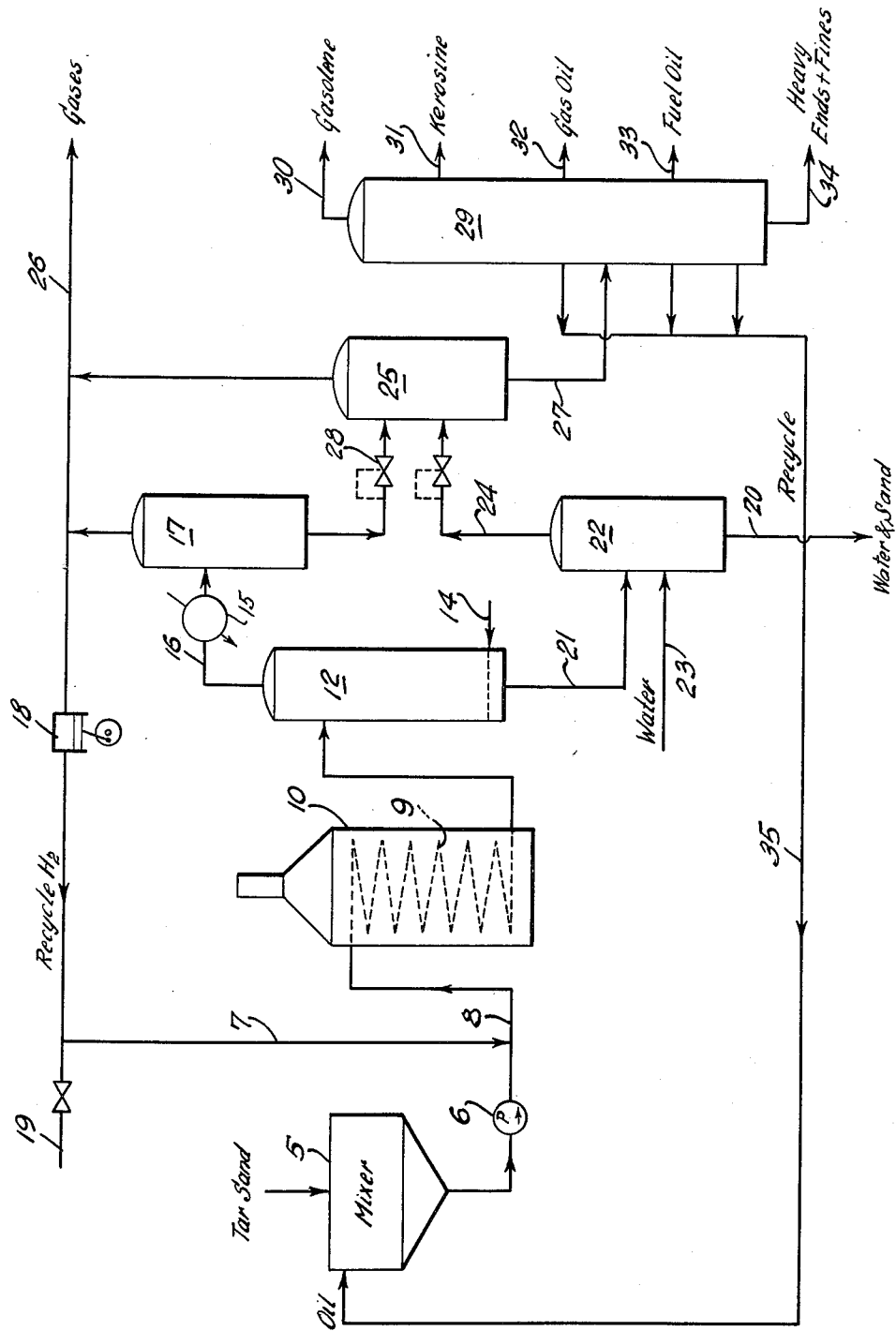


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DU BOIS EASTMAN ET AL
RECOVERY OF OIL FROM TAR SANDS

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RECOVERY OF OIL FROM TAR SANDS
Du Bois Eastman, Whittier, and Warren G. Schlinger,
Pasadena, Calif., assignors to Texaco Inc., a corpora-
tion of Delaware

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This invention relates to the recovery of oil from tar sands. The process of this invention involves simultaneous recovery of oil from tar sands and treatment of said recovered oil with hydrogen. The process results in the production of a recovered oil of reduced viscosity, lower sulfur and nitrogen content, and improved refinability as compared with oil recovered from tar sands by conventional methods involving separation of the oil from solid mineral matter by means of solvents or displacement with water.

In the process of this invention the tar sand is suspended in oil and subjected to highly turbulent flow at high temperature and pressure in the presence of hydrogen. As a result, oil of lower viscosity, specific gravity, and lower carbon residue and sulfur content is recovered. The general, all-around improvement in the quality of the oil is also accompanied by better recovery from the sand.

As is well known, oil recovered from tar sands is of poor quality as compared with most crude petroleum oils. In particular, the oil from tar sands generally is of low API gravity, and contains relatively little material in the distillate boiling range. In addition, the oil is relatively high in organic sulfur and nitrogen compounds. Yields of motor fuels from the oil by conventional petroleum refining processes are comparatively poor. Expensive treating and refining operations are necessary to remove nitrogen and sulfur and to obtain maximum yields of usable products from the crude oil. The process of this invention provides a method for recovery of oil of improved product quality directly from the tar sand by a combination hydrogenation and separation operation.

We are aware of the fact that it has been proposed heretofore to upgrade crude oil from tar sand by processing with hydrogen for the express purpose of improving product quality. Insofar as we are aware, however, such operations involve only the hydrogenation of the oil following its recovery from the tar sand. In our process, the hydrogen treatment is applied to the oil before separation from the inorganic solid residue or sand. The reduction of viscosity and specific gravity which results from this operation results in a cleaner and easier separation of the oil from the sand. Another advantage of the present process is the avoidance of large expensive pressure vessels required for such prior art processes. The present process provides for hydrogenation of oil from tar sands in a compact apparatus of relatively low cost.

One disadvantage of prior processes for treating heavy oils, such as oil from tar sands, with hydrogen results from the large volume-time relationship required in such processes. It is postulated that the long time requirements are dictated by the rates of solution and diffusion of hydrogen in the oil in large reactors. For example, in hydrocracking, if the rate of thermal decomposition is allowed to exceed the rate of solution of hydrogen in the liquid, the available supply of hydrogen is depleted and the undesirable thermal end-products, gas and coke, are produced. In the conventional hydrogenation of heavy petroleum oils, the operation is usually carried out in large unpacked reactors which contain a heavy viscous liquid phase through which the hydrogen slowly bubbles. The poor agitation in such a system limits the rate at which the reaction can proceed because of the local de-

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pletion of dissolved hydrogen. This limitation has been appreciated but efforts to provide a practical means to achieve agitation in the high pressure equipment required have not been successful.

A similar situation exists in packed beds, for example, where hydrogen-rich gas is used for mild hydrogenation of oils by flowing the oil downwardly over packing in a bed. In this system, the hydrogen must move through slowly moving, viscous oil film by diffusion. The reaction is slow at best and large vessels are required to provide ample reaction time.

In the process of this invention, a flowable mixture or slurry of hydrogen, oil, e.g. recycle oil, and raw tar sand (i.e. tar sand as mined) is passed through an elongated tubular reactor of relatively great length in comparison with its cross-sectional area. The volume of flow of feed material in the reaction zone is maintained at a rate such that highly turbulent flow conditions exist in the reactor. The velocity and turbulence are sufficient to completely disperse the sand particles in the oil-hydrogen composite fluid. A preferred form for the reactor is a tube of relatively small diameter, for example, one half to one inch in internal diameter. Under these conditions of highly turbulent flow, the rates of reaction of the desirable hydrogenation reactions are greatly increased. The oil is considerably upgraded, in particular, sulfur is decreased and the yield of lower boiling components increased without the concomitant formation of high boiling polymers or coke.

In the process of this invention, oil feed rate, hydrogen recycle rate, reaction tube diameter, and operating conditions of temperature and pressure all tend to affect velocity of flow and turbulence. It has been found convenient to express turbulence in terms of the ratio of the average apparent viscosity of the flowing stream

$$\frac{\bar{\epsilon}m}{\nu}$$

to the molecular or kinematic viscosity ν , viz.

$$\frac{\bar{\epsilon}m}{\nu}$$

Hereinafter, we shall refer to this ratio

$$\frac{\bar{\epsilon}m}{\nu}$$

as turbulence level. The apparent viscosity of the flowing stream, $\bar{\epsilon}m$, equals the sum of the eddy viscosity, ϵm , and the kinematic viscosity ν which may be shown in the expression $\bar{\epsilon}m = \epsilon m + \nu$. Under conditions of turbulence, $\bar{\epsilon}m$ has a finite value. If the magnitude of the apparent viscosity exceeds that of the kinematic viscosity at the point in question, the ratio of

$$\frac{\epsilon m}{\nu}$$

exceeds unity. For a given turbulent system, it follows that the average value of the ratio, as expressed by

$$\frac{\bar{\epsilon}m}{\nu}$$

exceeds unity. The average apparent viscosity

$$\bar{\epsilon}m$$

as employed herein is defined by the equation

$$\bar{\epsilon}m = \frac{1}{r_0} \int_0^{r_0} \epsilon m dr$$

where r_0 is the radius of the conduit. By substitution and integration, employing the parameters described by Cor-

coran et al., Industrial and Engineering Chemistry, 44, 410 (1952), this expression

$$\bar{\epsilon}m = \frac{1}{r_0} \int_0^{r_0} \epsilon m dr$$

may be rewritten

$$\bar{\epsilon}m = \frac{r_0}{15} \sqrt{\frac{r_0 g}{2\sigma}} \frac{dp}{dx}$$

The latter equation is in terms which may be readily determined for a given system; r_0 being the conduit radius, σ the specific weight of the flowing fluid, g the acceleration of gravity and

$$\frac{dp}{dx}$$

the pressure drop per unit of conduit length. In the process of this invention, turbulence levels above 10 may be employed but turbulence levels of 25 to 1,000 are preferable.

In the foregoing paragraph, the various symbols used in the formulas are defined as follows:

d =differential
 g =acceleration of gravity, feet per second per second
 p =pressure, pounds per square foot
 r =radial distance from center of conduit, feet
 r_0 =radius of conduit, feet
 x =distance, feet
 ϵ =eddy viscosity, square feet per second
 $\bar{\epsilon}m$ =apparent viscosity, square feet per second
 $\bar{\epsilon}m$ =average apparent viscosity, square feet per second
 ν =kinematic viscosity, square feet per second
 σ =specific weight, pounds per cubic foot

Temperatures of 700 to 1,500° F. may be employed. A preferred range of temperatures is from 800 to 1,000° F. Pressures of 1,000 to 20,000 p.s.i.g. may be employed, although pressures of 1,500 to 10,000 p.s.i. are preferred. Hydrogen feed rates of 1,000 to 100,000 standard cubic feet per barrel of slurry feed may be employed, but hydrogen feed rates of 2,000 to 50,000 standard cubic feet per barrel of feed slurry are preferred. Hydrogen may be supplied in pure form or in gas mixtures having hydrogen concentrations ranging from about 25 to about 95 percent hydrogen by volume. The hydrogen partial pressure in the system preferably is at least 1,500 p.s.i.g. Although reaction times from one second to one hour may be employed, reaction times of 20 to 300 seconds are preferred.

The figure is a diagrammatic elevational view illustrating a specific embodiment of apparatus suitable for carrying out the invention. With reference to the figure, raw tar sand is charged to a mixer 5 in which it is mixed with oil derived from the sand (as hereinafter described), optionally together with water, to form a pumpable slurry. If desired, a readily recoverable hydrogenation catalyst may be added to the slurry. Suitable catalysts include one or more of the following: iodine, a hydrogen halide, e.g. hydrogen iodide, organic iodine compounds, e.g. methyl iodide, and volatile halides of aluminum, zinc, boron, or phosphorus.

The amount of oil mixed with the sand to form a pumpable slurry may vary from about 50 to 200 percent by weight based on the weight of the deoiled sand. In general, a slurry comprising approximately equal parts by weight of oil and sand forms a satisfactory slurry for the present process. Stated another way, the mineral residue, or sand, content of the slurry may vary from about 35 to about 65 weight percent. About 35 weight percent oil (65 weight percent sand) is generally the minimum oil which may be used to form a flowable mixture. Larger amounts of oil than the indicated 65 weight percent may be employed but generally are not required nor desirable.

The resulting slurry is raised to an elevated pressure by

pump 6, mixed with hydrogen under pressure from line 7 and passed through tubular converter 9 at a velocity sufficient to develop highly turbulent flow. The velocity is such that a turbulence level (as defined hereinabove) above 10, preferably above 25, is maintained in the converter. As illustrated, converter 9 comprises a helical coil of pipe, a preferred form of the converter. Alternatively, the converter may comprise a pipe still type furnace with straight tubes and 180° return bends of the general type employed in petroleum refining operations.

Reactor coil 9 performs the dual functions of springing the oil from the tar sand and hydrogenation of the recovered and the recycled oil. The turbulent flow separates the sand particles and washes them with hydrogen and hydrogenated oil and, at the same time, hydrogenation of the oil takes place improving the quality of the oil for subsequent recovery. Heat from a suitable source, for example, furnace 10, is supplied to the heating coil to maintain the reaction temperature within the desired range of 700 to 1,500° F., preferably 800 to 1,050° F. The average pressure in the reaction coil 9 is of the order of several thousand pounds per square inch gauge, e.g. within the range of 1,500 to 10,000 p.s.i.g. and suitably 3,000 to 5,000 p.s.i.g. The resulting mixture of treated sand, oil, and residual hydrogen is discharged from conversion coil 9 into hot separator 12 without reduction in pressure or temperature.

The primary purpose of separator 12 is to effect separation between oil product, heavy liquid, and residual solid. At the base of separator 12, hydrogen from a suitable source is introduced through line 14 effecting stripping of oil and oil vapors from the residual sand and heavy residuum. All of the hydrogen required for the process is preferably introduced at this point. Generally an oil product comprising 80 to 95 volume percent or more, based on the oil in the feed, is taken overhead from hot separator 12.

Hydrogen and oil vapors are discharged from separator 12 through cooler 15 and line 16 to a gas-liquid separator 17. In separator 17, which preferably is operated at the same pressure as separator 12, unreacted hydrogen is separated from liquid products from the hot separator overhead. Hydrogen from separator 17 is recycled by compressor 18 to line 7 from which it flows into conversion coil 9. If desired, additional fresh feed hydrogen may be supplied to the system through line 19.

Residual solid from separator 12, together with the unvaporized portion of the oil, is withdrawn through line 21 to separator 22, preferably operated at the same pressure as separator 12, wherein hydrogen and oil are displaced from the residual solid by means of water. Water entering through line 23 preferentially wets the solid mineral residue or sand, displacing oil. The displaced oil containing dissolved hydrogen flows through line 24 provided with a pressure reducing valve, to separator 25. Oil from separator 22 may be recirculated to separator 12 as a carrier for the sand and also may be recycled directly to the mixer as part of the make-up oil. Water and sand are discharged through line 20 and discarded.

Separators 12 and 22 may be combined into a single vessel with hydrogen and water entering at intermediate points in the vessel and with the hydrogen, vapors, and oil going overhead to separator 17 as illustrated in connection with separator 12 and with water and spent shale particles being withdrawn from the bottom of the vessel as illustrated in connection with separator 22.

As will be evident from the data in Examples 1 to 3 below, the hydrogenation effected in reactor 9 reduces the gravity and viscosity of the oil so that the separation of heavy oil from the sand in separator 22 is more easily effected than water displacement of the original crude from the sand.

The separations which are effected in separators 12, 17, and 22 preferably are carried out at elevated pressure, for example, substantially at the reactor discharge pressure.

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Liquid separated in separator 17 passes through reducing valve 28 into separator 25. Here, the remaining gas is separated from the liquid and discharged through line 20. This gas may be processed for recovery of hydrogen in known manner, or used directly for fuel. Liquid from separator 25 is passed through line 27 to a fractionation

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The tar sand is mixed with additional oil in an amount sufficient to form a slurry containing approximately equal parts by weight of sand and oil. In Examples 1 to 3, additional crude oil from the sand is used to make up the slurry, whereas in Examples 4 and 5, hot separator bottoms are recycled to make up the slurry.

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
Average Pres., p.s.i.g.	5,250	4,860	4,800	4,640	5,735
Average Temp., ° F.	925	830	870	815	900
Fresh oil charge, g.p.h.	20.5	35.8	20.2	39.8	39.4
Recycle oil, g.p.h.				41.2	41.4
Hydrogen-rich gas:					
s.c.f.h.	7,771	10,125	9,028	9,827	10,382
s.c.f./Bbl. ¹	15,930	11,870	19,330	10,360	11,070
Hydrogen concentration, vol. percent	85.1	92.4	88.2	56.8	49.1
Hydrogen consumption, s.c.f./Bbl. ¹	3,435	478	1,339	296	607
Hot Separator Overhead Fraction:					
I.B.P. -400, vol. percent	50.56	14.8	38.95	11.39	19.47
400+ Fraction, vol. percent ¹	62.11	89.5	67.64	93.40	87.73
I.B.P. to 400° F. Fraction:					
API Gravity	64.7	56.1	57.7	57.3	60.4
Sulfur			0.45		
Research Octane—					
clear		67.7	70.7		
+3 cc TEL		77.1	84.1		
400+ Fraction:					
API Gravity	15.9		17.4	16.1	17.4
Vis. at 122° F., S.F.			59.7	64.9	21.7
Sulfur	1.36		1.68		2.8
Carbon Residue	3.89		2.08		
Hot Separator Bottoms Fraction:					
API Gravity	23.1	17.8	23.3		
Specific Gravity	.9153	.9478	.9181		
Vis. at 122° F.		SUS 115	SF 39.4		
Carbon Residue	4.07	8.9	1.17		
Sulfur		1.96			

¹ Basis fresh oil in feed.

system 29 where a final separation is made into various oil products. As illustrated, a gasoline fraction is taken from the fractionation system through line 30. Liquid products of intermediate boiling range are drawn from the fractionation system through lines 31, 32, and 33. Heavy oil, which may contain fine particles of sand which find their way through the various separators into the fractionation system, is withdrawn through line 34 for disposal in a suitable manner. This oil may be used directly as fuel, e.g. to supply heat for the process; it is also useful as fuel for the generation of hydrogen for the process by partial combustion with oxygen.

Recycle oil is drawn from the fractionation system at one or more points and passed through line 35 to mixer 5 for the preparation of the feed slurry for the process. Preferably the recycle oil is a fraction lower boiling than the heavy residuum, e.g. having a boiling range of 500 to 700° F.

The process disclosed in U.S. Patent 2,809,104 to Strasser et al. is particularly useful for the conversion of the heavy oil to carbon monoxide and hydrogen. Carbon monoxide so produced may be subjected to a shift conversion operation in the presence of an iron catalyst effecting reaction with steam to produce carbon dioxide and hydrogen. Following removal of carbon dioxide, hydrogen is obtained which is suitable for use in the process of this invention.

The beneficial results obtained by the process of this invention are illustrated in the following examples.

Examples

Tar sand with an oil content of 14 percent by weight is treated by the process of this invention. The original crude oil contained in the sand has the following characteristics.

Gravity, ° API	14.6
Viscosity, S.F., at 122° F.	342
Carbon residue, wt. percent	9.7
Sulfur, do.	2.6

ASTM distillation:

I.B.P., ° F.	400
10% —	584
20% —	609
400-780° F. vol. percent	41
Above 780° F. do.	59

In Examples 1 and 2, the reactor consisted of 1,000 feet of tubing having an internal diameter of 0.312 inch, while in Examples 3, 4, and 5 the reactor is made up of 1,750 feet of tubing having an internal diameter of 0.6 inch. In each of the examples, the turbulence level, as indicated by the above formulas, is above 100. The runs of Examples 1 to 3, inclusive, were carried out with hydrogen of high purity as make-up to the reactor, whereas Examples 4 and 5 were run with synthesis gas containing about 34 and 44 volume percent carbon monoxide, respectively, the balance consisting mainly of carbon dioxide with small amounts of inert atmospheric gases.

Obviously many modifications and variations of the invention as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A method of recovering oil of improved physical properties from tar sand which comprises forming a flowable mixture of tar sand in hydrocarbon oil, passing said mixture together with from 1,000 to 100,000 standard cubic feet of hydrogen per barrel of oil contained in said mixture through a tubular reaction zone of relatively small diameter under highly turbulent flow conditions wherein a turbulence level above 100 as expressed by the ratio

$$\frac{\bar{\epsilon}m}{\nu}$$

is maintained, wherein

$$\bar{\epsilon}m$$

is the average eddy viscosity and ν is the kinematic viscosity and wherein a temperature in the range of 700 to 1200° F. and a hydrogen pressure of 1,000 to 10,000 pounds per square inch gauge are maintained, and subjecting the mixture in said tubular reaction zone to non-catalytic reaction for a period of time within the range of 1 to 300 seconds effecting liberation of oil contained in said tar sand and simultaneous hydrogenation of said oil to yield a hydrocarbon product of improved physical properties, carrying out said reaction substantially completely within said tubular reaction zone, and separating

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hydrocarbon product from resulting treated tar sand at substantially said reaction zone temperature and pressure.

2. The method according to claim 1 wherein residual treated tar sand is stripped with feed hydrogen effecting vaporization of a substantial portion of the hydrocarbon content thereof, recovering vaporized hydrocarbon from said feed hydrogen, and thereafter passing said feed hydrogen to said tubular reaction zone.

3. A method of recovering oil of improved physical properties from tar sand which comprises forming a flowable mixture of tar sand in hydrocarbon oil, passing said mixture together with hydrogen in an amount within the range of about 2,000 to about 50,000 standard cubic feet per barrel of oil contained in said mixture through a tubular reaction zone at a velocity sufficient to develop highly turbulent flow wherein a turbulence level above 100 as expressed by a ratio

$$\frac{\bar{\epsilon}m}{\nu}$$

is maintained wherein

$$\bar{\epsilon}m$$

is the average eddy viscosity and ν is the kinematic viscosity and wherein a temperature in the range of 700 to 1200° F. and a pressure in the range of 1,000 to 10,000 pounds per square inch gauge are maintained for a

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period of 1 to 300 seconds effecting hydrogenation of oil contained in said tar sand to yield a hydrocarbon product of improved physical properties, carrying out said reaction substantially completely within said tubular reaction zone, discharging effluent from said reaction zone to a stripping zone maintained at a pressure within said range wherein unvaporized oil and residual sand are countercurrently contacted with feed hydrogen for the process, discharging hydrogen and oil vapors from said stripping zone to a separation zone operated at substantially the same pressure as said stripping zone and at a temperature sufficient to condense normally liquid hydrocarbons, separating hydrogen-rich gas from liquid hydrocarbon products in said separation zone, and passing said hydrogen-rich gas to said reaction zone as hydrogen for the process.

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