

[54] PROCESS FOR PRODUCING PRODUCT FROM FOSSIL FUEL

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[56] References Cited

UNITED STATES PATENTS

1,990,523	2/1935	Buswell et al.....	195/27 X
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3,342,257	9/1967	Jacobs et al.....	166/247
3,640,846	2/1972	Johnson.....	195/27
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[57] ABSTRACT

A process is disclosed for producing a valuable product from fossile fuel deposits which contain organic ring compounds. In the process, a fossil fuel deposit containing organic ring compounds is contacted in situ, preferably at a depth of at least 500 feet below ground surface, with an anerobic ring compound fermenting microorganism. An intermediate having a lower ring compound content and including paraffins and organic acids is produced. Generally, water is present during the fermenting and the intermediate is more soluble in the water than are the organic ring compounds. The intermediate is contacted either concurrently with the fermentation of the organic ring compounds or thereafter with a microorganism which converts paraffins to organic acids. The resulting organic acid composition is contacted with a microorganism which converts organic acids to valuable products. The conversion of the organic acids to valuable products can occur either concurrently with or after the microorganismic conversion of paraffins to organic acids. In a preferred embodiment of the invention a microorganism which converts carbohydrates, e.g., cellulose, to a valuable product is included in at least one of the contacting steps, most preferably during the ring compound fermenting.

12 Claims, No Drawings

PROCESS FOR PRODUCING PRODUCT FROM FOSSIL FUEL

BACKGROUND OF THE INVENTION

The invention relates to a process for making valuable products and in particular normally gaseous hydrocarbons from fossil fuel deposits containing organic ring compounds, especially from coal or shale oil deposits.

Methane is usually obtained from natural gas wells. Also, some methane is manufactured by conventional gasmaking processes from both liquid and solid fuels. The sources of natural gas are limited and the gas is becoming more costly to recover. Deeper wells are being drilled in more inaccessible locations. As a result, the demand for manufactured normally gaseous hydrocarbons is increasing.

Methane in the past has been manufactured by coal carbonization techniques (Lurgi process), the carburated water gas reaction, and by the destructive hydrocrocking of liquid hydrocarbon fuels such as naphtha. Bushwell et al. in U.S. Pat. No. 1,990,523 disclose the production of methane by sewage digestion with anaerobic bacteria.

Further, those processes using coal to make, e.g., methane, generally require that the coal be mined. The prior art fails to treat tar, asphalt, oil shales, crude oil, petroleum products generally, and other fossile fuels to convert them via the action of microorganisms to normally gaseous hydrocarbons. The prior art also fails to show the addition of hydrogen to the fermentation to increase the output of methane and other normally gaseous hydrocarbons. Earlier U.S. Pats. such as No. 3,640,846 do not disclose that the conversion of the organic ring compounds in coal and the branched chain hydrocarbons of crude oil and kerogen, to forms such as volatile and fatty acids or CO_3 suitable as substrates for methanogenic bacteria, is dependent upon the action of volatile acid, fatty acid, and CO_2 producing microorganisms, yeasts, and fungi.

In many cases, such as those of asphalts, it may be desirable to ferment initially with a microorganism which is either assimilable by volatile acid, CO_2 , or fatty acid forming microorganisms; or which forms a product capable of serving as a substrate for such microorganism. More complex fermentations, by groups of microorganisms, microbial ecoseptems, enrichment cultures, and selected pure strains of organisms may be required in some cases. The prior art does not disclose these facts.

As is taught by U.S. Pat. No. 3,540,983, it is possible to make an extract of coal for use as a medium for the support of microorganisms. These extracts support the growth of both aerobic and anaerobic microorganisms, e.g., yeasts, and fungi. Extracts of other hydrocarbon and petroleum products, as listed earlier, can also be used to support the growth of both anaerobic and aerobic microorganisms. Although U.S. Pat. No. 3,540,983 requires very small particle of coal for extraction, it has now been discovered that by the process of the present invention it is possible to make a satisfactory coal extract in situ with coal particles several orders of magnitude larger than those used by the process of U.S. Pat. No. 3,540,983. Oil shale is also treatable by the process of the present invention to form food for microorganisms. Other fossil fuels are also treatable by the process

of the present invention. These fossil fuel deposits are capable of anaerobic in situ fermentation to methane and other chemical products. It also is possible to pump water into a rubble chimney for in situ extraction and fermentation and then to pump the extract-ferment out and ferment it further above the ground.

The prior art teaches that there are many suitable methods of making rubble chimneys, tunnels, blockcaving mines and other wise providing for the extraction of desirable materials in situ. It is not desired to claim these methods, but rather to teach the use of the methods of in situ breakage and rubbing of native rock for use in the extraction and/or biological degradation of fossil fuel deposits to desired products.

The prior art does not disclose the conversion of fossil fuel deposits containing organic ring compounds, starting in situ, preferably at a depth of at least 500 feet below ground surface, into a valuable product. U.S. Pat. No. 3,640,846 discloses a process for producing methane by the anaerobic digestion of sewage sludge wherein coal is added to the sludge during the digestion step to improve methane production from the sludge. This patent is however concerned solely with the use of anaerobic methane producing bacteria and does not recognize, approach, or attack the problem of converting fossil fuel deposits containing organic ring compounds into a valuable product. This is particularly true since (1) methane producing anaerobic bacteria will not produce significant methane from organic ring compounds or for that matter from paraffins but will instead act substantially solely to convert organic acids into methane and (2) a simple water extraction will not remove a great deal of the convertible hydrocarbon materials and in particular most of the organic ring compounds and carbohydrates from coal and the like.

Accordingly, it is an object of the present invention to provide a process which will convert fossil fuel deposits containing organic ring compounds into a valuable product.

It is a further object of the invention to provide a process for producing normally gaseous hydrocarbons from fossil fuel deposits containing organic ring compounds.

It is a still further object of the invention to provide a process wherein by use of a plurality of types of microorganisms the organic ring compounds, paraffins, carbohydrates, and other constituents of fossil fuel deposits containing organic ring compounds are converted to a valuable product.

Another object of the invention is to provide a process featuring in situ conversion of organic ring compounds to intermediates which are convertible more easily than the organic ring compound to a valuable product.

It is a further object yet of the invention to provide a process for accomplishing all of the above objects in situ in a fossil fuel chimney.

GENERAL DESCRIPTION OF THE INVENTION

The invention comprises a process for producing a valuable product from fossil fuel deposits containing organic ring compounds, comprising contacting a fossil fuel deposit containing organic ring compounds, in situ, preferably at a depth of at least about 500 feet below ground surface, with an anaerobic organic ring compound fermenting microorganism under anaerobic fer-

mentation conditions to prepare an intermediate having a lowered organic ring compound content and including paraffins and organic acids. The intermediate is usually contacted either after or concurrently with the contacting of the fossil fuel deposit with the anaerobic organic ring compound fermenting microorganism, under fermentation conditions, with a microorganism which converts paraffins to organic acids to prepare an organic acid enriched composition. The organic acid enriched composition is usually contacted either after or concurrently with the contacting of the intermediate with the microorganism, which converts paraffins to organic acids, under fermentation conditions with a microorganism which converts organic acids to a valuable product. In a preferred embodiment of the invention a microorganism which converts carbohydrates to a valuable product, e.g., methane, is included in at least one of the above set out contacting steps, most preferably, during the organic ring fermenting.

The invention further comprises a novel combined extraction and fermentation process useful for leaching a valuable product from a fossil fuel deposit, said process comprising contacting a fossil fuel deposit in situ with water, an anaerobic microorganism which converts organic ring compounds to organic acids, and an anaerobic microorganism which converts carbohydrates to a valuable product preferably at a depth of at least about 500 feet below ground surface under anaerobic fermentation conditions, and producing a composition, said composition being useful as a food for other microorganisms which convert said composition into further valuable products, e.g. normally gaseous hydrocarbons, edible products, or the like.

DETAILED DESCRIPTION OF THE INVENTION

When the term "fossil fuel deposit" is used, this term is meant to include coal, shale oil, lignite, peat, asphalt, tar, and other deposits normally spoken of as fossil fuels. The process of the present invention is most useful in upgrading fossil fuel deposits of relatively low value, into a valuable product such as a normally gaseous hydrocarbon.

In the case of coal and shale oil, it will be desirable in many cases to first prepare the deposit, prior to the contacting steps of the process of the present invention, by setting off an explosive device in situ in the deposit reducing the size of the solid material forming the deposit so that said solid material, e.g., coal, oil containing rock, or the like will be in small enough pieces so that the organic ring compound, paraffin, carbohydrate, and other fermentable materials therein can be more easily contacted by the anaerobic organic ring compound fermenting microorganism. After the explosion, the coal and shale oil form what is commonly called a rubble chimney.

When the term "organic ring compound" is used, this term is meant to include cycloparaffin, cycloparaffene, aromatic, and heterocyclic ring containing compounds, which compounds may have various other chemical constituents attached thereto but to exclude carbohydrates (sugars, starches, cellulose, and the like). The organic ring compounds must include both carbon and hydrogen atoms in chemical combination with each other.

When the term "carbohydrate" is used, this term is meant broadly and includes cellulose, starch, partial

hydrolyzates of each, and derivatives of cellulose, starch, and their hydrolyzates.

When the term organic acid, paraffin, cycloparaffin, cycloparaffene, and the like are used, they are used in the broad sense and according to accepted chemical nomenclature.

As set out above, when the fossil fuel is a solid deposit and has been subjected to explosive action, a rubble chimney will result. Generally, the organic ring compound fermenting microorganism will be introduced into the rubble chimney in a water based solution. In general, the volume ratio of water to fossil fuel will be less than 2 to 1. More often there will be 10 to 30 volume percent water for 90 to 70 volume percent fossil fuel deposit, the water preferably containing the organic ring compound fermenting microorganism and in some embodiments of the invention also containing a paraffin converting microorganism and/or an organic acid converting microorganism, and/or a carbohydrate converting microorganism.

It will often be desirable to add essential nutrients for the microorganisms, e.g., suitable nitrogen, phosphorous, iron, potassium, etc. sources, along with or concurrently with the water. Water soluble salts such as ammonium, iron, and/or potassium phosphates may, for example, be used.

The contacting of the fossil fuel deposit with the organic ring compound fermenting microorganism is preferably carried out in situ at a depth of at least 500 feet to take advantage of the temperature and pressure conditions prevalent at this depth and of the natural (earth) fermenting vessel. By "a depth of at least 500 feet" it is meant that over 50 percent of the deposit being contacted is at least 500 feet below ground surface level. It is often desirable to perform the in situ contacting step in the presence of hydrogen to increase the yield of normally gaseous hydrocarbons.

The organic ring compound fermenting microorganism must be an anaerobic microorganism which converts organic ring compounds into organic acids and/or paraffins under anaerobic fermentation conditions thereby lowering the organic ring compound content of the fossil fuel deposit.

The action of the anaerobic organic ring compound fermenting microorganism upon the fossil fuel deposit will lead to the formation of an intermediate having a lowered organic ring compound content and including paraffins and organic acids, the amount of organic acids generally being increased by the action of the organic ring fermenting microorganism although it is recognized that some organic ring fermenting microorganisms produce paraffins or the like.

The intermediate may be contacted concurrently with the fermentation of the organic ring compounds by the anaerobic organic ring compound fermenting microorganism with a microorganism which converts paraffins to organic acids. Clearly if the contacting of the intermediate is concurrent with the contacting of the fossil fuel deposits with an anaerobic organic ring compound fermenting microorganism the two fermentations, i.e., the organic ring compound fermentation and the paraffin fermentation occur at the same time and can occur in situ in the same chimney. If this is the case, it will be advantageous to use a mixed culture of microorganisms including at least one organic ring compound fermenting microorganism and at least one paraffin converting microorganism. If these two fer-

menations occur together in a chimney then the paraffin fermenting microorganism must also be an anaerobic microorganism.

Alternatively, the intermediate may be pumped up from the chimney to ground level and contacted at ground level with a microorganism which converts paraffins to organic acids. This can still occur concurrently with the organic ring compound fermentation if liquid and organic ring compound fermenting microorganism is concurrently within the chimney or the paraffin conversion can occur after the organic ring compound fermenting is completed.

When the paraffin fermentation occurs after the organic ring compound fermentation is completed or on a sample on which the organic ring compound fermentation has been completed, then the microorganism used to accomplish the paraffin fermentation may be either an aerobic microorganism or an anaerobic microorganism. It is, of course, clear that when both the organic ring compound fermentation and the paraffin fermentation take place at the same time and in situ the microorganism which converts paraffins to organic acids must be an anaerobic microorganism.

The organic acid enriched composition from the paraffin fermentation can be fermented either after or concurrently with the paraffin fermentation. If the organic acid fermentation is carried out at the same time as is the paraffin fermentation, it may be carried out either in situ in the chimney along with both the paraffin fermentation and the organic ring compound fermentation or it can be carried out ex situ but at the same time as the paraffin fermentation. In the latter case, or if the organic acid fermentation is carried out after the paraffin fermentation, it is possible to use either an aerobic microorganism or an anaerobic microorganism to convert the organic acid enriched composition to a valuable product. When the organic acid fermentation occurs in situ, it is of course necessary that the microorganism used be an anaerobic microorganism and the fermentation be under anaerobic conditions.

The use of a carbohydrate fermenting microorganism in at least one of the contacting steps of the process of the invention is contemplated. Preferably, an anaerobic carbohydrate fermenting microorganism is present along with the organic ring fermenting microorganism in the first step of the invention whereby during the fermenting additional convertible material is removed or leached from the coal to form, when water is present, an extract-ferment composition of increased value.

Each of the steps of the process of the invention can be carried out concurrently and/or in situ or the first and second steps of the process can be carried out anaerobically in situ and the third step can be carried out aerobically or anaerobically ex situ. Also, if desired, the first step can be carried out anaerobically in situ and the second and third steps of the process can be carried out either anaerobically or aerobically ex situ.

Any of a number of valuable products can be produced by the process of the present invention, the particular valuable product produced being determined by the nature of the microorganism used to convert the organic acids in the third contacting step of the process of the present invention. One valuable product comprises a normally gaseous hydrocarbon or mixture of hydrocarbons. By normally gaseous hydrocarbon is meant, hydrocarbons which at one atmosphere pressure and 25° C exist in the gaseous state, e.g., methane,

ethane, propane, and butanes. When a normally gaseous hydrocarbon is the valuable product being produced it is desirable that the fermentation step which leads to the production of the normally gaseous hydrocarbon be performed in the presence of added hydrogen.

In some instances, for example, where a fossil fuel deposit has a high carbohydrate content, it is desirable to convert at least a portion of the carbon oxides produced into a valuable product, e.g., a normally gaseous hydrocarbon. One way of accomplishing this is to perform the contacting step wherein the carbohydrates are converted into a valuable product in an atmosphere which preferably contains considerable hydrogen and is substantially oxygen free. In a particular embodiment, hydrogen can be pumped into a rubble chimney along with an anaerobic carbohydrate converting microorganism thereby taking advantage of the natural vessel (the rubble chimney) and the natural temperature at a depth of at least 500 feet below ground level.

The use of a carbohydrate fermenting microorganism without the use of hydrogen is also contemplated and offers significant advantages of increased yield through increasing the amount of material extractable by a combined extraction fermentation step.

It is often advantageous to combine as part of the process of the present invention the conversion of sewage sludge by performing the contacting wherein the organic ring compound fermentation occurs in the presence of sewage sludge which is also converted by the overall process into a valuable product. Alternatively or additionally, sewage sludge may be present in the contacting whereby paraffins are converted to organic acids or where organic acids are converted to a valuable product. The use of sewage sludge in conjunction in the production of a valuable product from fossil fuel deposits is especially useful since sewage sludge will contact some or all of the microorganisms needed to carry out each of the fermentations of the present process as well as serving as an additional and an inexpensive source of valuable product. The carbohydrate content of sewage sludge is generally considerable. Thus, when sludge is converted along with a fossil fuel deposit it is particularly desirable that a carbohydrate converting microorganism be present.

If microorganisms spread unduly to nearby areas their growth can be controlled by chlorination and/or the addition of heavy metals.

A great number of the microorganisms within the genera listed below are facultative, i.e., can grow under either aerobic or anaerobic conditions. Further, not all of the microorganisms of each genera listed below will perform the listed conversion. Simple laboratory testing of particular strains with model compounds, wherein the model compounds are fed to a particular microorganism and the product produced by the microorganism is determined will serve to show whether a particular strain is useful for the desired conversion. Also in many cases, and especially with anaerobic microorganism, mixed strains will be used, the exact strain composition not being known. This is common practice with anaerobic microorganisms, pure strains of only a handful of which are stored at strain depositories.

The exact conditions of temperature, pressure, pH, etc under which the above set out fermentations occur

will differ somewhat depending on the precise microorganism being used. In general, the temperature will be above 0° C and below the temperature at which the particular microorganism is deactivated or killed, usually below about 100° C. More usually the temperature will fall within the range 10° C to about 70° C and more usually from about 15° C to about 60° C. The pH will generally fall within the range from about 2 to about 12 and more usually from about 3 to about 9.

Representative genera of anaerobic organic ring compound fermenting microorganisms are from the bacteria: *Pseudomonas*, including *arvilla*, *dacunhae*, *desmolytica*, *rathones*, *salopia*, *crucivial*, *indoloxidans*, *pictorum*, and *lacunogens*; *Vibrio*, including *neocistes*, *cyclosites*, and *cuneatias*; *Agarbacterium*, *Beueckea*, *Bacteroides*; and *Achromobacter*, including *iophagus* and *cyloclastes*; from the fungi (fungi imperfecti): *Actinomyces*, *Myrothecium*, *Mycobacterium*, *Myococcus*, *Nocardia*, *Sporocytophaga*, *Streptomyces*, *Trichoderma*, *Oscillospira*, and *Aspergillus*; and from the yeasts: *Gospora*, *Candida*, *Debaryomyces*, *Pichia*, *Saccharomyces*, *Dekkera*, and *Hauseniaspora*.

Representative genera of aerobic and anaerobic microorganisms that convert paraffins to organic acids are from the bacteria: *Mycobacterium*, *Cornebacterium*, and *Pseudomonas* and from the yeasts: *Rhodotorula*, *Lipomyces*, *Candida*, *Debaryomyces*, *Hansenula*, *Schizoblastosporion*, *Trichosporon*, *Torulopsis*, *Saccharomyces*, *Gospora*, and *Pichia*.

Representative genera of anaerobic microorganisms that convert organic acids to valuable products are from the bacteria: *Pseudomonas* including *riboflavina*, *Xanthomonas*, *Spirillum*, *Selenomonas*, *Rhodomicrobium*, and *Propionibacterium* and from the yeasts: *Candida*, *Torulopsis*, *Rhodotorula*, *Lipomyces*, and *Saccharomyces*.

Representative genera of aerobic microorganisms that convert organic acids to valuable products are from the bacteria *Pseudomonas*, *Nitroceptis*, *Xanthomonas*, *Protaminobacter*, *Escherichia*, *Erwinia*, *Streptococcus Zooglea*, and *Bordetella* and from the yeasts: *Candida*, *Torulopsis*, *Rhodotorula*, *Saccharomyces*, *Citeromyces*, *Debaryomyces*, *Eudomycopsis*, *Hausanuela*, *Lipomyces*, *Lodderomyces*, *Netsclenkowia*, and *Wadsonia*.

Representative genera of microorganisms that ferment carbohydrates are from the bacteria: *Pseudomonas* including *tralucida* and *lacia*, *Cellfalcicula*, *Flavobacterium* including *ferrugineum*, *Cellulomonas*, and *Clostridium*.

The invention will be better understood by reference to the illustrative examples that follow.

EXAMPLES

EXAMPLE 1. OIL SHALE

An oil shale extract was prepared to simulate that derived from a rubble chimney from in situ leaching coupled with in situ microorganism fermentation-extraction. For about 5 weeks, about 500 grams of ¼ inch oil shale chips were incubated at 35° C with 1½ liters of anaerobic methane filter effluent (a mixture of cellulose fermenters, organic acid producer and methanogens produced according to the method described by J. C. Young and P. L. McCarty (Department of Civil Engineering, Stanford University, Palo Alto, CA, Technical Report No. 87 (1968) p 252)).

The culture liquid was separated by filtration. The filtrate was inoculated heavily with a mixed *Candida* yeast. The resulting yeast culture was aerated for 4 days with a sparger at room temperature. Following this 4 day period, 25 ml of the yeast culture was filtered through a tared glass fiber filter paper. The filter paper was dried at 100° C overnight, and the dry weight suspended solids value was found to be 42.2 milligrams per 25 ml or 1,688 milligrams per liter.

The oil shale chips which were separated from the culture liquid by the filtering were inoculated with 800 ml of a crude enrichment culture of petroleum fermenters (a mixture of organic ring fermenters, organic acid producers, cellulose fermenters, paraffin fermenters and methanogens produced in a coal enrichment culture originally inoculated with the anaerobic sludge. A portion of this mixed culture was freeze dried and sent for storage to NRRL, Peoria, Ill.).

The resulting culture was fermented anaerobically and the gas produced was trapped by gas displacement of an acid-salt solution. The quantity of gas produced was not measured but the composition of the gas was measured by vapor phase chromatography. It was found that of the combined CH₄ and CO₂ produced, over 85 percent was CH₄.

This example demonstrates that through in situ fermentation-extraction by the process of the present invention valuable products such as CH₄ and/or *Candida* yeast can be produced when the ferment-extract composition is further fermented, either aerobically or anaerobically with microorganisms.

EXAMPLE 2. COAL

A coal extract was prepared to simulate that derived from a rubble chimney through in situ leaching coupled with in situ microorganism fermentation-extraction. To prepare the extract, for 2 weeks, 15 Kilograms of average size ¼"-½" bituminous coal was shaken at 35° C with a mixture of two liters distilled water, six liters of the anaerobic methane filter effluent described in Example 1, and an innoculum of mixed *Candida* yeast.

After this period, a 100 ml portion of the extract was filtered and heavily inoculated with the mixed *Candida* yeast, shaken, and aerobically fermented at 35° C for 1 week. Following filtration through a tared glass fiber filter, and overnight drying at 100° C, the dry-weight suspended solids from the yeast culture of the 100 ml portion of the extract was determined. The 100 ml portion of the extract, after aerobic growing of *Candida* yeast thereon, contained 21.1 milligrams of dry weight suspended solids per 100 ml, or 211 milligrams per liter.

Over 15 liters of CH₄ rich gas (87% to 96% of the combined CO₂ and CH₄ was CH₄) was produced during the fermenting of all but the 100 ml portion removed and aerobically used as a food for the *Candida* yeast.

This example demonstrates that microorganisms grow on coal to ferment and extract the coal and to produce considerable CH₄ rich gas under conditions similar to those to be encountered in situ in a rubble chimney. The example further demonstrates the production of considerable of an edible yeast.

While the invention has been described in connection with specific embodiments thereof, it will be understood that it is capable of further modification, and this application is intended to cover any variations, uses or adaptations of the invention following, in general,

the principles of the invention and including such departures from the present disclosure as come within known or customary practice in the art to which the invention pertains and as may be applied to the essential features hereinbefore set forth, and as fall within the scope of the invention and the limits of the appended claims.

That which is claimed is:

1. A process for producing a valuable product from a fossil fuel deposit containing organic ring compounds comprising the steps of:

1. contacting a fossil fuel deposit containing organic ring compounds in situ, with an anerobic organic ring compound fermenting microorganism under anaerobic fermentation conditions to prepare an intermediate having a lowered organic ring compound content and including paraffins and organic acids; and thereafter
2. contacting said intermediate under fermentation conditions with a microorganism which converts paraffins to organic acids to prepare an organic acid enriched composition; and
3. contacting said organic acid enriched composition, either after or concurrently with the contacting of step (2), under fermentation conditions with a microorganism which converts organic acids to a valuable product.

2. A process as in claim 1, wherein step (3) is carried out after step (2).

3. A process for producing a valuable product from a fossil fuel deposit containing organic ring compounds comprising the steps of:

- A. concurrently (1) contacting a fossil fuel deposit containing organic ring compounds in situ, with an anaerobic organic ring compound fermenting microorganism under anaerobic fermentation conditions to prepare an intermediate having a lowered organic ring compound content and including paraffins and organic acids, and (2) contacting said intermediate under fermentation conditions with a microorganism which converts paraffins to organic acids to prepare an organic acid enriched composition; and thereafter

B. contacting said organic acid enriched composition under fermentation conditions with a microorganism which converts organic acids to a valuable product.

4. A process for producing a valuable product from a fossil fuel deposit containing organic ring compounds comprising the steps of:

1. Contacting a fossil fuel deposit in the presence of water and with less than about 2 to 1 ratio, volume-wise, of water to fossil fuel, the fossil fuel deposit containing organic ring compounds, in situ, with an anaerobic organic ring compound fermenting microorganism under anaerobic fermentation conditions to prepare an intermediate having a lowered organic ring compound content and including paraffins and organic acids;
2. contacting said intermediate in the presence of water, either after or concurrently with the contacting of step (1), under fermentation conditions with a microorganism which converts paraffins to organic acids to prepare an organic acid enriched composition; and
3. contacting said organic acid enriched composition in the presence of water, either after or concur-

rently with the contacting of step (2), under fermentation conditions with a microorganism which converts organic acids to a valuable product.

5. A process as in claim 4, wherein said in situ contacting is performed at a depth of at least about 500 feet below ground surface.

6. A process as in claim 4, including performing at least one of the contacting steps in the presence of a carbohydrate fermenting microorganism.

7. A process for producing a valuable product from a fossil fuel deposit containing organic ring compounds comprising the steps of:

1. contacting a fossil fuel deposit containing organic ring compounds, in situ, with an anaerobic organic ring compound fermenting microorganism under anaerobic fermentation conditions to prepare an intermediate having a lowered organic ring content and including paraffins and organic acids;
2. contacting said intermediate, either after or concurrently with the contacting of step (1), under fermentation conditions with a microorganism which converts paraffins to organic acids to prepare an organic acid enriched composition; and
3. contacting said organic acid enriched composition and added hydrogen, either after or concurrently with the contacting of step (2), under fermentation conditions with a microorganism which converts organic acids to a valuable product comprising a normally gaseous hydrocarbon.

8. A process as in claim 7, wherein said fossil fuel is coal, oil shale asphalt, tar, peat, or lignite.

9. A process for producing a valuable product from a fossil fuel deposit containing organic ring compounds comprising the steps of:

1. contacting a fossil fuel deposit containing organic ring compounds in the presence of sewage sludge, in situ, with an anaerobic organic ring compound fermenting microorganism under anaerobic fermentation conditions to prepare an intermediate having a lowered organic ring compound content and including paraffins and organic acids;
2. contacting said intermediate, either after or concurrently with the contacting of step (1), under fermentation conditions with a microorganism which converts paraffins to organic acids to prepare an organic acid enriched composition; and
3. contacting said organic acid enriched composition, either after or concurrently with the contacting of step (2), under fermentation conditions with a microorganism which converts organic acids to a valuable product the sewage sludge also being converted by the overall process into said valuable product.

10. A process for producing a valuable product from a fossil fuel deposit containing organic ring compounds comprising the steps of:

1. contacting a fossil fuel deposit containing organic ring compounds in situ, with an anaerobic organic ring compound fermenting microorganism under anaerobic fermentation conditions to prepare an intermediate having a lowered organic ring compound content and including paraffins and organic acids;
2. contacting said intermediate, in the presence of sewage sludge, either after or concurrently with the contacting of step (1), under fermentation conditions with a microorganism which converts paraf-

fins to organic acids to prepare an organic acid enriched composition; and

3. contacting said organic acid enriched composition, either after or concurrently with the contacting of step (2), under fermentation conditions with a microorganism which converts organic acids to a valuable product, said sewage sludge also being converted by the overall process into said valuable product.

11. A process for producing a valuable product from a fossil fuel deposit containing organic ring compounds comprising the steps of:

- 1. contacting a fossil fuel deposit containing organic ring compounds in situ, with an anaerobic organic ring compound fermenting microorganism under anaerobic fermentation conditions to prepare an intermediate having a lowered organic ring compound content and including paraffins and organic acids;
- 2. contacting said intermediate, either after or concurrently with the contacting of step (1), under fermentation conditions with a microorganism which converts paraffins to organic acids to prepare an organic acid enriched composition; and
- 3. contacting said organic acid enriched composition, in the presence of sewage sludge, either after or concurrently with the contacting of step (2), under

fermentation conditions with a microorganism which converts organic acids to a valuable product, said sewage sludge also being converted by the overall process into said valuable product.

12. A process for producing a normally gaseous hydrocarbon from a fossil fuel deposit containing organic ring compounds comprising the steps of:

- 1. contacting a fossil fuel deposit containing organic ring compounds in situ, with an anaerobic organic ring compound fermenting microorganism under anaerobic fermentation conditions to prepare an intermediate having a lowered organic ring compound content and including paraffins and organic acids;
- 2. contacting said intermediate, either after or concurrently with the contacting of step (1), under fermentation conditions with a microorganism which converts paraffins to organic acids to prepare an organic acid enriched composition; and
- 3. contacting said organic acid enriched composition, either after or concurrently with the contacting of step (1), under fermentation conditions with a microorganism which converts organic acids to a gaseous product, said gaseous product including at least 85 percent of a normally gaseous hydrocarbon.

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