinary sea water, an economic readily available fluid, due to the precipitation of various cation hydroxides such as iron, calcium, and magnesium under alkaline conditions. Such prior art processes either imply or explicitly state that fresh water, or perhaps brine in which the above cations are absent, must be used.

The aforementioned patent to Coulson discloses that water containing neutral salts may be used, but separation must be accomplished by centrifugation. In many locales, large amounts of fresh water are not available except at a prohibitive cost, and it is thus highly desirable to provide a process for extracting oil from a tar sand which employs either brine or sea water, especially in an acidic condition. Also, many tar sands, such as those located at Edna, Calif., contain connate water that is highly buffered on the acid side and which therefore requires unusually large and costly amounts of alkaline material to raise the pH above the neutral point. Moreover, for many reasons, including high maintenance costs and the fact that extremely large volumes of tar sand ore and water must be handled to recover a small volume of tar, centrifugation is not a satisfactory method in most cases.

SUMMARY OF THE INVENTION

It is an object of our invention to provide an improved method of separating or breaking oil from bituminous sands.

It is a further object of our invention to provide an economic method of separating or breaking oil from bituminous sands by aqueous extraction using neutral or acidic brine or sea water.

It is an even further object of our invention to provide such an aqueous extraction using neutral or acidic brine or sea water.

It is an even further object of our invention to provide such an aqueous extraction process which avoids the necessity for using alkaline material, high pH control of at least 8 or more, or centrifugation.

It is a still further object of our invention to provide a tar sand extraction process which results in the production of a final hydrocarbon product which is free of significant amounts of water or solids.

These objects are preferably carried out by mixing pulverized tar sand with a liquid hydrocarbon diluent. For example, the diluent may be one of a number of common or convenient substances including, but not limited to, fuel oil, stove oil, kerosene, toluene, etc., and may be used, for example, in quantities of the order of 10 percent to 200 percent by weight of tar present. The hydrocarbon-diluted tar sand is mixed with a first volume of hot brine having a controlled pH. The materials which float in the first volume of hot brine are isolated and mixed with a second volume of hot brine which contains a surfactant. The second volume of hot brine also has a controlled pH. Any hydrocarbon materials that are substantially free of solids and aqueous liquids and float in the second volume of hot brine are isolated.

Any of the hydrocarbons that are substantially as volatile as the liquid hydrocarbon diluent are preferably evaporated and the remaining oil is recovered.

BRIEF DESCRIPTION OF THE DRAWING

The drawing is a diagrammatic illustration of a suitable arrangement for carrying out a preferred embodiment of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

When oil-bearing tar sand is mixed with a suitable solvent, the oil can then be displaced with water under certain conditions. A discussion of this phenomenon appears in the aforementioned patent to Coulson. In the

process of our invention, referring now to the drawing, tar sand ore is pulverized as by crushing or grinding in any conventional manner at a pulverizing station 10. The method of crushing or grinding the tar sand is not critical and a suitable process is disclosed in U.S. Pat. No. 2,924,565 to Steagemeir et al.

The pulverized ore is next milled at mulling station 11 with a suitable hydrocarbon diluent as will be discussed further hereinbelow in a conventional manner for a period long enough to allow the tar and diluent to mutually dissolve. The tar sand is substantially uniformly diluted to an oil phase exhibiting a viscosity of less than about 100 cp. at a temperature of less than 200° F.

At this point, if desired, the ore-diluent mixture may be milled at station 13 with hot liquid brine or sea water, received from a sea water source 12, having a pH of not more than about 7 and a volume sufficient to extend between materials which float and sink in the brine or sea water so as to change the slurry characteristics of the ore. This step is optional and not necessary for carrying out the process of our invention. The resulting ore-diluent mixture (or slurry) at station 13 is introduced into a flotation stage or process comprising one or more flotation cells (such as skimming stage 14, countercurrent washer 15, and aeration cell 16) which may employ in cell 16 aeration from any convenient air source or other conventional techniques as indicated to create a froth or emulsion upon the introduction of brine or sea water into the cell.

The resultant froth or emulsion is then treated by countercurrent washing at washer 15 with a preferably hot liquid brine or sea water solution of a detergent or surfactant received from a surfactant-sea water make-up station 17. The surfactant used is one that exhibits a significant amount of solubility in both brine and oil, the second volume of brine also having a pH of not more than about 7, and a volume sufficient to extend between materials which float and sink in the brine or sea water. The washed froth-surfactant slurry from washer 15 is separated, by conventional settling, into a solid and aqueous-free oil, surfactant in sea water and tailings mixture at station 18 as indicated in the drawing. The oil is removed and, at station 19, any hydrocarbons that are as substantially as volatile as the hydrocarbon employed as the diluent are evaporated and the remaining oil is recovered by passing it to a diluent recovery station 20. The silt-water, separated from the solid-free oil at station 19, is clarified with water at station 21 and the water and tailings are disposed of by conventional disposal means. Thus, the water is passed to a water disposal station 22 and the tailings to a tailings disposal station 23. The sea water removed from the oil-surfactant-sea water slurry at station 18 is also clarified with water at station 21 while the tailings disposed of to station 23 as indicated in the drawing. The surfactant in the sea water is passed from station 18 to surfactant make-up station 17. Finally, at the diluent recovery station 21, any necessary diluent is added from a diluent make-up station 24 while any surplus diluent is passed to a processing station such as a desalting and refining station 25 for further processing by conventional means. The necessary diluent for mulling station 11 is supplied from the diluent recovery station 20. Tailings from skimming stage 14 are also passed to tailings disposal station 23. In all of the above steps, although the invention has been described diagrammatically, it is to be understood that conventional processing equipment, such as pumps, valves, settling devices, etc., are used to carry out the process herein disclosed.

Thus, as can be seen from the foregoing, a clean hydrocarbon product with good recovery yields is obtained at the diluent recovery station 20. The diluent from station 20 contacts the tar sand at mulling station 11 before any water is added. This is an important feature of our invention since, if the diluent is added after water is introduced, recovery may be reduced. Once the diluent has been added

and well mixed, water may be added from station 12, as desired, to improve the slurry characteristics.

It is also important that the surfactant used to upgrade the froth or emulsion produced in the flotation stages is not added at an earlier stage in the process, such as during the mulling process at station 11 and 13 or the skimming stage 14. In these cases, such an addition would be ineffective for improving the froth quality and may actually interfere with the flotation process by causing an increase in the amount of solids being floated and in the volume of froth due to inclusion of excess air. Suitable surfactants for use in the froth upgrading of our process are disclosed in a copending application Ser. No. 760,493 filed Sept. 18, 1968 to Jorda et al., the pertinent subject matter therein being incorporated herein by reference. Such surfactants may comprise an aqueous solution of an anionic surface-active material which is a free acid or salt of a complex organic phosphate ester (as for example, Gafac RE-610, manufactured by the Antara Chemical Division of the General Aniline and Film Company and described in U.S. Pat. Nos. 3,331,896 and 3,168,478). Further, any suitable closely related compound, as for example, any surfactant material in which ethylene oxide groups, acyl radicals and from about 10 to 22 carbon atoms are contained in each of the molecules of a surfactant that exhibits a significant amount of solubility in both oil and brine in addition to having a pH of not more than about 7 and a volume sufficient to extend between materials which float and sink in the brine may be used.

The addition of water or brine from water source 12 to station 13 is optional since certain tar sand ores, such as those from the Edna, Calif., region as well as other regions, commonly contain from 3 to 10 percent water by weight in their natural state. The addition of more water, especially before contact with the hydrocarbon diluent, either reduces the recovery of tar from the sand or, if it is a very small amount, has no effect. It is believed that, in the former case, it hinders adequate solution of the tar and diluent by filling and blocking the pore volume. The diluent is generally required to effect complete separation of tar, although, with some tar sands, it may be possible to obtain separation without diluent by careful operation of the flotation process.

As discussed hereinabove and illustrated diagrammatically in the drawing, the flotation stage or process includes a first skimming station 14, an aeration station 16 and a countercurrent washing station 15. Obviously, various other devices or combinations of these stations may be used.

The water in the flotation stage (stations 14 through 16) may contain certain surfactants, but it has been generally found that sea water is quite satisfactory by itself. Certain cations in sea water, such as calcium, serve to suppress the flotation of clays which are a serious contaminant in the froth and a cause of emulsion stability.

The temperatures which may be employed in the various steps of our process may range from ambient to 212° F., although improved recovery and separation are favored by higher temperatures.

We claim as our invention:

1. A process for recovering oil from a tar sand comprising the steps of:

pulverizing said tar sand;

mixing said pulverized tar sand with liquid hydrocarbon diluent;

mixing the hydrocarbon-diluted tar sand with a first volume of hot brine at a controlled pH;

isolating the materials which float in the first volume of hot brine and mixing them with a second volume of hot brine which contains a surfactant, the second volume of hot brine having a controlled pH; and isolating any hydrocarbon materials that are substantially free of solids and aqueous liquids and float in the second volume of hot brine.

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2. The process of claim 1 including the steps of: evaporating for reuse any hydrocarbons that are substantially as volatile as the liquid hydrocarbon diluent; and

recovering the remaining oil.

3. The process of claim 2 including the step of clarifying any water recovered during the steps of isolating any hydrocarbon materials which float in the second volume of hot brine and evaporating any hydrocarbons substantially as volatile as the diluent; and

disposing of any tailings recovered during the steps of clarifying any water recovered and isolating any hydrocarbon materials floating in the first and second volumes of hot brine.

4. The process of claim 1 wherein the steps of mixing the diluted tar sand with first and second volumes of brine includes mixing said diluted tar sand with first and second volumes of hot liquid sea water.

5. The process of claim 1 including the step of mulling said hydrocarbon-diluted tar sand with hot brine having a pH of not more than about 7 and a volume sufficient to extend between materials which float and sink in the brine in an amount sufficient to change the slurry characteristics of said tar sand prior to mixing with a first volume of hot brine.

6. The process of claim 1 wherein the step of isolating the materials which float in the first volume of hot brine includes the step of aerating the mixture of the hydrocarbon-diluted tar sand and hot brine.

7. The process of claim 1 wherein the step of mixing the materials which float in the first volume of hot brine includes the step of countercurrent washing said materials which float in the first volume of brine while mixing with the second volume of hot brine containing a surfactant.

8. The process of claim 1 including the step of recovering brine containing said surfactant during the step of isolating any hydrocarbon materials that float in the second volume of hot brine; and

using said recovered brine containing said surfactant as the brine containing a surfactant required in the step of mixing materials which float in a first volume

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of hot brine with a second volume of hot brine containing a surfactant.

9. The process of claim 1 wherein all of the foregoing steps are carried out at temperatures in the range of ambient to 212° F.

10. In a process for recovering oil from a tar sand comprising the steps of:

pulverizing said tar sand;

mixing said pulverized tar sand with liquid hydrocarbon diluent in an amount sufficient to substantially uniformly dilute all of said tar sand to an oil phase exhibiting a viscosity of less than about 100 cp. at a temperature of less than about 200° F.;

mixing the hydrocarbon-diluted tar sand with a first volume of hot brine having a pH of not more than about 7 and a volume sufficient to extend between any materials which float and sink in the hot brine; isolating the materials which float in the first volume of hot brine and mixing them with a second volume of hot brine which contains a surfactant exhibiting a significant amount of solubility in both brine and oil, the second volume of hot brine having a pH of not more than about 7 and a volume sufficient to extend between any materials which float and sink in the hot brine; and

isolating any hydrocarbon materials that are substantially free of solids and aqueous liquids and float in the second volume of hot brine.

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