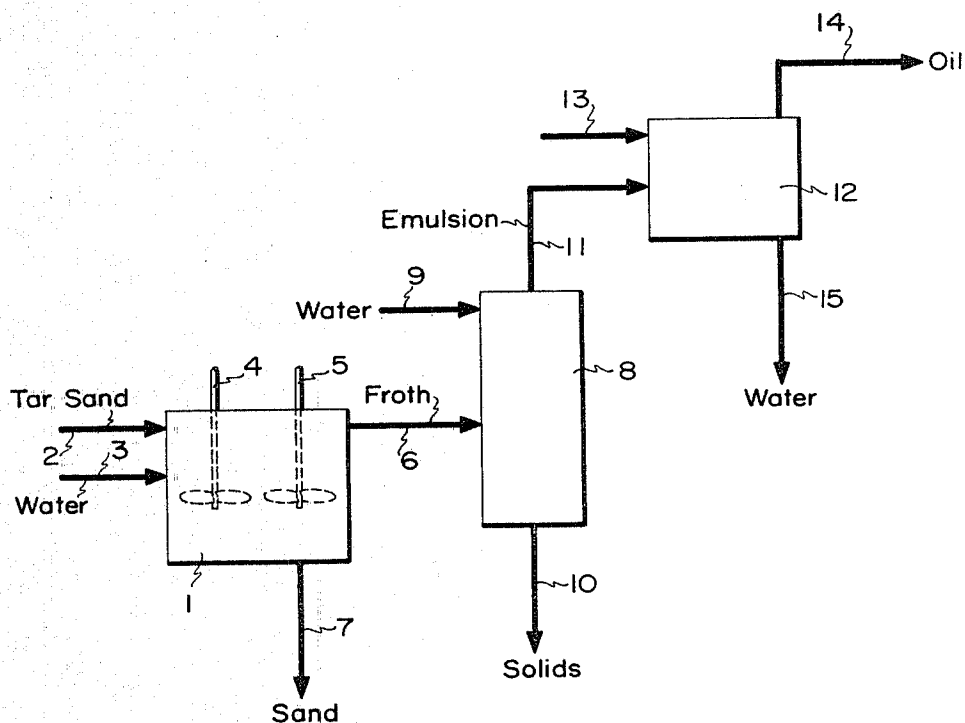


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SANDS FROTH BY A TWO-STEP
CHEMICAL TREATMENT
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DEWATERING/UPGRADING ATHABASKA TAR SANDS FROTH BY A TWO-STEP CHEMICAL TREATMENT

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6 Claims. (Cl. 208—11)

The present invention is broadly concerned with the recovery of hydrocarbons from tar sands. The invention is more particularly concerned with an improved technique of efficiently removing hydrocarbons such as bitumen, tars and the like from tar sands containing the same, such as Athabaska tar sands. These sands may contain clay, etc. in the range from about 0–30% by weight as, for example, about 5% clay.

The invention is more particularly concerned with an improved integrated process for the recovery of oil from tar sands wherein the oil is removed from the sands in an initial stage or phase comprising a treatment with water to produce a froth containing an appreciable amount of water and solids (sand/clay) particles. This froth is subsequently treated in a secondary phase or stage with water containing a selected chemical agent. In a tertiary stage the now substantially solids-free oil and water phase are separated by treatment with a selected chemical demulsifier.

In various areas of the world, tar sands exist which contain various types of hydrocarbons as, for example, the heavy deposits of Athabaska tar sands existing in Canada. These sands contain tremendous reserves of hydrocarbon constituents. For example, the oil in the sands may vary from about 5% to 21% by volume, generally in the range of about 12% by volume. The gravity of the oil ranges from about 6° to 10° API, generally about 8° API. These sands may lie from about 200 to 300 ft. below an overburden and the beds may range from about 100 to 400 ft. thick. A typical oil recovered from the sands has an initial boiling point of about 300° F., 1.0% distilled to 430° F., 20.0% distilled to 650° F. and 50.0% distilled to 980° F. However, the recovery of hydrocarbons in the past has not been effective to any great extent due to the deficiencies in operating techniques for the recovery of these hydrocarbons. For example, a relatively small amount of clay (from about 0% to 30%, usually about 5%) in the sand greatly retards recovery of the oil utilizing conventional water techniques. Apparently the oil and the clay form skins which envelop small pockets of water often containing finely divided sand; then the enveloped pockets are distributed in water, thus forming a type of emulsion.

Numerous attempts have been made in the past to recover bitumen from the Athabaska tar sands in various manners. For example, it has been suggested that a solvent be added in order to reduce the viscosity of the bitumen, and in conjunction with water, to float the bitumen solvent mixture away from the sand. Although this technique achieves a good separation of clean sand, the addition of water results in problems with the formation of stable emulsions and sludges which have been very difficult to separate. Thus, extensive supplementary processing has been required in order to avoid large oil losses.

It has also been suggested in the past that tar sands as they are mined be handled by a thermal process in order to recover the bitumen therefrom. However, this process has been uneconomical due to the large amount of heat which is lost due to the fact that the heat is imparted to the sand and cannot be effectively and efficiently recovered therefrom. It has been suggested for example that

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tar sands be handled in a direct fluid coking operation. However, as pointed out, this process is uneconomical for the reasons given above. Also, any process that will effectively handle tar sands must have the ability to handle a very wide range of tar sand and compositions which occur even in an immediate location. Some processes as, for example, direct fluid coking are able to handle these widely different compositions and, in accordance with the present process, employing a two-phase operation wherein in an initial phase a substantially enriched tar sand is produced and wherein in the second phase the enriched sand is for example handled in a fluid coker, surprisingly effective results are secured.

Thus in the treatment of natural tar sands with water at temperatures in the range from about 160° F. to 200° F., as for example 180° F., a froth is produced which consists of approximately 30–40% by weight of water, approximately 10% sand/clay particles and the remainder oil. In the subsequent processing of this stream as feedstock to a fluid coker, the large water content is a large economic debit. Attempts to dewater this stream have either been expensive (i.e., thermal dehydration) or only partially effective (i.e., mechanical rollers).

The simple addition of a selected chemical surfactant to "break" the oil-water-sand matrix is an obvious and economical solution, but it has been limited by the physical characteristics of the system. It has been found that the emulsifying surfactants in the oil produce a plastic skin or membrane about the water droplets, thereby preventing their coalescence. A chemical demulsifier (anti-surfactant) has been found that will destroy this film and eliminate this coalescence barrier. However, the high viscosity of the oil and almost negligible differential in water/oil specific gravity due to the presence of the sand/clay limits the settling and separation of the coalesced water droplets. The sand/clay solid particles also adsorbed some of the demulsifier, necessitating the addition of greater quantities of the demulsifier.

A two-step chemical treatment was invented which first separates these solid particles. The solids-free oil and water phases are then very effectively treated with the selected chemical demulsifier.

The present invention will be more fully understood by reference to the diagrammatical drawing illustrating one embodiment of the same. Referring to the drawing, tar sands are introduced into treating zone 1 by means of feed line 2. Water is introduced into zone 1 by means of line 3. Zone 1 may comprise any number of stages, either in parallel or series. Intimate contact is secured between the tar sand and the water by means of mixers 4 and 5 which may be of any conventional design such as vibrators, stirrers, countercurrent means and the like. The tar sands introduced by means of line 2 may be also introduced by any conventional means such as conveyors, tumblers, etc.

The amount of water used based upon the volume of tar sands may be varied appreciably as, for example, from 0.5 to 2.0 volumes of water, preferably 0.8 to 1.2 volumes such as 1 to 1 volume of water per volume of tar sands. Temperatures maintained in zone 1 are in the range from about 140° F. to 200° F., preferably in the range from 170° F. to 190° F. such as about 180° F.

Under these conditions, a froth comprising water, sand and oil is produced which is removed from zone 1 by means of line 6. As pointed out heretofore, the froth comprises about 35% by weight of water, 10% by weight of sand and clay, the remainder being bitumen. Separated sands are removed by means of line 7. The froth is introduced into a water washing zone 8 wherein the same is countercurrently contacted with additional water which is introduced into zone 8 by means of line 9. The amount of water used in zone 8 as compared to the

volume of froth is in the range from about 0.5 to 1.5 volumes of water, preferably 0.8 to 1.2 such as 1 to 1 volume of water per volume of froth. The temperature in zone 8 is maintained in the range from 160° F. to 200° F., such as about 180° F.

In accordance with the present invention, the water introduced into zone 8 contains a selected solids remover or "transfer" agent which will promote the transfer of the solid particles for the oil environment to the aqueous phase. Tetrasodium pyrophosphate is one such transfer agent; other examples are trisodium polyphosphate and sodium silicate. The amount of tetrasodium pyrophosphate added to the water introduced by means of line 9 is in the range from about 0.1 to 2.0%, preferably 1.0%. The solids removed are settled in zone 8 and are removed from the system by means of line 10.

The substantially solids-free emulsion comprising oil and water is removed overhead from zone 8 by means of line 11 and introduced into zone 12. In this zone, the emulsion is contacted with the selective demulsifier mixture which is introduced by means of line 13. The addition of the demulsifier is in the range from 0.05 to 0.5% as, for example, 0.1% of the total emulsion. A substantially water-free oil phase is removed by means of line 14 while the oil-free water phase is removed by means of line 15.

The demulsifying solution comprises a mixture of: (1) one part of the reaction product of diethyl ethanol amine with premixed propylene oxide and ethylene oxide. (Propylene oxide/ethylene oxide can range from 40/60 to 60/40, preferably 55/45.) (2) approximately three parts of a palmitic acid ester of the reaction product of an alkyl phenol formaldehyde resin with ethylene oxide

$$\left(\frac{\text{alkyl phenol formaldehyde}}{\text{ethylene oxide}} = \frac{1}{1.5} \right)$$

The mixture may be varied in the range from about 1 part of the reaction product to 2 parts of the acid ester to 1 part of the reaction product to 4 parts of the palmitic acid ester. A preferred mixture is 1 part by weight of the reaction product to 3 parts by weight of the palmitic acid ester.

In order to further illustrate the invention, a froth comprising 46.6% by weight of bitumen, 42.6% of water and 10.8% sand was contacted in a number of operations; namely, A, B, C, D and E. The results of these operations are illustrated in the following table.

TABLE I.—EFFECTS OF "TRANSFER" AGENTS AND DEMULSIFYING AGENTS UNWASHED FROTH

Operations	Water, percent wt.	Solids, percent	Bitumen
A. Untreated Sample (Control).....	42.6	10.8	46.6
B. Water Washing With 1% TSPP Solution ¹	36.0	1.79	62.21
C. Water Washing+Addition 0.4% Demulsifying Mixture ²	18.0	-----	-----
D. Water Washing With 1% Na ₂ SiO ₃ +Addition 0.4% Demulsifying Mixture ²	7.5	-----	-----
E. Water Washing With 1% TSPP Solution ¹ +Addition 0.4% Demulsifying Mixture ²	0.3	0.1	99.6

¹ Tetrasodium pyrophosphate.

² Mixture.

(1) one part of the reaction product of diethyl ethanol amine with premixed propylene oxide and ethylene oxide. (Propylene oxide/ethylene oxide can range from 40/60 to 60/40, preferably 55/45.)

(2) approximately three parts of a palmitic acid ester of the reaction product of an alkyl phenol formaldehyde resin with ethylene oxide

$$\left(\frac{\text{alkyl phenol formaldehyde resin}}{\text{ethylene oxide}} = \frac{1}{1.5} \right)$$

From the preceding it is apparent that far superior results are secured if the froth is contacted initially with water containing a transfer agent to remove substantially all the solid and then contacted in the subsequent stage with a demulsifying agent. In Operation B a substantial amount of solids was removed but the bitumen contained an appreciable amount of water. The same situation occurred in Operation C, as well as in Operation D. However, when employing the technique of the present invention by washing the froth in an initial phase containing tetrasodium pyrophosphate and thereafter removing the sand and treating the same in the secondary phase, the oil phase was about 99.6% oil, containing only 0.1% by weight of solids and 0.3% by weight of water. The palmitic acid ester is preferably secured from a phenol formaldehyde resin wherein the alkyl group contains from about 3 to 4 carbon atoms and is secured from isopropyl alcohol or alkyl butyl alcohol. The molecular weight is in the range from about 1200–1600, preferably about 1400.

What is claimed is:

1. In a process for the recovery of oil from tar sands wherein tar sands are treated with water at an elevated temperature and wherein a froth consisting essentially of water, sand-clay and oil is secured, the improvement which comprises contacting said froth in a first stage with water containing from about 0.1 to 2% by weight of a transfer agent selected from the class consisting of tetrasodium pyrophosphate, trisodium pyrophosphate, and sodium silicate, whereby the sand and clay separate, removing a substantially sand-clay free emulsion from said first stage and contacting the same in a secondary stage with a mixture consisting of (1) about 1 part by weight of the reaction product of diethyl ethanol amine with premixed propylene oxide and ethylene oxide and (2) from about 2 to 4 parts by weight of a palmitic acid ester of the reaction product of an alkyl phenol formaldehyde resin with ethylene oxide whereby an oil phase substantially free of water and sand-clay separates, thereafter removing said oil phase.

2. Process as defined by claim 1 wherein the premixed propylene oxide and ethylene oxide are present in the range from 40/60 to 60/40% by weight.

3. Process as defined by claim 1 wherein the amount of alkyl phenol formaldehyde resin is present in the range from about 0.5 to 1.5 parts by weight as compared to 1.5 parts by weight of ethylene oxide.

4. Process as defined by claim 1 wherein about 1 part by weight of the reaction product is used with about 3 parts by weight of the palmitic acid ester.

5. Process as defined by claim 1 wherein said tar sands are treated with water at a temperature in the range from about 140° F. to 200° F.

6. Process as defined by claim 5 wherein said froth is countercurrently washed in said first stage with water at a temperature in the range from about 160° F. to 200° F.

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