United States Patent

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[54] **PROCESS FOR REMOVING THE HYDROCARBON CONTENT OF CARBONACEOUS MATERIALS**
20 Claims, 5 Drawing Figs.

[52] **U.S. Cl.** **208/11,** 208/16
[51] **Int. Cl.** **C10b 53/06**
[50] **Field of Search** 201/29, 31, 32, 36; 208/11

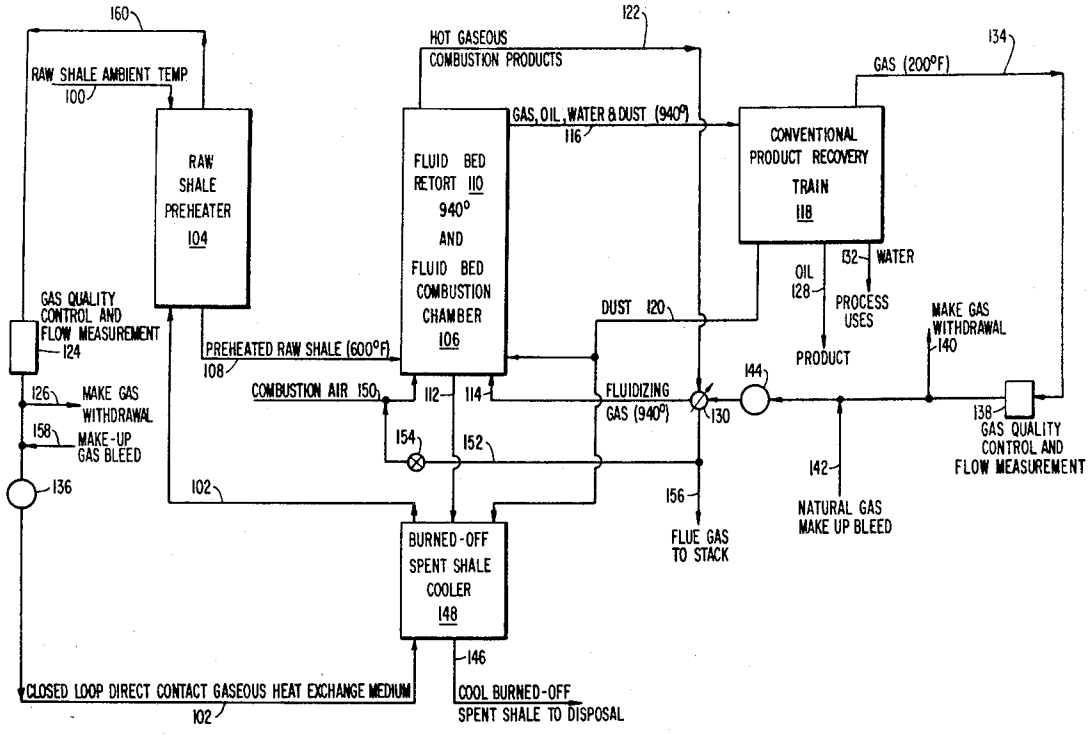
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ABSTRACT: A process for the recovery of volatile material from solid carbonaceous material, such as oil shale, tar sands, coal, lignite and the like, which comprises introducing the solid carbonaceous material into a retorting zone and fluidizing the solid carbonaceous material within the retorting zone. The fluidized solid carbonaceous material in the retorting zone is heated and volatile material is retorted therefrom and withdrawn from the retorting zone. The spent solid carbonaceous material is withdrawn from the retorting zone and transferred to a burnoff zone. The spent solid carbonaceous material is fluidized in the burnoff zone and carbon is burned off the fluidized spent solid carbonaceous material therein. The burned-off spent solid carbonaceous material and combustion products are then withdrawn from the burnoff zone.



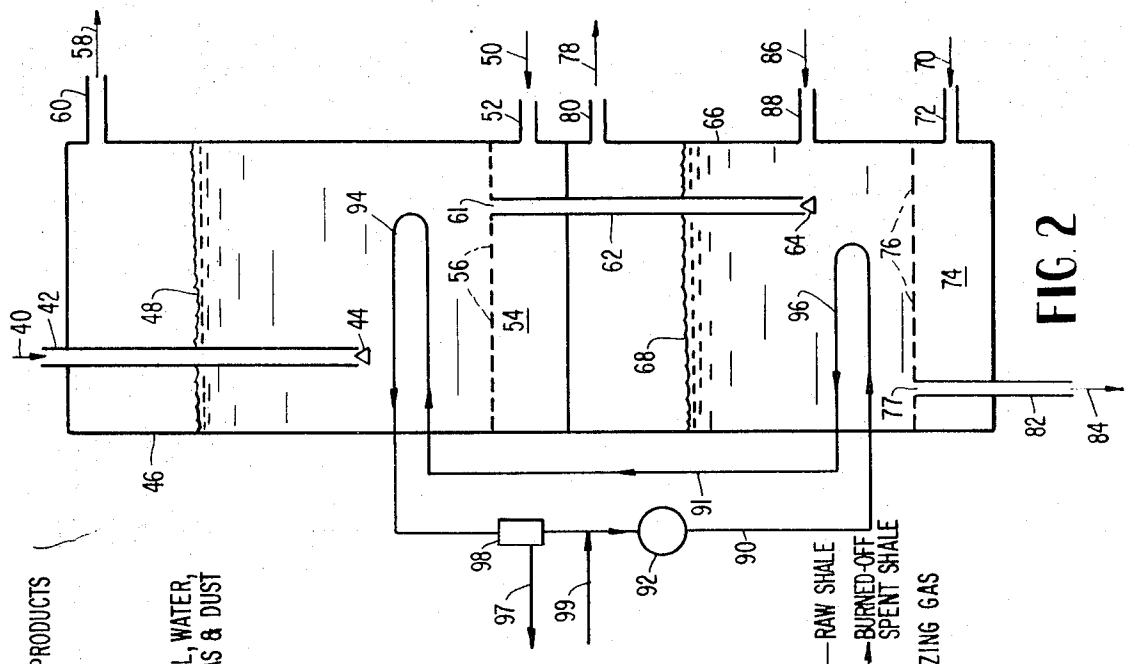


FIG. 2

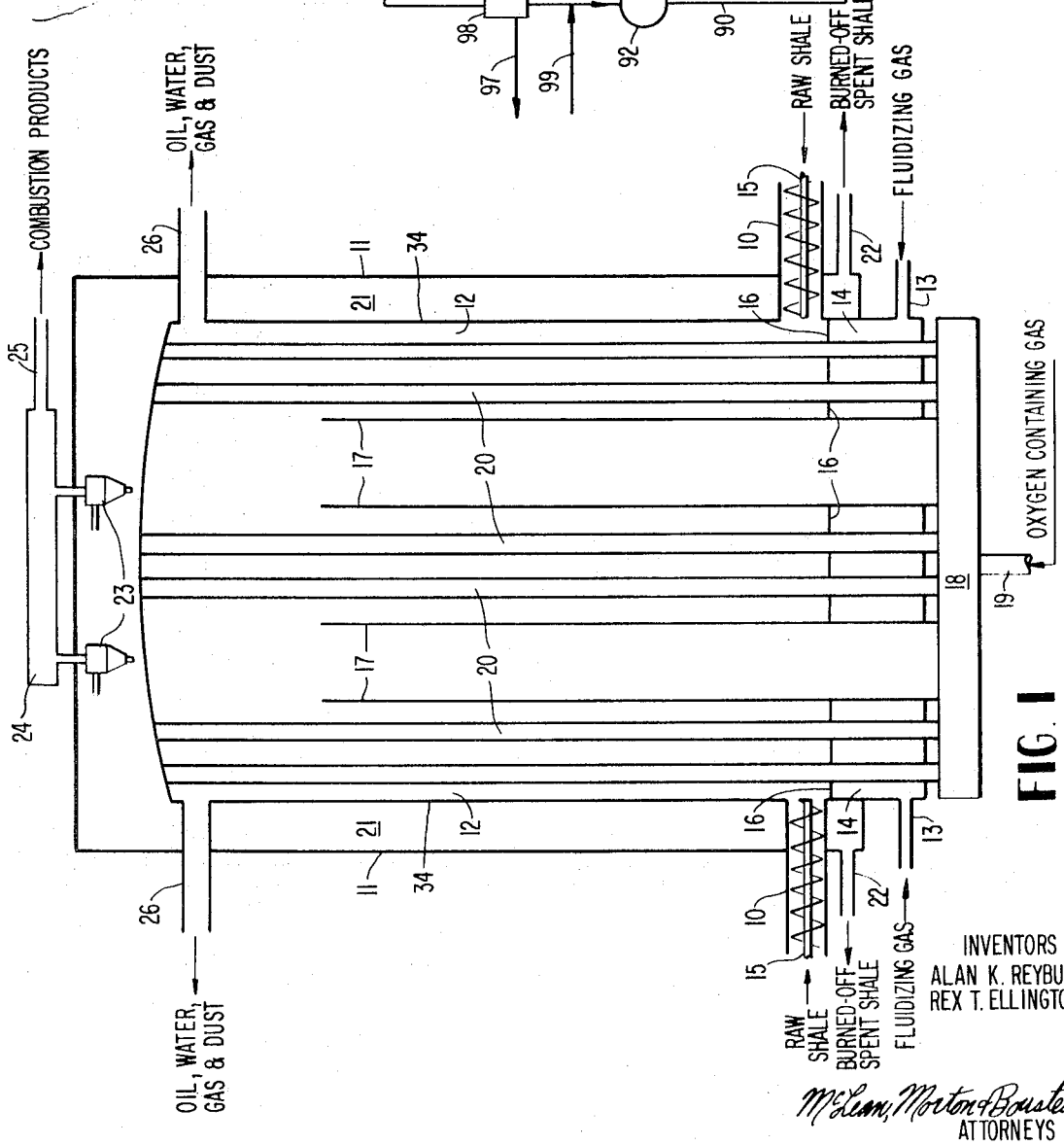


FIG. 1

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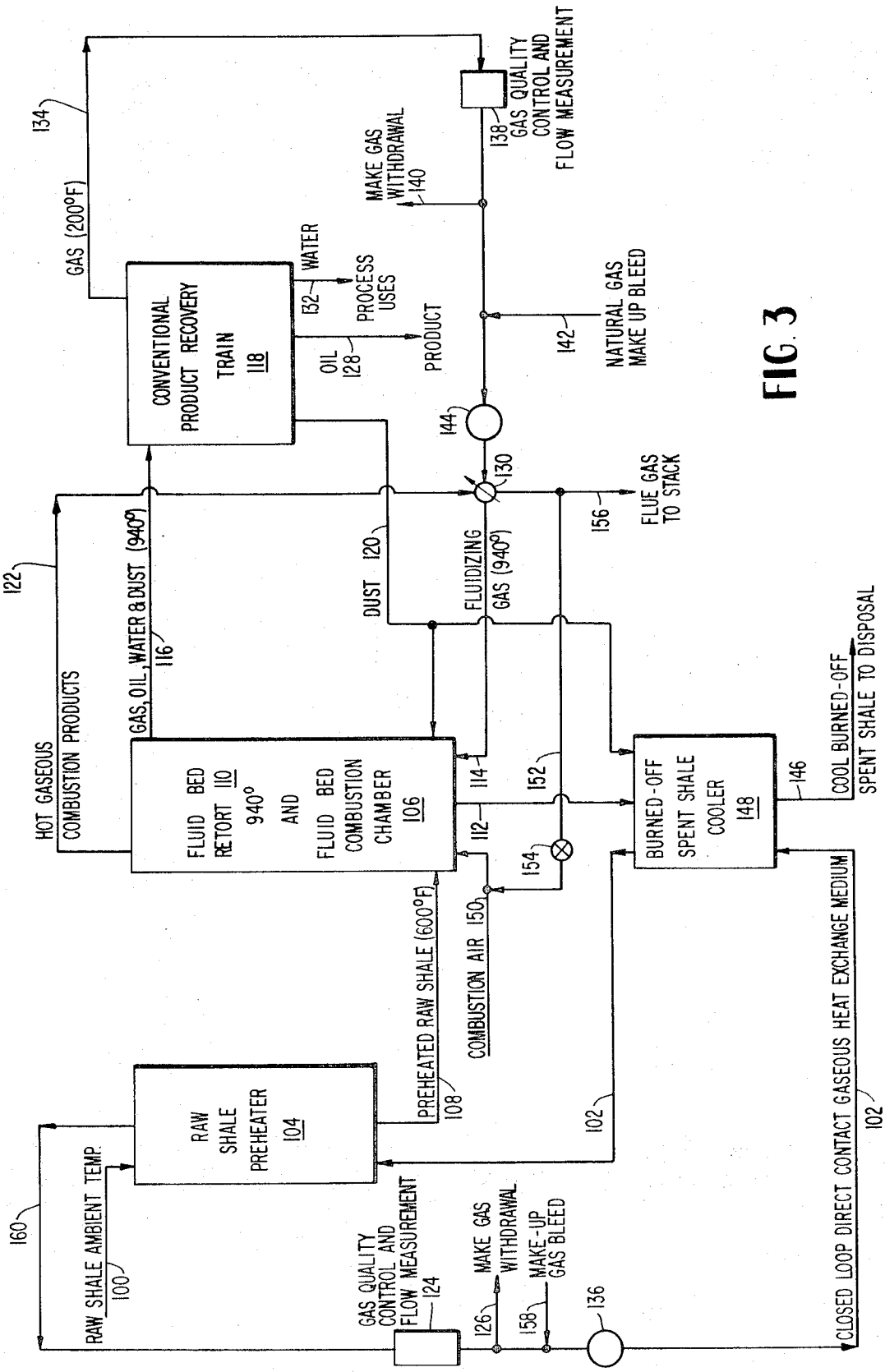

RAW SHALE AMBIENT TEMP.
100
160
RAW SHALE PREHEATER 104
PREHEATED RAW SHALE (600°F)
108
COMBUSTION AIR 150
FLUID BED RETORT 110 940° AND FLUID BED COMBUSTION CHAMBER 106
HOT GASEOUS COMBUSTION PRODUCTS
122
GAS, OIL, WATER & DUST (940°)
116
DUST 120
FLUIDIZING GAS (940°)
114
112
152
154
BURNED-OFF SPENT SHALE COOLER 148
146
COOL BURNED-OFF SPENT SHALE TO DISPOSAL
102
CLOSED LOOP DIRECT CONTACT GASEOUS HEAT EXCHANGE MEDIUM
102
GAS QUALITY CONTROL AND FLOW MEASUREMENT
124
MAKE GAS WITHDRAWAL
126
MAKE-UP GAS BLEED
158
136
CONVENTIONAL PRODUCT RECOVERY TRAIN 118
GAS (200°F)
134
WATER
132
PROCESS USES
OIL
128
PRODUCT
MAKE GAS WITHDRAWAL
140
GAS QUALITY CONTROL AND FLOW MEASUREMENT
138
NATURAL GAS MAKE UP BLEED
142
144
130
FLUE GAS TO STACK
156

FIG. 3

FIG. 4

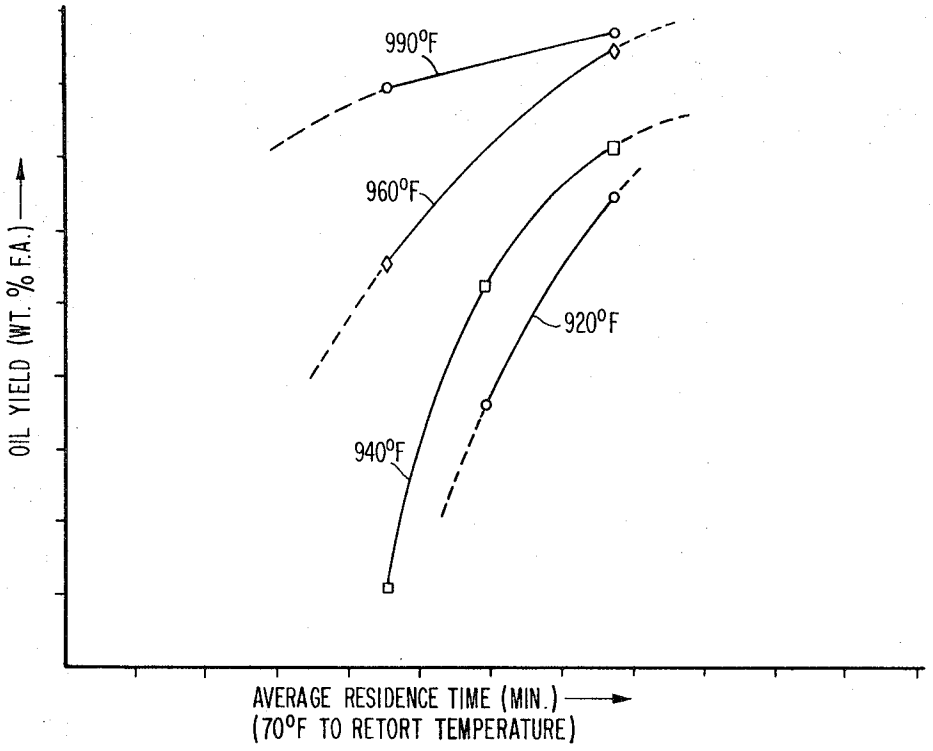
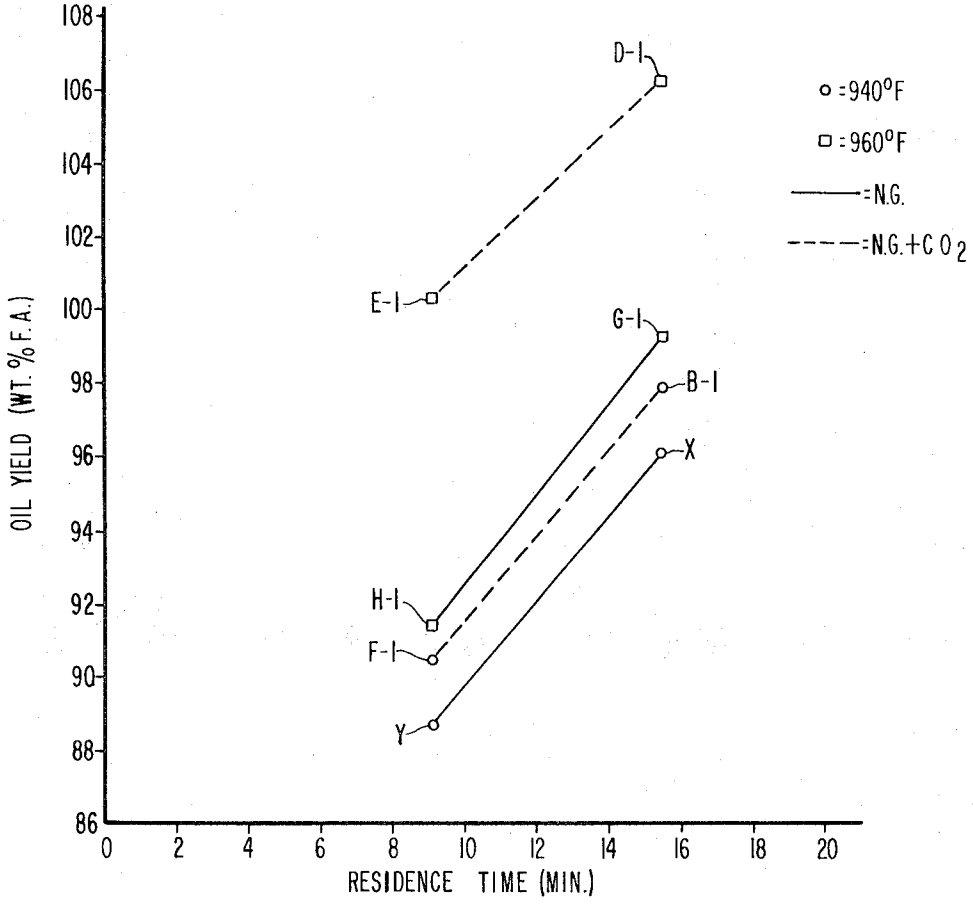

990°F
960°F
920°F
940°F
OIL YIELD (WT. % F.A.)
AVERAGE RESIDENCE TIME (MIN.)
(70°F TO RETORT TEMPERATURE)

FIG. 5


108
106
104
102
100
98
96
94
92
90
88
86
0
2
4
6
8
10
12
14
16
18
20
OIL YIELD (WT. % F.A.)
RESIDENCE TIME (MIN.)
D-I
E-I
G-I
B-I
X
H-I
F-I
Y
o =940°F
□ =960°F
——=N.G.
----=N.G.+C O 2

PROCESS FOR REMOVING THE HYDROCARBON CONTENT OF CARBONACEOUS MATERIALS

This invention relates to the removal of volatile material from solid carbonaceous material. More particularly, this invention relates to an improved process for the recovery of volatile material, such as combustible gases, liquid motor fuels, and various grades of oil, from solid carbonaceous material, such as oil shale, tar sand, coal, lignite and the like.

Many techniques have been employed for the beneficiation of solid carbonaceous material. For example, oil shale has been retorted in batch-type fixed-bed operations, rotating drums, chain grate kilns, moving-bed retorts, and fluidized beds.

Previously proposed fluidized-bed solid carbonaceous material retorts have several disadvantages. Some of these disadvantages are found in the heating methods, control of retorting atmosphere and location of the solids inlet and outlet.

Some retorts utilize the sensible heat of the fluidizing gas to supply the heat of retorting, necessitating the use of large volumes of gas to carry out the retorting of the volatile material from the carbonaceous material because the solid particles and the gas used in these processes have a similar heat capacity per unit mass. The high gas flow rates may be reduced by introducing into the retorting bed a combustion-supporting gas and allowing limited combustion to occur in the bed, thus supplying the heat of retorting. But in this case, some of the volatile material products are lost through combustion and the gaseous material from the retort is seriously diluted with combustion products. In still another method, it is proposed that hot solids, either spent solid carbonaceous material from a combustion unit or other hot inert solids, be added to the retort to supply heat. This method involves additional solids-handling costs and, when burned-off spent solid carbonaceous material is added, considerable fly ash will be generated and will be difficult to remove from the liquid and gaseous products. In addition, there is evidence that the burned-off spent solid carbonaceous material absorbs some of the volatile material products and thus contributes to a loss of yield.

In cases in which inert gas is used as the fluidizing medium, it may be heated indirectly by burning product, which is highly disadvantageous. Although most of the previous fluidized-bed retorting methods used either air or a combination of air and recycled combustion products as the fluidizing medium, as mentioned above, such fluidizing media cause loss of product through combustion and the off-gas from the retort is of little or no value. In the prior art it was not feasible to control the chemical composition of the fluidizing gas in order to enhance the quantity and/or quality of the liquid product or to facilitate the processing of the product stream (oil, gas, water and dust) outside of the retort.

Also, in previous fluidized-bed retorts, the solids inlet has usually been at the top of the bed. In such a process, the produced oil vapors must pass through a zone of relatively cold, incoming solid carbonaceous material. While this has the advantage of effecting some of the cooling necessary to condense the oil vapors and preheat the cold incoming raw solid carbonaceous material by direct contact, there are overriding disadvantages. Some of the mist droplets formed when the vaporous material condenses impinge on the raw solid carbonaceous material and are carried back into the retort bed where product loss can occur. An even more serious disadvantage is the fact that the mist droplets in the off-gas stream will be removed in large part by the equipment that removes the dust particles from the off-gas. The problem of removing the dust from the oil can be difficult and costly.

Fluid bed operation has a number of inherent advantages, including uniformity of temperature in both the horizontal and vertical directions, excellent heat transfer, uniform solid and gas distributions, intimate solid-gas contacting, convenient solids handling, large surface area per unit weight of solid for heat and mass transfer, and rapid transport of the evolved hydrocarbon from the retorting zone. In view of foregoing prior art, it is a major advantage of the present invention to retort solid carbonaceous material and the like in a fluidized bed in a process which eliminates many of the disadvantages of former processes discussed above. Another advantage of the process of he present invention is the control of the composition of the fluidizing gaseous material in order to increase the amount of product, and the control of gas velocities so that product is withdrawn from the retorting zone before cracking can occur through prolonged residence at high temperatures thereby maximizing product yield. Another benefit of rapid withdrawal of product from the retorting zone is the fact that raw shale oil has a marked instability at temperatures up to cracking temperatures and has a tendency to form polymerization or condensation products with high boiling points. Another advantage of the process of the present invention is the transfer of heat generated by burning off carbon on the spent solid carbonaceous material to the retorting zone and its use to heat the retorting zone without contaminating the fluidizing atmosphere of the retorting zone. Still another advantage of the process of the present invention is the ability to control the residence time of the shale in the retorting zone to maximize yield while minimizing equipment size. In a preferred embodiment, the fluidized solid carbonaceous material in the retorting zone is heated by means of a single heat transfer barrier separating the fluidized spent solid carbonaceous material in the burn-off zone and the fluidized solid carbonaceous material in the retorting zone thereby benefiting from the high heat transfer coefficients obtainable. The process of the invention is further advantageous in that heat from the burned-off spent solid carbonaceous material and its combustion products can be used to preheat cold gaseous fluidizing medium and cold raw solid carbonaceous material and other process streams to increase the thermal efficiency of the process and the burnoff process can be controlled so that maximum cementing properties are developed in the burned-off spent solid carbonaceous material to facilitate disposal. Finally, the raw solid carbonaceous material feed inlet can be positioned so that product comes into minimum contact with cold solid carbonaceous material thereby reducing loss of volatile material product. Relatively wide particle size ranges of solid carbonaceous material may be employed in this process, e.g. ½ inch to 10 microns, as contrasted to the narrow size ranges of solid particles employed in fluidized-bed catalytic cracking units, e.g. about 10 to 100 microns. Each retort can be designed to process a certain particle size range of interest, the main difference among the various retort designs being the flow rate of fluidizing gas used. It also is possible that there would be only one particle size range of interest, said one-half inch minus, or one-fourth inch minus, and that all the raw solid carbonaceous material would be crushed to this size range and processed in retorts of one design.

In general, the process for the recovery of volatile material from solid carbonaceous material, such as oil shale, tar sands, coal, lignite and the like of this invention comprises introducing the solid carbonaceous material into a retorting zone and fluidizing the solid carbonaceous material within the retorting zone by introducing a gaseous material. The fluidized solid carbonaceous material in the retorting zone is heated and volatile material is retorted and withdrawn from the retorting zone. The spent solid carbonaceous material is withdrawn from the retorting zone and transferred to a burnoff zone. The spent solid carbonaceous material is fluidized in the burnoff zone by introducing oxygen-containing gas into the burnoff zone and carbon is burned off the fluidized spent solid carbonaceous material therein. The burned-off spent solid carbonaceous material and combustion products are then withdrawn from the burnoff zone. A part of the stream of gaseous combustion products from the burnoff zone can be recycled and mixed with air to provide the oxygen-containing gas which is introduced into the burnoff zone. In this manner, the partial pressure of oxygen in the oxygen-containing gas can be controlled in such a way as to limit the peak temperature in the burnoff zone to a desired value.

A portion of the gaseous material introduced into the retorting zone can be a portion of the gaseous material withdrawn from the retorting zone. In such an embodiment, the gaseous material is noncombustion supporting and the chemical composition and gas velocity of the fluidizing gaseous material can be controlled to maximize product yield as is taught in our copending U.S. Pat. application Ser. No. 781,901, filed of even date herewith. The product yield would be maximized by these methods because the gas composition to be used, as has been proven in the laboratory and shown in the aforesaid copending application, gives greater oil yields than gases used heretofore in such a process. When the fluidizing gaseous material is a noncombustion-supporting material, there is no loss of product through combustion in the retorting zone. The fluidizing gaseous material can be preheated prior to introduction to the retorting zone, preferably by indirect heat exchange with the gaseous products from the combustion in the burnoff zone. Some heat will also be supplied to the fluidizing gaseous material from that portion of the gaseous material withdrawn from the retorting zone which is mixed with it.

The solid carbonaceous material can be preheated with a hot gaseous medium prior to introduction of the solid carbonaceous material into the retorting zone. The fluidized solid carbonaceous material in the retorting zone can be heated by indirect heat exchange with the fluidized spent solid carbonaceous material in the burnoff zone either by circulating a liquid or gaseous heat transfer medium in indirect heat exchange with the fluidized spent solid carbonaceous material in the burnoff zone and the fluidized solid retorting zone or by means of a single heat transfer barrier separating the fluidized spent solid carbonaceous material in the burnoff zone and the fluidized solid carbonaceous material in the retorting zone thereby benefiting from the high heat transfer coefficients obtainable.

The temperature of the fluidized solid carbonaceous material in the retorting zone is maintained at retorting temperature, e.g. within the range of about 800° to 1,000° F., preferably about 900° to 950° F. The solid carbonaceous material is retained in the retorting zone for a time sufficient to retort the kerogens, e.g. shale oil, from the material. Average residence times within the range of about 3 to 20 minutes, preferably about 5 to 10 minutes, are generally sufficient, at the desired retorting temperatures, for all of the volatile and gaseous products to be evolved. The burning in the burnoff zone is frequently carried out at a maximum temperature within the range of about 1,000° to 1,500° F., generally within the range of 1,200° to 1,400° F., to develop maximum cementing properties in the burned-off spent solid carbonaceous material to facilitate disposal.

The solid carbonaceous material can be introduced adjacent the bottom of the retorting zone providing minimum contact with the volatile material withdrawn adjacent the top of the retorting zone thereby reducing loss of volatile material product. Relatively wide particle size ranges of solid carbonaceous material may be employed in this process, e.g. one-half inch to 10 microns, preferably one-eighth inch to −400 mesh, as contrasted to the narrow size ranges of solid particles employed in fluidized-bed catalytic cracking units, e.g., 10 to 100 microns. Each retort can be designed to process a certain particle size range of interest, the main difference among the various retort designs being the flow rate of fluidizing gas used. It also is possible that there would be only one particle size range of interest, say one-half inch minus, or one-fourth inch minus, and that all the raw solid carbonaceous material would be crushed to this size range and processed in retorts of one design.

The invention will be described in more detail with reference to the appended drawings in which:

FIG. 1 schematically illustrates a retort designed for carrying out the preferred process of the invention wherein the retorting chamber and burnoff chamber are contained in one process vessel and the retorting chamber is heated by means of a single heat transfer barrier separating the fluidized spent solid carbonaceous material in the retorting chamber;

FIG. 2 schematically illustrates a retort for carrying out the preferred process of the invention wherein the fluidized solid carbonaceous material in the retort is heated by circulating a liquid or gaseous heat transfer medium in indirect heat exchange therewith and with the fluidized spent solid carbonaceous material in the burner;

FIG. 3 is a flow diagram illustrating the process of the instant invention using the retort and combustion chambers of either FIG. 1 or FIG. 2;

FIG. 4 is a graph of the effect of average residence time on oil yield for unpreheated oil shale at various temperatures for the continuous feed unit, using natural gas as the fluidizing gas; and

FIG. 5 is a graph of the effect of average residence time on oil yield for unpreheated oil shale at various temperatures for the continuing feed unit, using either natural gas or 90 percent natural gas–10 percent CO_2 as the fluidizing gas.

Referring to FIG. 1, solid carbonaceous material, crushed to a suitable size range and preheated to a desirable temperature, is introduced into process vessel **11** through conduits **10**, of which there may be several, by screw feeders **15** into retorting chamber **12**. Introduction of solid carbonaceous material can also be accomplished using a gas drive similar to that used in supplying solids to fluid bed catalytic cracking units, or it can be accomplished by using gravity feed through vertical tubes discharging somewhere in the retorting bed, as in FIG. 2. The fluidizing gaseous material, preheated to a suitable temperature and of a suitable flow rate and composition, is introduced into vessel **34** through conduits **13** into chamber **14**. The composition of the fluidizing gas can be controlled by an online chromatograph to hold its carbon dioxide content to particular values in the range of 0.5 to 20 volume percent, preferably 10 to 15 volume percent, with the bulk of the remaining gaseous material being light hydrocarbons and hydrogen, as is taught in our copending application Ser. No. 781,901, filed of even date herewith. This mixture can be obtained by mixing natural gas or another light hydrocarbon gas with the gaseous product from the retort, which contains carbon dioxide, to obtain the desired concentration of carbon dioxide in the retort fluidizing gas. In some cases, the concentration of carbon dioxide in the gaseous product from the retort will be the concentration desired in the retort fluidizing gas. In such cases, natural gas or another light hydrocarbon gas is used only to start the unit, and for occasional makeup necessitated by upsets or leaks. The noncombustion-supporting fluidizing gaseous material of the process of the invention is advantageous because there is no need for combustion within the retorting chamber for heat generation. Such combustion tends to consume volatile material product in preference to carbon on the spent carbonaceous material. For example, oil shale was retorted in the laboratory in a 4-inch-diameter batch fluidized bed at temperature of 915° F. A fluidizing gas was used containing about 5-percent oxygen, as might be used in a gas-combustion retort, and the oil yield was about 85 to 88 weight percent of Fischer Assay oil as is frequently obtained in a gas-combustion retort. When heat of retorting was supplied by other means and a mixture of 10-volume-percent carbon dioxide and 90-volume-percent natural gas was used as the fluidizing gaseous material, the oil yield was about 107 weight percent Fischer Assay oil. Similarly, natural gas yielded about 102 weight percent Fischer Assay oil. In these batch tests, a total residence time in the retort bed of about 7 to 9 minutes was necessary for the unpreheated oil shale to completely evolve the volatile and gaseous material products to give the stated yields. When this 4-inch-diameter fluidized bed was operated as a continuous feed unit, the effect of average residence time in the retort bed on oil yields could be studied at different temperatures. The average residence time in the continuous unit is a composite of a wide range of actual particle residence times, whereas all the oil shale was in the retort bed for the stated residence time in the batch tests. FIG. 4 shows

the effect of average residence time on oil yield for unpreheated oil shale at various temperatures for the continuous feed unit, using natural gas as the fluidizing gas. There are no numbers on the yield axis in FIG. 4 because the data obtained for the runs depicted in FIG. 4 were weight percent Fischer Assay oil yield loss to the spent shale, as shown in table I, rather than actual oil recovered. In other words, the success of a particular run was gauged by how much oil did not get produced. Such results give relative comparisons among various combinations of temperature and residence time. Once this screening procedure narrowed the ranges of interest in temperature and residence time, runs were made in which the oil was actually recovered. In this series of runs the variable of fluidizing gas composition was added. The results of these runs may be seen in table II, and FIG. 5.

TABLE I

Retort Temp. (° F.)	Average Resid. Time (min.)	Approx. Oil Yield Loss in Spent Shale (Wt. % F.A.)
920	11.88	10.74
920	15.44	5.12
940	9.12	15.77
940	11.88	7.49
940	15.44	3.65
960	9.12	6.90
960	15.44	1.08
990	9.12	2.07
990	15.44	0.59

TABLE II

Run	Fluidizing gas Compositions	Retort temp. (° F.)	Average residence time (min.)	Oil yield (wt. percent F. A.)
X	Natural gas	940	15.44	96.09
Y	do	940	9.12	88.67
G-1	do	960	15.44	99.28
H-1	do	960	9.12	91.42
B-1	90 vol. percent N.G. plus 10 vol. percent CO_2.	940	15.44	97.87
F-1	do	940	9.12	90.52
D-1	do	960	15.44	106.32
E-1	do	960	9.12	100.38

The fluidizing gaseous material passes from chamber **14** through gas distributor **16** into retorting chamber **12**, thereby fluidizing the carbonaceous material in retorting chamber **12**. The gas distributor can be any of several types now in use on commercial fluidized beds or it can be made up of sections of sintered metal such as Inconel thereby giving an excellent distribution of gaseous material entering retorting chamber **12**. Volatile and gaseous product material containing dust and water are withdrawn from retorting chamber **12** through conduits **26**.

The retorting fluidized carbonaceous material passes upward through retorting chamber **12** until it reaches the tops of standpipes **17**. The height of standpipes **17** is determined by the residence time required and the raw carbonaceous material feed rate through feeders **15**. The spent carbonaceous material falls over standpipes **17** and passes down into catch basin **18**. As an alternative to standpipes **17**, a shroud could be placed around and openly connected with retort shell **34**, into which the spent solid carbonaceous material would spill from retorting chamber **12**. This spent solid carbonaceous material would then be conveyed via appropriate piping to catch basin **18**. As another alternative to standpipes **17**, the above setup can be used with a concentric cylinder replacing the shroud mentioned above. Oxygen-containing gas is introduced through conduits **19** into catch basin **18** at a sufficient rate that spent carbonaceous material is fluidized, passed upward into and through tubes **20**, and the carbon on the fluidized spent carbonaceous material is burned off at a temperature level between 1,000° and 1,500° F., preferably 1,200° and 1,400° F., to supply heat to retorting chamber **12**. If the heat derived from burning the carbon off the spent carbonaceous material is insufficient to supply the heat of retorting, then enough other fuel, such as fuel oil, natural gas, coke, etc., to supply the retorting heat requirements can be added to the oxygen-containing gas in conduit **19**. The burned-off spent carbonaceous material overflows from tubes **20** into chamber **21** and passes down through the chamber **21**, helping to maintain retorting chamber **12** temperature at the desired value, and exits chamber **21** and vessel **11** through conduits **22**. The combustion products given off by burning the carbon on the spent carbonaceous material pass through cyclones **23** or other devices which remove most of the entrained dust and then pass out through manifold **24** and conduit **25**.

Referring to FIG. **2**, solid carbonaceous material **40**, crushed to a suitable size range and preheated to a desirable temperature, is introduced into fluid bed retort **46** through conduits **42**, of which there may be several, at some point below the bed level **48**. The feed rate of the solid carbonaceous material **40** into the fluid bed retort **46** can be controlled by cone valves **44** or some other suitable device. Introduction of solid carbonaceous material can also be accomplished using a gas drive similar to that used in supplying solids to fluid bed catalytic cracking units, or it can be accomplished by using screw feeders, as in FIG. **1**.

The fluidizing gaseous material **50**, preheated to a suitable temperature and of a suitable flow rate and composition, is introduced into chamber **54** through conduits **52**. The composition of the fluidizing gas can be controlled by an online chromatograph to hold its carbon dioxide content to particular values in the range of 0.5 to 20 volume percent, preferably 10 to 15 volume percent, with the bulk of the remaining gaseous material being light hydrocarbons and hydrogen similar to that done with the apparatus of FIG. **1**. This mixture can be obtained by mixing natural gas or another light hydrocarbon gas with the gaseous product from the retort, which contains carbon dioxide, to obtain the desired concentration of carbon dioxide in the retort fluidizing gas. In some cases, the concentration of carbon dioxide in the gaseous product from the retort may be the concentration desired in the retort fluidizing gas. In such cases, natural gas or another light hydrocarbon gas is used only to start the unit, and for occasional makeup necessitated by upsets or leaks.

The fluidizing gaseous material passes from chamber **54** through gas distributor **56** into the retorting bed, thereby fluidizing the carbonaceous material in the retorting bed. The gas distributor can be any of several types now in use on commercial fluidized beds or it can be made up of sections of sintered metal such as Inconel thereby giving an excellent distribution of gaseous material entering the retorting bed. Volatile and gaseous material containing dust and water are withdrawn from retorting chamber **46** through conduits **60** as streams **58**.

The retorting fluidized carbonaceous material is entrained in the various solids flow patterns in the retorting bed until it reaches the inlets **61** to spent carbonaceous material downcomers **62**. These inlets **61** can be located at the level of the gas distributor **56**, as shown in FIG. **2**, or anywhere within the retorting bed up the bed level **48**. The spent carbonaceous material passes through downcomers **62** into fluid bed combustion chamber **66**. The feed rate of the spent solid carbonaceous material into the fluid bed combustion chamber **66** can be controlled by cone valves **64** or some other suitable device. Oxygen-containing gas **70** is introduced through conduits **72** into chamber **74**, and passes through gas distributor **76** at a sufficient rate that the spent carbonaceous material in

the combustion chamber is fluidized, and most if not all of the combustible carbon left on the spent carbonaceous material is combusted at a temperature level between 1,000° and 1,500° F., preferably 1,200° and 1,400° F., to provide the heat necessary to carry out the retorting in retorting chamber **46**. The heat of combustion so generated is transferred to a plurality of horizontal tubes **96**, containing a flowing liquid or gaseous heat transfer medium, preferably a liquid such as molten sodium. This hot heat transfer medium is circulated by pump **92** through pipe **91** to a plurality of horizontal tubes **94** in retorting chamber **46**, where enough heat is transferred from it to the bed of solid carbonaceous material to effect complete retorting at the desired temperature level. The heat transfer medium, now cooled, exits retorting chamber **46** and is circulated to cleanup system **98** in which contaminants **97** are removed, and then makeup heat transfer medium **99** is supplied as necessary and the resulting stream passes through pump **92** and line **90** as it is circulated back to the combustion bed to be reheated. The burning spent carbonaceous material is entrained in the various solids flow patterns in the fluid bed combustion chamber until it reaches the inlets **77** of the burned-off spent carbonaceous material downcomers **82**, from which it exits as stream **84** and goes to further cooling and disposal. These inlets **77** can be located at the level of the gas distributor **76**, as shown in FIG. **2**, or anywhere within the retorting bed up to the bed level **68**. The combustion products given off by burning the carbon on the spent carbonaceous material pass out of combustion chamber **66** through conduits **80** as streams **78** and are circulated to conventional heat recovery devices. If the heat derived from burning the carbon off the spent carbonaceous material is insufficient to supply the heat of retorting, then enough other fuel **86**, such as fuel oil, natural gas, coke, etc., to supply the retorting heat requirements can be added to combustion chamber **66** through conduits **88**.

In FIG. **2** retorting chamber **46** and combustion chamber **66** are shown as being stacked vertically, as preferred, but they can also be built side by side. In addition, retorting chamber **46** and combustion chamber **66** are shown as being the same size, although they can be of different heights and diameters. The heat transfer loop shown in FIG. **2** is the preferred method of transferring heat from combustion chamber **66** to retorting chamber **46**. However, if desired, this heat transfer can be accomplished by a different method; for example, steam can be generated in tubes **96**, which would then be used to generate electricity, which in turn would be used to heat the retorting bed by operating in-bed electrical heaters in place of tubes **94**.

FIG. **3** is an example of what a process flow chart built around the retort and combustion chamber of either FIG. **1** or **2** might look like. The temperature levels cited constitute one example of the process but the process is not limited to this example and can be used within the levels discussed above.

Referring to FIG. **3**, crushed solid carbonaceous material, oil shale in this example, of a suitable particle size range **100** is preheated to about 600° F. in the raw shale preheater **104** by the hot gaseous closed-loop heat exchange medium **102**. The preheated raw shale **108** is introduced into the fluid bed retort **110**, where it is fluidized by preheated fluidizing gas **114** and retorted, and the carbon is burned off the spent shale in the separated combustion zone **106** by oxygen-containing gas stream **150**. A bypass line **152** to carry flue gas from the flue gas exhaust line **156** to the air inlet through control valve **154** is provided so that the temperature in the combustion chamber can be controlled as desired by varying the partial pressure of the oxygen in the combustion supporting air plus flue gas stream into the combustion chamber.

The product stream **116**, consisting of gas, oil vapors, dust, and water exits the fluid bed retort **110** and is introduced into the conventional product recovery train **118**. The first unit or units in the conventional product recovery train would be the dust removal equipment. This dust removal equipment is operated at the retorting temperature so that the dust can be removed from the product stream while the oil is still in the vapor state, and consists of mechanical separators such as cyclones, or electrostatic precipitators, or a combination of the two. The dust so removed **120** is transferred to the combustion chamber **106** or to the burned-off spent shale cooler **148**. The remainder of the product stream, consisting of oil, gas, and water, is transferred to a system of recovery equipment such as heat exchangers, fractionation towers, etc., resulting in the effluent streams of oil **128**, water **132**, and gas **134**. The gas stream **134** is sent through the gas quality control and flow measurement section **138**, which is an online chromatograph and a standard flow measurement device, and which regulates the flow rates of the make gas withdrawal stream **140** and the light hydrocarbon gas makeup bleed stream **142**, as necessary, and therefore also regulates the flow rate and composition of the fluidizing gas stream **114**. The fluidizing gas stream **114** is heated to retorting temperature in heat exchanger **130** by indirect heat exchange with the hot gaseous combustion products **122** from the combustion zone **106**, and is then introduced into the fluid bed retort **110**. The hot burned-off spent shale **112** exits combustion chamber **106** and is fed to the burned-off spent shale cooler **148**, from which the cooled burned-off spent shale **146** exits and is sent to disposal. The burned-off spent shale is cooled by the closed loop direct contact gaseous heat exchange medium **102**. This can be any gaseous medium as long as oxygen content is minimized or preferably eliminated. The heat transferred to the closed-loop gas stream **102** in the burned-off spent shale cooler **148** is then transferred to the raw shale in the raw shale preheater **104**. The cool closed-loop gas stream **160** exiting from the raw shale preheater **104** is passed through a gas quality control and flow measurement section **124**, which could consist of an online chromatograph, H_2S removal equipment, and a standard flow measurement device, and which regulates the flow rates of the make gas withdrawal stream **126** and the makeup gas bleed stream **158**, as necessary, and therefore also regulates the flow rates and composition of the closed-loop gaseous heat exchange medium **102** to be fed to the burned-off spent shale cooler **148**.

As a more specific illustration of the process described above, the following examples are presented.

EXAMPLE I

In the modification shown in FIG. **1**, oil shale, crushed to a suitable size range, say −12+60 mesh, is introduced into process vessel **11** at a suitable rate to give an average particle residence time in the bed of about 10 minutes and is fluidized with a gaseous material. The composition of the fluidizing gaseous material is controlled to an online chromatograph and is held constant at 10-volume-percent carbon dioxide and 90-volume-percent light hydrocarbons and hydrogen. The fluidizing gaseous material is introduced into process vessel **11** at a rate of 3,370 s.c.f./ton of raw shale. The fluidized oil shale is retorted in retorting chamber **12** at a temperature of 925° F., yielding 107 weight percent of the Fischer Assay oil. Air is introduced into vessel **11** at a rate sufficient to fluidize the spent shale in catch basin **18**. The spent shale is burned at a temperature of 1,300° F. in tubes **20** to supply the heat required to maintain the 925° F. temperature in retorting chamber **12**.

EXAMPLE II

In the modification shown in FIG. **2**, crushed oil shale with relatively wide particle size range (e.g., one-eighth inch minus) is introduced into retort **46** at a suitable rate to give an average particle residence time in the bed of about 10 minutes. Preheated fluidizing gaseous material is introduced into the bottom of retort **46** at a rate of 3,370 s.c.f./ton of raw shale, and its composition is controlled by an online chromatograph and is held constant at 10-volume-percent carbon dioxide and 90-volume-percent light hydrocarbons and hydrogen. Molten sodium is circulated through pipe **90** at a suitable rate and transfers from burner **66** to retorting bed **46**

the heat required to bring the inlet oil shale to retorting temperature and retorting heat. The fluidized oil shale is retorted in retorting bed **46** at a temperature of 925° F., yielding 107 weight percent of the Fischer Assay oil. Air is introduced into burner **66** at a rate sufficient to fluidize the spent shale transferred from retort **46**. The spent shale is burned at a maximum temperature of 1,400° to 1,500° F. in burner **66** to supply the heat required to maintain the 925° F. temperature in retorting bed **46**.

It is claimed:

1. A process for the recovery of volatile material from solid carbonaceous material, which comprises the steps of:

introducing the solid carbonaceous material into a retorting zone;

fluidizing the solid carbonaceous material within the retorting zone;

heating the fluidized solid carbonaceous material in the retorting zone thereby retorting volatile material therefrom;

withdrawing volatile material from the retorting zone;

withdrawing and transferring spent solid carbonaceous material from the retorting zone to a burnoff zone;

fluidizing the spent solid carbonaceous material in the burnoff zone by introducing oxygen-containing gas into the burnoff zone and burning carbon off the fluidized spent solid carbonaceous material therein; and

withdrawing burned-off spent carbonaceous material and gaseous combustion products from the burnoff zone.

2. The process of claim **1** wherein the solid carbonaceous material is oil shale and the volatile material contains oil.

3. The process of claim **2** wherein the oil shale is fluidized within the retorting zone by a noncombustion-supporting gaseous fluidizing material taken from the group consisting of natural gas or a gas of similar composition to natural gas and natural gas containing up to 20-volume-percent carbon dioxide.

4. The process of claim **3** wherein the volatile material is treated to remove any dust, oil and water contained therein and part of the remaining volatile material is reintroduced into the retort zone as a portion of the noncombustion-supporting gaseous material.

5. The process of claim **3** wherein a portion of the noncombustion-supporting gaseous material introduced into the retorting zone is a portion of the volatile material withdrawn from the retorting zone.

6. The process of claim **1** wherein the fluidized solid carbonaceous material in the retorting zone is heated by indirect heat exchange with the fluidized spent solid carbonaceous material in the burnoff zone.

7. The process of claim **3** wherein the noncombustion-supporting gaseous material is preheated prior to introduction to the retorting zone.

8. The process of claim **7** wherein the said gaseous material is preheated by indirect heat exchange with the gaseous combustion products withdrawn from the burnoff zone.

9. The process of claim **2** wherein the burning in the burnoff zone is at a temperature of about 1,000° to about 1,500° F. to develop maximum cementing properties in the burned-off spent solid carbonaceous material to facilitate disposal.

10. The process of claim **6** wherein the fluidized solid carbonaceous material in the retorting zone is heated by means of a single heat transfer barrier separating the fluidized spent solid carbonaceous material in the burnoff zone and the fluidized solid carbonaceous material in the retorting zone.

11. The process of claim **6** wherein the fluidizing solid carbonaceous material in the retorting zone is heated by circulating a heat transfer medium in indirect heat exchange therewith and with the fluidized spent solid carbonaceous material in the burnoff zone.

12. The process of claim **11** wherein heat transfer medium is liquid sodium.

13. The process of claim **1** wherein the solid carbonaceous material is introduced adjacent the bottom of the retorting zone and the volatile material is withdrawn adjacent the top of the retorting zone to provide minimum contact between the two materials thereby reducing loss of volatile material product.

14. The process of claim **1** wherein the burned-off spent carbonaceous material is withdrawn to a cooling zone and the solid carbonaceous material is preheated by direct contact with a closed-loop gaseous heat exchange medium which is in direct contact with said spent carbonaceous material in its cooling zone.

15. The process of claim **3** wherein the noncombustion-supporting gaseous material contains 0.5 to 20-volume-percent carbon dioxide and the bulk of the remainder consists essentially of light hydrocarbons and hydrogen.

16. The process of claim **15** wherein the carbon dioxide content of the noncombustion-supporting gaseous material is 10 to 15 volume percent.

17. The process of claim **2** wherein the solid carbonaceous material in the retorting zone is maintained at a temperature level within the range of about 850° to about 1,000° F. and is retained in the retorting zone for an average residence time within the range of about 3 to about 20 minutes.

18. The process of claim **17** wherein the temperature level is within the range of about 900° to about 950° F. and the average residence time is within the range of about 5 to about 10 minutes.

19. The process of claim **3** wherein the noncombustion-supporting gaseous fluidizing material is natural gas.

20. The process of claim **15** wherein the light hydrocarbons and hydrogen are produced by the retorting of the oil shale.

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