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TREATMENT OF SHALE

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This invention relates to the treatment and recovery of hydrocarbons, bituminous substances, and the like from shale and similar formations. The recovery and improvement of oil or so-called kerogen, supposedly a complex bituminous mixture, from shale is a major problem of long standing because of the close association of the kerogen with, the inorganic mineral aggregate and the necessity of handling such large quantities of the latter. Processes such as destructive distillation, solvent extraction at high temperatures and high pressures, and hydrogenation at high temperatures and pressures in the presence of a catalyst have been practiced to some extent but are generally regarded as unsatisfactory because of the relatively low yields obtained and the large quantities of aggregate that must be handled and brought up to the required high temperatures. In some cases the mineral aggregate may run as high as 75% or more.

It is an object of this invention to provide a novel process wherein the hydrocarbon and bituminous contents of shale and like materials can be separated therefrom and recovered at minimum expense and without the necessity of bringing the mineral aggregate up to and handling it at high temperatures.

Another object of the invention is to provide a novel process for handling shale wherein the kerogen content thereof can be separated and recovered at relatively low temperatures, the physical characteristics thereof being materially improved.

Other objects and advantages of the invention will become apparent from the following description and claims taken in connection with the attached drawing wherein

Figure 1 illustrates one method of practicing the process of the invention.

Figure 2 illustrates a modification of the method of Figure 1, both methods being illustrated diagrammatically.

Broadly stated, the present invention relates to a method of processing shale and like material wherein the shale is subjected to the action of microorganisms capable of metabolizing certain constituents of the kerogen content of the shale and effecting both separation and recovery of the kerogen as well as alteration products thereof while simultaneously improving the properties of the kerogen and converting it to satisfactory types of oils. More specifically stated, the invention involves treatment of shale with microorganisms capable of metabolizing certain hydrocarbons, sulfur-containing, and nitrogen-containing constituents thereof in the presence of a microbiological nutrient medium capable of supporting such metabolism whereby the bulk of the kerogen is released and made available for recovery. Such processing is preferably carried out at substantially atmospheric temperature or at temperature slightly above to avoid the loss of heat incident to heating the inorganic aggregate.

The term "microorganisms" as used herein is intended to include mold, fungi, and bacteria as well as the enzymes and other products thereof that are capable of effecting alterations or modifications in the structures of selected compounds or mixtures thereof, usually termed "substrates.”

While the exact mechanisms of the various reactions or modifications is not entirely understood, it is believed that the bacteria, enzymes and other microorganisms, preferably anaerobic, tend to break up large molecular aggregates which may be bound together through S or N by attacking them at the sulfur and nitrogen, and tend to split any adsorbed hydrocarbons at the site of a carbon-carbon bond with the liberation of lighter and more mobile hydrocarbons from the shale aggregate. The former is indicated by reaction products containing sulfur, hydrogen sulfide, and ammonia, and the latter by the apparent reduction in viscosity of the hydrocarbon. An additional theory regarding the latter is that the microorganisms tend to split the long chain hydrocarbons into shorter chains. There is also some basis for believing that the microorganisms produce some acids or acidic substances from the nutrient medium and constituents of the kerogen as through a reduction of the sulfur or nitrogen in the shale and those acids or acidic substances attack and dissolve certain constituents of the mineral aggregate, thus releasing the kerogen. This is indicated by the presence of some carbon dioxide in the gaseous reaction products.

Suitable microorganisms for the process include Clostridium sporogenes, Clostridium histolyticum, Clostridium lentoputrecaes and facultative anaerobic microorganisms such as Pseudomonas fluorescens which are able to metabolize the desired constituents in a nutrient medium such as a mineral type medium of the following general composition:

- \((\text{NH}_4)_2\text{SO}_4\) 2.0 g
- \(\text{Na}_2\text{HPO}_4 \cdot \text{H}_2\text{O}\) 1.0 g
- \(\text{K}_2\text{HPO}_4\) 2.0 g
- \(\text{MgSO}_4 \cdot 7\text{H}_2\text{O}\) 0.25 g
- \(\text{MnCl}_2 \cdot 4\text{H}_2\text{O}\) 0.01 g
- \(\text{CuCl}_2 \cdot 2\text{H}_2\text{O}\) 0.01 g
- \(\text{Fe}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}\) 0.01 g
- \(\text{KI}\) 0.00001 g
- \(\text{CuSO}_4 \cdot 5\text{H}_2\text{O}\) 0.00001 g
- Distilled water 1000 ml

To the above, 5% yeast extract by weight is preferably added as a source of biotic factor.
Such microorganisms function best at a pH of about 5.5 to 8, and a temperature in the range of 20° to 45° C., the precise conditions differing slightly with different microorganisms as is well known in the art. The pressure appears variable over a considerable range, substantially atmospheric pressure being preferred for economic and engineering reasons.

An example of one method of carrying out the process, attention is called to Fig. 1 of the accompanying drawing wherein 11 indicates a hopper for the shale or similar material as originally mined; 12 is a mill for grinding the shale into relatively fine particles; 13, 14 and 15 are treating receptacles or tanks to which the ground shale is distributed by conduits 16, 17 and 18 leading from a manifold 19 connected in turn to mill 12 by connection 21; 22, 23 and 24 are connections for charging nutrient medium with its contained microorganisms to the treating tanks; 25, 26 and 27 are manifolds connected to the several tanks for removing liquid reaction products at different levels; 28 is a manifold connecting the individual manifolds 25, 26 and 27 to a manifold discharge 29; 31, 32 and 33 are valve-controlled outlets for the processed aggregate and its surrounding nutrient medium after the processing is completed; and 34, 35 and 36 are outlets for the gaseous products, all being connected to a common conduit 37.

In carrying out the process, shale in hopper 11 is ground in mill 12 into fine particles and charged to tanks 13, 14 and 15; conditions differing slightly with the microorganisms to be used is preferably charged first to the tanks through connections 22, 23 and 24 so that the shale falls into the medium, although it is to be understood that the medium may be added after the shale. The nutrient medium, when charged, is preferably the desired pH. If it is found that the shale constituents have an appreciable effect on the pH of the medium, the pH of the medium, as introduced, can be so adjusted that the pH attained by the medium mixture in the desired range.

The shale and medium are combined in proportions to form a slurry which can be agitated as by mechanical means to maintain the solid particles of the shale in suspension. This insures intimate and continued contact of the microorganisms with the shale particles. Agitation can also be accomplished by the introduction of a suitable gas.

Any gaseous products formed are removed through outlets 34, 35 and 36. Separated oil or processed kerogen rises to the top of the nutrient medium and is withdrawn through the valved connections leading to outlets 25, 26 and 27. These liquid products may be subsequently processed and refined as desired in accordance with recognized refinery practice.

Suitable heating means may be provided in the form of steam coils or the like to maintain the temperature in the tanks within the desired range.

After the shale has been processed, the valves at the bottom of the tanks are opened and the aggregate and medium withdrawn. The valves are closed and new charges of inoculated medium and shale charged to the tanks.

Dependent upon the processing time and the capacity and number of the tanks used, the process may be made substantially continuous as regards the shale fed by hopper 11 and the liquid products taken off through outlets 34, 35 and 36. Obviously many modifications and variations...
of the invention as above 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.

I claim:

1. A method for treating kerogen-type oil shales for the purpose of facilitating the separation and recovery of hydrocarbon, bituminous substances and the like associated therewith, which comprises subjecting said materials to the action of microorganisms selected from the group consisting of Clostridium sporogenes, Clostridium histolyticum, Clostridium lentoputrescens, Pseudomonas fluorescens and mixtures thereof, in the presence of a microbiological nutrient medium capable of supporting the metabolism of said microorganism.

2. The method according to claim 1 in which the microbiological nutrient medium has a pH in the approximate range of 5.5 to 8.

3. A method according to claim 1 in which a temperature in the approximate range of 20 to 45°C is maintained during the action of the microorganisms on said kerogen-type oil shales.

4. A method for treating kerogen-type oil shales for the purpose of facilitating the separation and recovery of hydrocarbon, bituminous substances and the like associated therewith, which comprises subjecting said materials to the action of microorganisms selected from the group consisting of Clostridium sporogenes, Clostridium histolyticum, Clostridium lentoputrescens, Pseudomonas fluorescens and mixtures thereof, in the presence of a microbiological nutrient medium capable of supporting the metabolism of said microorganisms and separating resulting products from the inorganic aggregate of said material.

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