MASTER

IMPROVED SOLVENT EXTRACTION RECOVERY OF SHALE OIL

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DISCLAIMER

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Background of the Invention:

The present invention relates to an improved process for the recovery of organic matter from oil shale. More particularly, the present invention relates to the recovery of sorganic matter at relatively low temperatures. Still more particularly, the present invention relates to high recoveries of organic matter from oil shale at relatively low temperatures using solvent extraction.

The organic matter in oil shale has been described in the scientific literature as bitumen, kerogen, or shale oil. These terms describe portions of the organic matter removed from the oil shale under specific conditions. The term "bitumen" is defined as the portion of organic matter that is soluble in organic solvents at their refluxing temperature; kerogen is the portion of organic matter that is not soluble in organic solvents at their refluxing temperature; and shale oil is the liquid product produced from the organic matter by thermal degradation or solvent extraction under supercritical conditions.

The generally recognized shortage of conventional petroleum resources in the world has necessitated the focus of attention on other fossil-based deposits for petroleum-type or petroleum precursor resources.

One of the most abundant carbonaceous deposits around the world is oil shale that contains solid organic matter admixed with, or bound in, shale, a relatively tight inorganic matrix of marine deposits or rock strata found both at the earth's surface and at various depths in the crust.

The organic matter in oil shale is a solid because of its high molecular weight. Accordingly, recovery of the organic matter requires its liquefaction as a means of separating it from the solid inorganic matrix.

The liquefaction can be achieved, to varying degrees, either by thermal means mentioned above or by solvent extraction. Heretofore, thermal liquefaction has been far more successful. Thermal liquefaction involves retorting, either in-place (i.e., in situ retorting) or surface retorting in a vessel after mining the organic-laden shale. Those methods, while meeting with a measure of success, are energy-intensive and consume substantial amounts of the organics (or equivalent energy from another source). The organic matter is consumed in two ways: 1) in heating the organic-inorganic composite sufficiently in temperature to enable separation; and 2) unavoidably converting some of the organic matter into carbon (i.e., char and/or coke and similar immobile carbonaceous matter) and low molecular weight gas. Solvent extraction, while not consuming as much of the kerogen and thus not being so destructive as retorting, has not recovered as much of the organic matter as in retorting. In solvent extraction, less organic matter such as bitumen or other products is recovered and a greater residual of the original organics is left on the rock. A method of recovering relatively high proportions of the organic materials in liquid form, as distinguished from carbonaceous solids and/or gases, is desirous.

It is a principal object of the present invention to provide a process for the recovery of high percentages of organic material as a liquid, and relatively small amounts of carbon and low molecular weight gas.

It is another object of this invention to provide an efficient solvent extraction process for the recovery of shale oil.

Another object of the present invention is to provide a process for the recovery of shale oil from shale at a temperature below which significant thermal degradation of the organic matter occurs.

Still another object is to provide a process for efficient solvent extraction for the recovery of oil from shale which does not require grinding or otherwise breaking up the shale into extremely fine particles preparatory to the solvent treatment.

It is still another object to provide an efficient solvent extraction process for the recovery of oil wherein relatively inexpensive and readily available solvents can be employed.

Yet another object is to provide an efficient solvent extraction process for the recovery of oil from shale wherein good percentages of the solvents can be recovered in a relatively inexpensive and facile manner.

Other objects, advantages and novel features of the invention will become apparent to those skilled in the art from the description herein taken as a whole.

Summary of the Invention

In brief, the foregoing and other objects are

achieved by an improved solvent extraction process for recovering shale oil from shale comprising:

(a) treating a shale containing organic matter with a solvent system comprising a combination of water and an alcohol at a temperature of about 375°-425°C;

(b) treating the product of (a) with a solvent system comprising a combination of an alcohol and another organic solvent at an elevated temperature, but not above about 425°C; and

(c) separating the solid shale from the solvent-oil extract.

Description of the Preferred Embodiments

Before proceeding with a discussion of the process or treatment parameters, some discussion of the process in general terms may be beneficial. Some of this will involve theory(ies) of the mechanism or how otherwise the invention is believed to work; however, applicants are not bound by any such theory(ies). In the end, persons skilled in the art will find this description sufficient to enable them to practice the invention regardless of the operative technical principals involved.

It is believed that the first treatment of the shale pregnant with organic material [i.e., step (a)] accomplishes the major portion of breaking up the inorganic matrix through the combined action of the alcohol and water on the matrix. In the second treatment [i.e., step (b)], the alcohol and other organic solvent operate primarily to dissolve the organics but some breakdown of the shale matrix due to the alcohol also occurs in this step.

The chemical breakdown of the shale matrix is believed responsible, at least in part, for the increased recovery of shale oil because of increased accessibility and actual contact by the solvent for the organic material in the second treatment. The chemical breakdown of the shale matrix is more efficient than a mechanical method such as grinding. For the foregoing reason, shale pieces which are relatively large can be used in the present invention. While pieces of shale larger than about 1 inch in size can be employed by adjusting the treatment, for example, by extending the time of this treatment, generally about 1-inch pieces of shale and smaller will be used. In most cases, pieces of shale on the order of about 1/2 inch and less will be found not only suitable but advantageous. We prefer pieces of shale of about 1/4 inch or less.

The temperature for either of the two treatments should not significantly exceed about 425°C in order to avoid thermally altering the organic material. In order to achieve dissolution rates generally required for commercially acceptable operation in step (a), the temperature should be about 375°C. Also, temperatures above the critical temperature of water (i.e., about 374°C) are believed to be beneficial in respect to how the water performs. Under high pressures, the water is in a dense vapor phase which appears to enhance the desired effect of the water on the shale matrix. Preferred temperatures with the preferred solvent systems in the first solvent treatment is about 390°-400°C. The preferred temperatures in the second treatment [i.e., step (b)] are to be sufficient to dissolve the various organic components, particularly the higher molecular weight compounds therein and is easily determined by routine tests. This temperature will, as a practical matter, normally be the reflux temperature of the lowest boiling solvent. This is discussed further in connection with specific solvents later herein.

Temperature and time of both treatments vary inversely. The higher the temperature the shorter the time required. Of course, the size of the pieces of shale also has a significant effect on the time needed for the first treatment. The ratio of the solvents in a system, as well as the quantity relative to the weight of solvent system to the shale being treated also affects the time required for the treatments. The desired or optimum treatment time for any given case can be readily determined by routine experimentation aided by the teachings herein.

In the first solvent treatment step, the pressure in a closed system (i.e., batch operation) will be autogenous and will vary in the range of about 4,000 to 5,200 psi. Preferably, the pressure in the first treatment is sufficient to maintain the water in a dense vapor phase. Generally this is in the range of about 3,200 to 5,200 psi in either a batch or a continuous operation.

The solvent system in the first treatment is to be comprised of water and an alcohol. The alcohol can be a mixture of one or more aliphatic alcohols. The more suitable alcohols comtemplated are the alkyl alcohols of about 1 to 4 carbon atoms. Examples are methanol, ethanol, propanol, isobutyl alcohol and n-butyl alcohol. Methanol is the preferred alcohol for a number of reasons. Among those reasons are that methanol is quite effective and is a commodity chemical which is now obtainable from many technical and commercial sources, and is expected to continue to be so available. The alcohol and water can be used in a wide range or ratios, for example, 0.5/1 to 1/3. Preferably, however, the alcohol is used in a 0.8/1 ratio by weight with water, but other ratios can be used especially when other shales and/or alcohols than methanol are involved. The quantity

of solvent system to shale will vary based on such factors as the particular shale and alcohol used. In the case of Green River oil shale and a solvent system of methanol and water (0.8/1)), at a ratio of about 2/1 to 10/1 solvent to shale by weight will normally be used. We prefer a ratio of about 6/1 solvent.

The solvent system for the second treatment is comprised of an alcohol like that discussed above in combination with an organic solvent other than an alcohol. By organic solvent is meant those having good solvency for the high molecular weight components of shale oil (e.g., molecular weights on the order of about 500). The organic solvents thus include polar solvents, aromatic solvents, and the halogenated hydrocarbon solvents. Examples of the organic solvents are methylene chloride, ethylene chloride, trichloroethylene, carbon tetrachloride, benzene, toluene, xylene, cyclohexane, tetralin and other partially or fully hydrogenated single and multiple ringed compounds, although aliphatics such as hexane can be admixed therewith. Hydrocarbon fractions containing substantial amounts of partially hydrogenated aromatics derived from a shale oil as a recycle stream is a particularly suitable and preferred as a step (b) solvent, although similar streams from coal or conventional petroleum are also suitable. Other solvents include the various oxygenated solvents (i.e., other than alcohols which are required in combination with this solvent). Oxygenated solvents include ketones such as methyl ethyl ketone, methyl hexyl ketone; ethers such as diethyl ether, methyl hexyl ether; esters such as the methyl ester of butyl alcohol, the butyl ester of dodecyl alcohol, and the counterpart esters of similar acids; and phenolic compounds represented by phenol itself.

The preferred solvent combination in the second extraction is benzene and methanol, about 60/40% by weight, respectively. The reason for this is that the mixture can be easily refluxed at mild temperatures of about 58°C to achieve very good extraction. In turn, the solvent is readily recovered from the crude shale oil by distillation since it forms a constant boiling azeotrope.

In order to disclose more clearly the nature of the present invention and the advantages thereof, reference will hereinafter be made to certain specific embodiments which illustrate the herein described process. It should be clearly understood, however, that this is done by way of example and is not to be construed as a limitation upon the spirit and scope of the appended claims.

Examples

The oil shale used in these experiments was a 65-gallon per-ton* Green River oil shale from the Mahogany zone of the Piceance Creek Basin. Mineral carbon in the shale was determined by perchloric acid digestion followed by coulimetric titration. Total carbon was determined by heating the shale in a Lindberg furnace at 950°C and coulimetric titration of the released carbon dioxide. Organic carbon content was calculated as the difference between total carbon and mineral carbon. Elemental analyses for C, H, N, O, and S were determined by a commercial laboratory: C, H, and S by a combustion methods; nitrogen by a modified Dumas method; and oxygen by a modified Unterzacher method. The raw shale contained 37 weight percent organic matter. Prior to treatment, the oil shale was crushed to pass a minus 100 mesh screen. This was accomplished

by crushing to 0.3- to 0.6-mm particle size using a jaw-crusher and then ground to minus 100 mesh with a Siebtechnik ring-mill and sieved.

Powdered (-100 mesh) Green River oil shale (40 g.) was placed in an Inconel-600 high-pressure autoclave (1 liter batch reactor) together with methanol (120 ml) and water (120 ml). The vessel was purged with argon to remove air and then sealed. The room-temperature pressure of the autoclave was 500 psi argon, neglecting the vapor pressure of methanol and water. The autoclave was heated from 20°C to 400°C (except Experiment 2 below) over a period of 2-3/4 hours and held at 400°C for 1 hour. The operating pressure at 400°C was 4550 psi. After cooling the autoclave to about 25°C a gas sample was taken.

The alcohol/water-treated shale slurry was removed from the autoclave by vacuum suction and the autoclave was washed with water (550 ml). The slurry was then filtered using a Buchner suction filtration apparatus to recover the treated shale as a dry powder and the alcohol/water as a clear liquid. The dry shale was transferred to a Soxhlet extraction apparatus and extracted for 48 hours with benzene/methanol (60%/40%), 300 ml, to recover the heavy liquid organic material. The alcohol/water solution recovered during filtration was extracted first with diethyl ether and then methylene chloride (200 ml each) to recover organic materials soluble in alcohol/water. After removal of organic solvents by rotary evaporation the water soluble organics and the heavy liquid organics were combined as a total recovered organic material. Yield of total organic material was calculated using the gravimetric amount of total organic material recovered, which was divided by the amount of organic material in the raw shale.

The results are set forth below in the table.

TABLE OF EXPERIMENTS

Experiment	Temp.	Time	Wt. % Total Organics Recovered	% Fishcher* Assay
1. Methanol/Water	400°C	1 hr	89.5	138
2. Methanol/Water	375°C	1 hr	52.3	81
3. Ethanol/Water	400°C	1 hr	86.5	133

* Fischer Assay yield considered to be 65 wt. percent of total organic matter in the shale.

While particular embodiments of the invention have been described, it will be understood, of course, that the invention is not limited thereto, since many modifications may be made; and it is therefore contemplated to cover by the appended claims any such modifications as fall within the true spirit and scope of the invention.

Abstract

An improved process for solvent extraction of organic matter from shale by two extraction steps in sequence. The extraction steps are: (a) treating a kerogen-containing shale with a solvent system comprising a combination of water and an alcohol at a temperature of about 375°-425°C; and (b) treating the product of (a) with a solvent system comprising a combination of an alcohol and another organic solvent at an elevated temperature, but not above about 425°C. The organic matter is recovered by separating the liquid which results from step (b) from the shale solids.