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RECOVERY OF LOW-GRAVITY VISCOUS
HYDROCARBONS

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ABSTRACT OF THE DISCLOSURE

A process for the recovery of the low-gravity, viscous crudes and oils from tar sands by contacting the hydrocarbon-bearing formation or tar sands with an aqueous carrier containing an alkaline agent and a solubilizing agent.

FIELD OF THE INVENTION

This invention relates to an improved process for the recovery of petroleum products from hydrocarbon-bearing formations. More particularly, this invention pertains to a process for increasing the recovery of low-gravity petroleum fluids, including highly viscous crudes, which are substantially immobile under ordinary conditions, oils from tar sands, and residual asphaltic crudes in hydrocarbon-bearing formations, from which varying amounts of the more mobile fractions of the original hydrocarbons in place have been recovered.

DESCRIPTION OF THE PRIOR ART

The production of petroleum products is usually accomplished by drilling into a hydrocarbon-bearing formation and utilizing one of the well-known recovery methods for the recovery of hydrocarbons. However, it is recognized that these recovery techniques may recover only a minor portion of the petroleum products present in the formation, particularly when applied to reservoirs of viscous crudes, e.g. hydrocarbons having gravities less than 25° API. Even the use of improved recovery practices involving heating, miscible flooding, water flooding and steam processing may still leave up to 70–80% of the original hydrocarbons in place.

Thus, many large reserves of petroleum fluids, e.g. heavy crude from which only small recoveries have been realized by present commercial recovery methods, are yet to reach a potential recovery approaching their estimated oil-in-place.

Known recovery processes applied to the recovery of hydrocarbons from tar sands are even more inefficient and may result in recovery of less than 10% of the oil-in-place. This type of hydrocarbon is a viscous, tarry material, which has a density of approximately 1.00 to 1.04. Since the material in its crude state does not command a high price, many recovery processes are not attractive commercially at the very low estimates of recovery. Heretofore, proposed methods involving mining and handling of the tar sands to recover the hydrocarbons are likewise expensive and have not resulted in commercial successes. Consequently, the extensive deposits of tar sands still await commercial development.

It is well known in the art that improved recovery methods include so-called secondary recovery techniques which are applied after the natural drive of a reservoir has been depleted. The application of these techniques permits additional recovery of hydrocarbons from partially depleted formations.

Water flooding is one of the more widely practiced secondary recovery methods. A successful water flood may result in recovery of 30–50% of the original hydrocarbons left in place. However, generally the application

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of water flooding to heavy crudes results in much lower recoveries.

The newer development in recovery methods for heavy crudes is the use of steam injection which has been applied in several modifications, including the "push-pull" technique and through-put methods, and has resulted in significant recoveries in some areas of heavy crude reservoirs. Crude recovery by this process is enhanced through the beneficial effects of the drastic viscosity reduction that accompanies an increase in temperature which is characteristic of heavy crudes. This reduction in viscosity facilitates the production of hydrocarbons, since it improves their mobility, i.e., it increases their ability to flow.

However, the application of these secondary recovery techniques to depleted formations may leave major quantities of oil-in-place, since the crude is tightly bound to the sand particles of the formation, that is, the sorptive capacity of the sand for the crude is great. In addition, interfacial tensions between the immiscible phases result in entrapping crude in the pores, thereby reducing recovery. Another disadvantage is the tendency of the aqueous drive fluid to finger, since its viscosity is considerably less than that of the crude, thereby reducing the efficiency of the processes.

Consequently, process modifications have been developed which may incorporate additives to lessen the above cited disadvantages and thereby improve the efficiency of these processes. For example, surface-active agents and miscible liquids are utilized to decrease the interfacial tension between the water and the reservoir crude, and thickeners have been developed to adjust viscosity so as to inhibit fingering.

The practiced methods for the injection of additives, commonly consists of injection of a slug of additive, contained in a transporting medium, e.g. water, into the formation and then following this injection with a flood water to move the additive slug through the formation. In its ideal effect, the so-called slug moves through the formation as an additive bank, thereby imparting its beneficiating effects to the recovery process.

In many hydrocarbon-bearing formations, it is common to find the oil sands to be preferentially wetted by oil. It is well known in the art to inject into these preferentially oil-wetted formations certain chemicals to reverse the wettability characteristics of the formation, thereby increasing the effectiveness of a water flood to remove the residual crude. For example, a dilute alkaline aqueous solution is known to increase the wetting characteristics of sand surfaces, and promote a leaching action and emulsification of the tarry materials. Those solutions have been used as slugs in conjunction with subsequent steam injection processes to force the emulsion thus formed through the formation to a production well.

Improved recoveries from heavy crudes or tar sands have been realized also by the use of dilute aqueous alkaline solutions containing an effective amount of a non-ionic surfactant, whereby extraction is effected by the spontaneous emulsification when the aqueous liquid comes into contact with the tar in the sand.

However, some of the disadvantages of those additive recovery processes include the problem that the additive may be strongly absorbed in the surfaces of the sand formation, resulting in a large or excessive amount of additive being required. The costs involved of these additives, which may be relatively expensive, may become excessive early in the life of the recovery process necessitating its termination. Other disadvantages include the unfavorable viscosity ratio between the flooding medium and the crude.

Accordingly, it is an object of the present invention to overcome the disadvantages of the prior art by providing

a recovery method whereby highly viscous, low-gravity crudes, and oils from tar sands can be recovered by a more efficient process.

SUMMARY

The invention comprises contacting the heavy crude in the formation or the oil in tar sands with an aqueous carrier containing an alkaline agent and a solubilizing agent.

DESCRIPTION OF THE PREFERRED EMBODIMENT

More specifically, it has been found that the combination of an alkaline agent and a solubilizing agent results in a beneficial and synergistic effect in the action of the extraction of heavy crudes from sands.

The alkaline agent is selected from the group consisting of an alkali metal hydroxide, an alkaline earth metal hydroxide, and a basic salt of the alkali or alkaline earth metal which is capable of hydrolyzing in an aqueous medium to give an alkaline solution, the concentration of the alkaline agent being about 0.001 molar to 0.5 molar to give the required alkaline solution.

A variety of solubilizing agents may be used in the process of the present invention and includes pyridine, quinoline, closely related derivatives of these, coal tar fractions containing at least one member of the group consisting of pyridine and quinoline, and mixtures thereof, which show a solubilizing and/or emulsifying effect at least upon the asphaltene portions of the crude.

The solubilizing agent should be present in the aqueous solution in sufficient concentration to effect the emulsification of the hydrocarbon materials and maintain them in this state during passage through the formation. Concentrations in solution of from about 0.1 to about 10.0% by volume are usually sufficient, although other amounts may be required in some cases.

The beneficiating results of the aqueous carrier containing the alkaline agent and the solubilizing agent are believed to derive from the wettability-improving characteristics of the alkaline agent and the solubilizing action of the solubilizing agent. The solubilizing agent is effective in releasing the crude from the sand surfaces so that the surfaces can be exposed to the alkaline agent, which in turn improves the wettability of the surface, thereby improving the recovery possibility of the crude.

A further advantage of the aqueous solution is believed to result from its ability to emulsify the extracted crude to form an oil-in-water emulsion with its attendant benefits including improved mobility. Emulsions are mechanical mixtures of two immiscible liquids, one of them being dispersed in the other in the form of droplets. Their apparent viscosities are functions of the continuous phase and the interaction of the dispersed droplets. Generally, the viscosity of the emulsion is greater than that of its continuous phase. In the case of a water-in-oil emulsion, the viscosity of the emulsion increases as the volume fraction of the water is increased to about 60-75%. Further increase in water content results in a sharp drop in viscosity to a value comparable with water. This reduction is related to the inversion of the emulsion from a water-in-oil type to an oil-in-water type.

Experiments using an emulsion of a crude oil (San Ardo) and an aqueous carrier consisting specifically of an alkaline agent and a solubilizing agent, 10% 0.2 molar sodium hydroxide and 90% quinoline saturated aqueous solution, showed that the viscosities of the emulsion measured when the emulsions were in an agitated state approximated a straight line on a Fisher/Tag blending chart. The results of the viscosity measurements showed that by adding small amounts of an aqueous carrier consisting of an alkaline agent and a solubilizing agent, substantial decreases in viscosity were obtained.

The effectiveness of the aqueous carrier is further believed to result in large part from its action on the heavier, complex hydrocarbon-type materials present in low-grav-

ity, viscous crudes and oils from tar sands which are difficult to recover. Chromatographic analyses indicate that these types of viscous crudes have large or relatively large fractions of the heavier complex hydrocarbon-type materials, referred to as asphaltenes. The term asphaltenes includes the more aromatic and polar materials of moderate molecular weight (~2000-10,000) dispersed in a lower molecular weight medium, the material together being commonly referred to as asphalt.

It has been shown that these asphaltene fractions of heavy crudes are responsible in large part for the adhesive force which heavy crudes and tars have for the mineral surfaces of the hydrocarbon-bearing formation. This accounts for the fact that in the comparison of recoveries between two crudes with similar viscosities, the residual hydrocarbon saturation for the crude having the larger asphaltene content will be greater.

Experiments were performed to obtain a general idea of the nature of the adhesive force between various crude oils and a silica surface. Flat glass surfaces cleaned with chromic acid were chosen for the tests. The tests consisted of putting equal drops of the crudes to be examined on the horizontal glass surface, then placing the glass in a vertical position and measuring the distance the drop traveled as a function of time. Although the initial rate of flow of the crudes depends upon viscosity, the total flow length depends upon the amount of crude left on the glass as the drop proceeds down the glass. The total lengths of the crude columns were measured when there was no more flow for a length of time. This distance, called for convenience the equilibrium distance, is an indication of the adhesive force between the respective crudes and the surface. The results of these tests showed that crudes with higher asphaltene contents had a greater tendency to coat the mineral surface.

Further experiments demonstrated the effectiveness of the alkaline solubilizing agent to remove the asphaltene from the silica surface. A glass flat surface cleaned with chromic acid was covered with a 10° API crude containing 41.5% asphaltenes. The glass was placed in a vertical position and the excess crude was allowed to drain from the glass for a period of one week. Three aqueous solutions and one distilled water standard were then allowed to flow over the crude-covered face of the glass in separate streams at a rate of approximately 0.5 ml. per hour. The three aqueous solutions or treated waters consisted of:

- (1) 0.2 molar NaOH
- (2) Quinoline saturated H₂O ~0.5 vol. percent
- (3) 90% quinoline saturated H₂O ~0.45 vol. percent
10% 0.2 molar NaOH = 0.2 molar NaOH.

Observations from this demonstration indicated that the distilled water standard and the alkaline water solution had no apparent effect upon the crude covered surface. The quinoline saturated water penetrated through the surface and removed minor portions of the crude which were exposed to the treated water. However, the quinoline-alkaline water effectively removed most of the crude from the glass which was exposed to the treated water.

This experiment showed that the distilled water standard and the alkaline water solution were ineffective in removing the crude layer on the glass. The quinoline saturated water acted as a solvent and removed some of the crude. The quinoline-alkaline water removed the most of the crude layer because of the increased wetting ability of the alkaline water.

A further demonstration of the effectiveness of treated water to remove a tar sand (Sunnyside, Okla.) utilized a series of three glass centrifuge tubes into each of which was placed approximately 20 ml. of the crushed tar sand. An alkaline solution containing 0.2 molar NaOH was added to the first centrifuge tube to the 100 ml. mark. A quinoline saturated water was added to the second

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centrifuge tube to the 100 ml. mark. A quinoline-alkaline water was added to the third tube to the 100 ml. mark.

Observations indicated that the tube containing the 0.2 molar NaOH solution showed little or no effective extraction with the tar sand. The tube containing the quinoline saturated water showed some of the oil had been removed from the tar sand. The tube containing the quinoline-alkaline water showed almost complete removal of the oil from the tar sand in the form of an emulsion. Further centrifuge tests have demonstrated a similar effectiveness of a 5% pyridine-alkaline solution in extracting oil from a tar sand.

Similar tests have demonstrated comparable effectiveness of a coal tar base to remove hydrocarbons from a tar sand in the form of an emulsion when the aqueous carrier contained the coal tar base, thus presenting an attractive commercial possibility.

In utilizing the above disclosed alkaline and solubilizing agents in an aqueous carrier to exploit an underground hydrocarbon-bearing formation, one embodiment may consist of drilling an injection well into the formation, through which the aqueous carrier with the agents is injected into the formation. The injected quality may vary within relatively wide limits, and will depend on a number of conditions, including the thickness of the formation, its characteristics, and the conditions for the subsequent injection of the aqueous drive medium.

The carrier is then pushed through the formation by the drive medium, e.g. H₂O in the form of either water or steam, the temperature of the water may range up to higher than even 200° F., although in some cases it may be desirable to use even higher temperatures, up to 500° F., the temperatures being fixed by optimum conditions of operation.

In the passage of the carrier through the formation, hydrocarbons are stripped from the formation, forming an oil-in-water emulsion which can then be produced at neighboring wells. Separation of the hydrocarbons from the emulsion is accomplished by one of several emulsion breaking techniques.

Another embodiment of the invention is the recovery of hydrocarbon materials from tar sands by utilizing the aqueous medium in an extractive technique in combination with well-known techniques for the mining of the tar sand, and well-known techniques for the recovery of the oil from the tar sand following its extraction.

In demonstrating the effectiveness of this invention, experiments were performed to measure the displacement efficiency of heavy crudes mixed with silica sand and the efficiency of various concentrations of an alkaline agent and a solubilizing agent in water. In these experiments, the alkaline agent was sodium hydroxide and the solubilizing agent was quinoline. Three of each type of apparatus were used and consisted of a glass tube 7 inches long and ½" in diameter, the top and bottom of each of these tubes being closed by 100 mesh wire screens. Each tube contained a silica sand pack having an initial crude saturation of about 32%, and a pore volume of about 8 ml. The properties of the crudes used are shown in Table I.

TABLE I

Crude	° API	Viscosity (cs.)		Percent asphaltene
		100° F.	210° F.	
A	13.0	3,700	59	33.1
B	10.0	71,000	275	41.5
C	10.3	28,000	278	38.6

The various tubes prepared as described above were treated by saturating the sands according to the following procedure:

(a) 150 ml. of distilled water was passed through the sand pack. No oil was produced during this phase of the experiment.

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(b) 200 ml. of the treated aqueous solution was passed through the sand pack in the following sequence:

- (1) 100 ml;
- (2) after 1 hour, 50 ml;
- (3) after 1 hour, 50 ml.

(c) 150 ml. of distilled water was passed through the pack to remove the aqueous solution.

Additional experiments were performed using a similar set up, but utilizing different concentrations of the said alkaline agent and said solubilizing agent. The results of these displacement experiments are indicated in Table II.

TABLE II

CRUDE A

[Displacements at 78° F.]

	Conc. of Quinoline, Vol. percent				
	0	0.1	0.25	0.5	1.0
Percent Oil Recovery					
Conc. of NaOH Molar:					
0.002	1.2	0.1	0.1	0.6	0.7
0.005	66	48	51	54	68
0.01	76	68	64	71	72
0.02	61	61	71	69	72
0.05	43	58	59	74	79
0.1	31	52	45	49	64
0.2	4	11	10	16	44
0.5	0.1	1	1	13	29

CRUDE B

[Displacements at 78° F.]

	Conc. of Quinoline, Vol. percent				
	0	0.1	0.25	0.5	1.0
Percent Oil Recovery					
Conc. of NaOH Molar:					
0.002	0.4	1.7	1.9	4.2	9
0.005	1.5	9	26	64	83
0.01	3.0	11	23	42	82
0.02	6	8	19	43	61
0.05	0.4	0.6	1.5	8	62
0.1			1.6	7	23
0.2	0	0.2	0.3	3	23

CRUDE C

[Displacements at 78° F.]

	Conc. of Quinoline, Vol. percent				
	0	0.1	0.25	0.5	1.0
Percent Oil Recovery					
Conc. of NaOH Molar:					
0.002	0	0.1	0.2	.1	0.4
0.005	0	0.3	0.6	4	49
0.01	TR		7.8	71	82
0.02	0	0.7	1.7	7	46
0.05	0	0.5	1	11	38

The results show that effective maximum displacements can be obtained by utilizing optimum concentrations of the alkaline agent and the solubilizing agent for the type of crude involved. Different crudes require the aqueous medium to have different compositions. The required optimum compositions can be determined prior to field operations by the use of experiments similar to those described above.

Besides the embodiments of the invention described above, others are possible. Thus, the foregoing description is not to be considered as limiting since other variations may be made within the scope of the following claims by one skilled in the art.

I claim:

1. A process for recovering hydrocarbons from a subterranean hydrocarbon-bearing formation which comprises contacting said formation with an aqueous alkaline medium containing a solubilizing agent selected from the group consisting of pyridine, quinoline, closely related derivatives of pyridine and quinoline, coal tar fractions containing at least one member of the group consisting of pyridine and quinoline, and mixtures thereof, forming an emulsion in said formation thereby enhancing the

mobility of said hydrocarbons, recovering said emulsion thus formed, and thereafter separating said hydrocarbons from said emulsion.

2. The process of claim 1 wherein said aqueous alkaline medium comprises an aqueous medium containing an alkaline agent selected from the group consisting of alkali metal hydroxides, alkaline earth metal hydroxides, basic salts of alkali metal hydroxides, basic salts of alkaline earth metal hydroxides and mixtures thereof.

3. The process of claim 2, wherein said alkaline agent is contained in the aqueous carrier in amounts in the range of from about 0.001 molar to 0.5 molar.

4. The process of claim 3 wherein said alkaline agent is sodium hydroxide.

5. The process of claim 1 wherein said solubilizing agent in solution is in the range from about 0.1% to 10.0% by volume.

6. A process for recovering hydrocarbons from a subterranean hydrocarbon-bearing formation penetrated by an injection well and a production well which comprises injecting into said formation through said injection well an aqueous alkaline medium containing a solubilizing agent selected from the group consisting of pyridine, quinoline, closely related derivatives of pyridine and quinoline, coal tar fractions containing at least one member of the group consisting of pyridine and quinoline, and mixtures thereof, thereafter injecting an aqueous drive medium into said formation through said injection well and driving the same toward said production well.

7. The process of claim 6 wherein said aqueous alkaline medium comprises an aqueous medium containing an alkaline agent selected from the group consisting of alkali metal hydroxides, alkaline earth metal hydroxides, basic salts of alkali metal hydroxides, basic salts of alkaline earth metal hydroxides and mixtures thereof.

8. The process of claim 6, wherein said alkaline agent is contained in the aqueous carrier in amounts in the range of from about 0.001 molar to 0.5 molar.

9. The process of claim 8 wherein said alkaline agent is sodium hydroxide.

10. The process of claim 6 wherein said solubilizing agent in solution is in the range from about 0.1% to 10.0% by volume.

11. The process of claim 6 wherein said aqueous drive medium is H_2O .

12. The process of claim 11 wherein the H_2O is water, steam, and mixtures thereof, the temperatures thereof being fixed by optimum conditions of operation.

13. A process for recovering hydrocarbons from a hydrocarbon-bearing sand matrix having heretofore undergone mining processing which comprises contacting said hydrocarbon-bearing sand matrix with an aqueous alkaline medium containing a solubilizing agent selected from the group consisting of pyridine, quinoline, closely related derivatives of pyridine and quinoline, coal tar fractions containing at least one member of the group consisting of pyridine and quinoline, and mixtures thereof, thereby emulsifying and extracting said hydrocarbons from said sand matrix in said aqueous alkaline medium, recovering the emulsion thus formed, and separating hydrocarbons from said emulsion.

14. The process of claim 13 wherein said aqueous alkaline medium comprises an aqueous medium containing an alkaline agent selected from the group consisting of alkali metal hydroxides, alkaline earth metal hydroxides, basic salts of alkali metal hydroxides, basic salts of alkaline earth metal hydroxides and mixtures thereof.

15. The process of claim 14, wherein said alkaline agent is contained in the aqueous medium in amounts ranging from about 0.001 molar to 0.5 molar.

16. The process of claim 15 wherein said alkaline agent is sodium hydroxide.

17. The process of claim 13 wherein said solubilizing agent in solution is in the range from about 0.1% to 10.0% by volume.

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