United States Patent [19]

Squires

[11] **3,855,070**

[45] **Dec. 17, 1974**

[54] **HYDROPYROLYSIS OF HYDROCARBONACEOUS FUEL AT SHORT REACTION TIMES**

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[22] Filed: **Oct. 26, 1973**

[21] Appl. No.: **410,070**

Related U.S. Application Data

[63] Continuation of Ser. No. 167,686, July 30, 1971, abandoned, which is a continuation-in-part of Ser. No. 812,786, April 2, 1969, Pat. No. 3,597,327.

[52] **U.S. Cl.** **201/23,** 201/31, 201/37, 208/127

[51] **Int. Cl.** **C10b 49/22**

[58] **Field of Search** 201/31, 21–23, 201/30, 28, 36–38, 12–17, 10, 3, 4, 20; 208/127, 8–11; 48/197, 77

[56] **References Cited**

UNITED STATES PATENTS

2,793,173	5/1957	Fritz	201/12 X
2,537,153	1/1951	Nelson et al.	201/4
3,431,197	3/1969	Jahnig et al.	201/31 X

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[57] **ABSTRACT**

Coal or residual oil may be hydropyrolyzed at short reaction times to produce relatively high yields of methane and liquids and relatively low yield of coke. A bed of coke pellets, fluidized with a gas containing hydrogen, operates at 1100° to 1800°F and preferably at a pressure greater than 20 atmospheres. The coal or residual oil is fed to the bed and is heated practically instantaneously to the bed temperature, hydropyrolyzing to yield gaseous products and a coke product accreting upon the pellets. A fine solid is supplied to a space provided above the fluidized bed of coke pellets, the fine solid flowing at a temperature and rate to maintain the temperature of the fluidized bed substantially constant. The dimensions of the fluidized bed and space are such that the overall residence time of gaseous products of hydropyrolysis, including unreacted hydrogen, in the bed and space is less than 20 seconds. A residence time less than 5 seconds can be provided.

7 Claims, 3 Drawing Figures

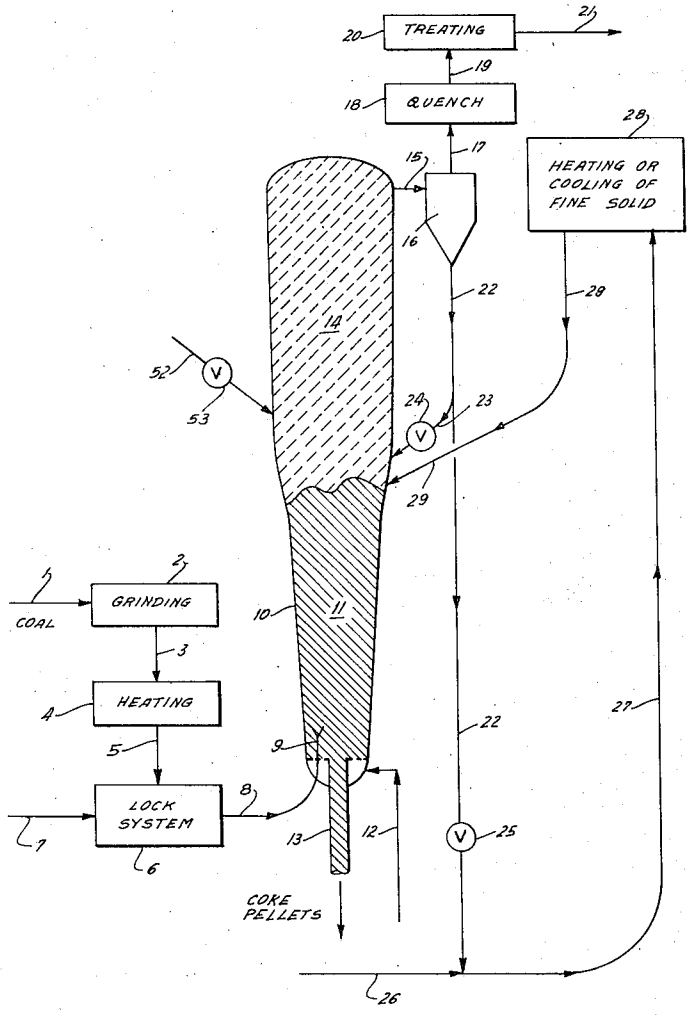
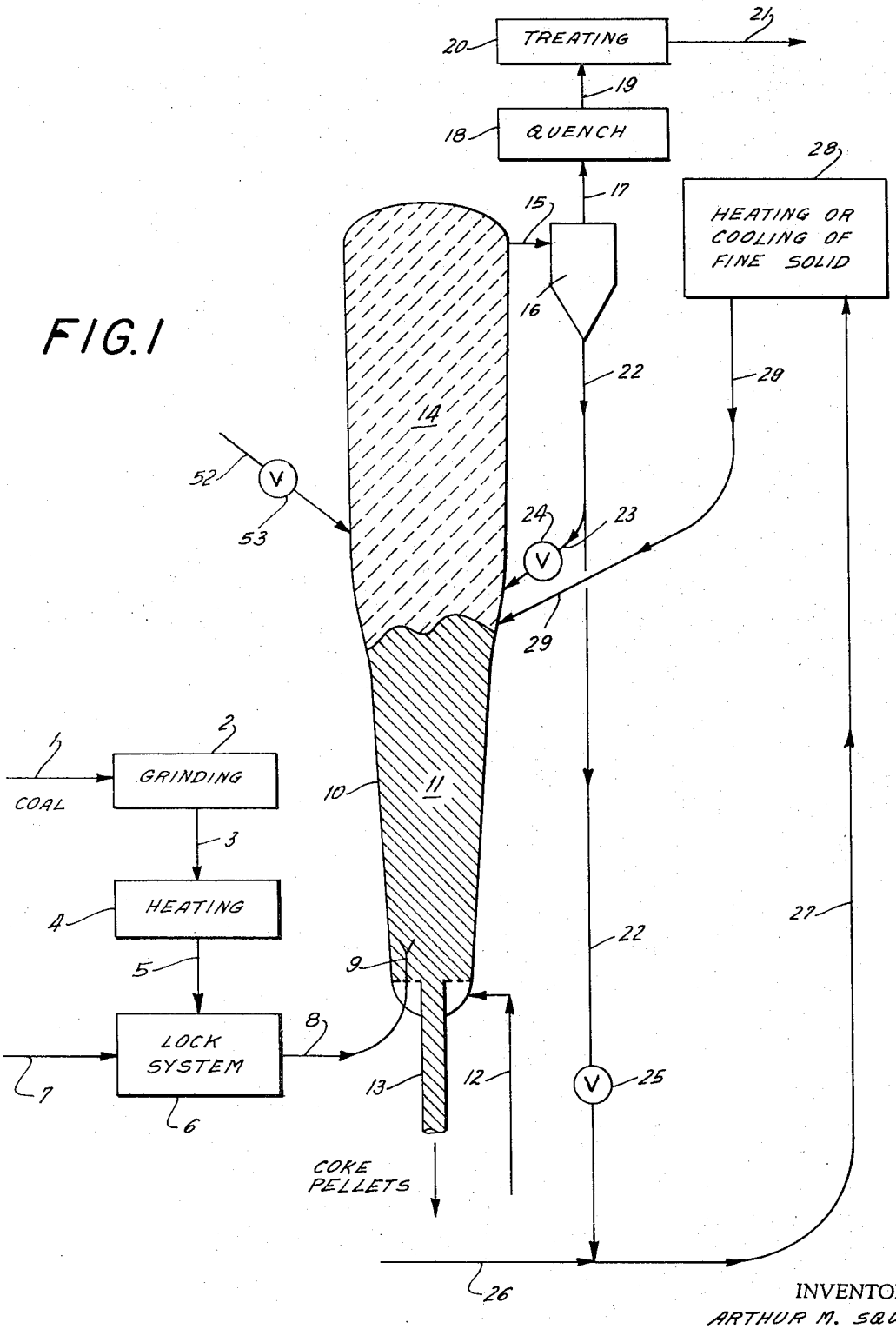
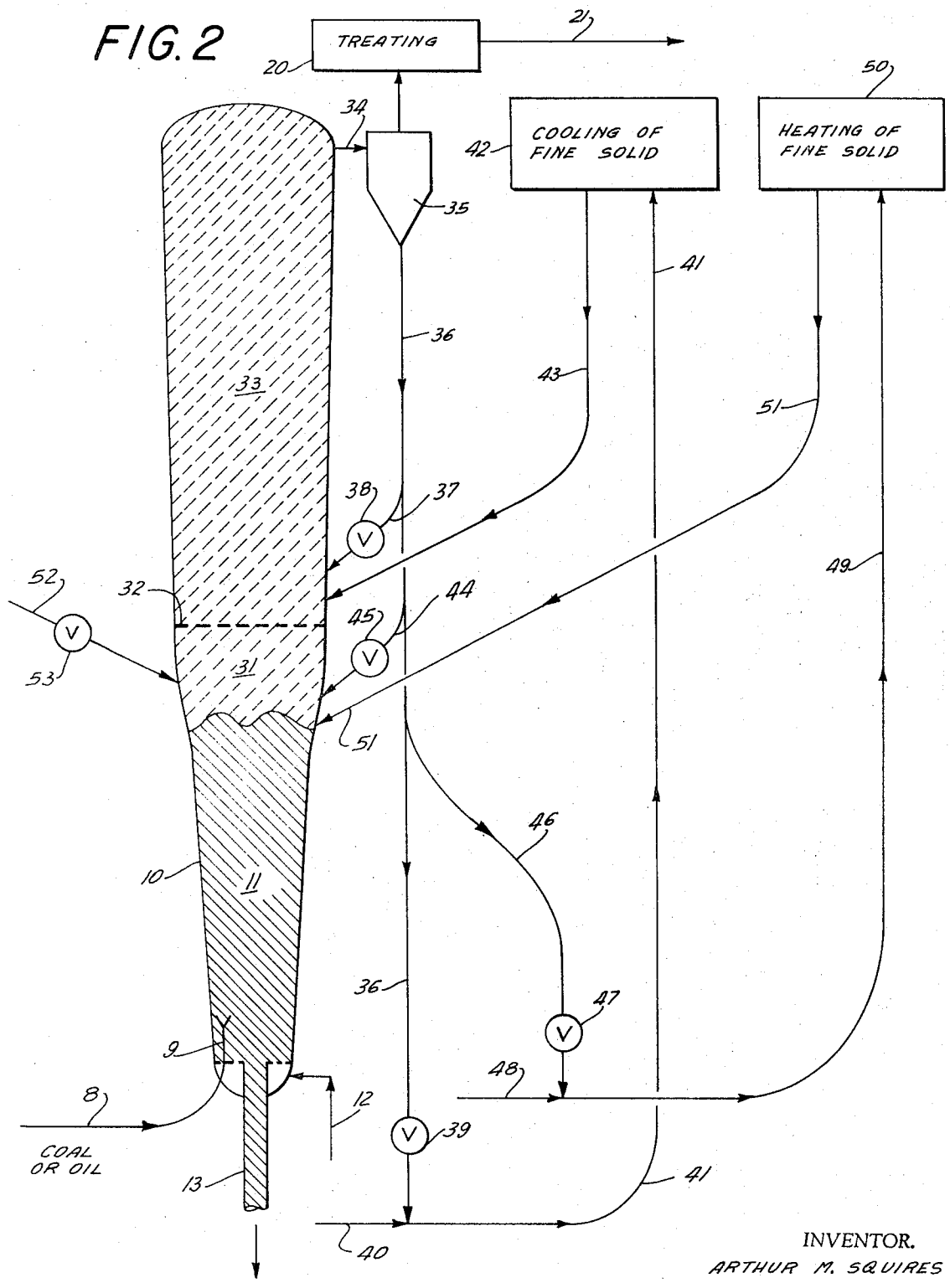


FIG. 1



INVENTOR.
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FIG. 2



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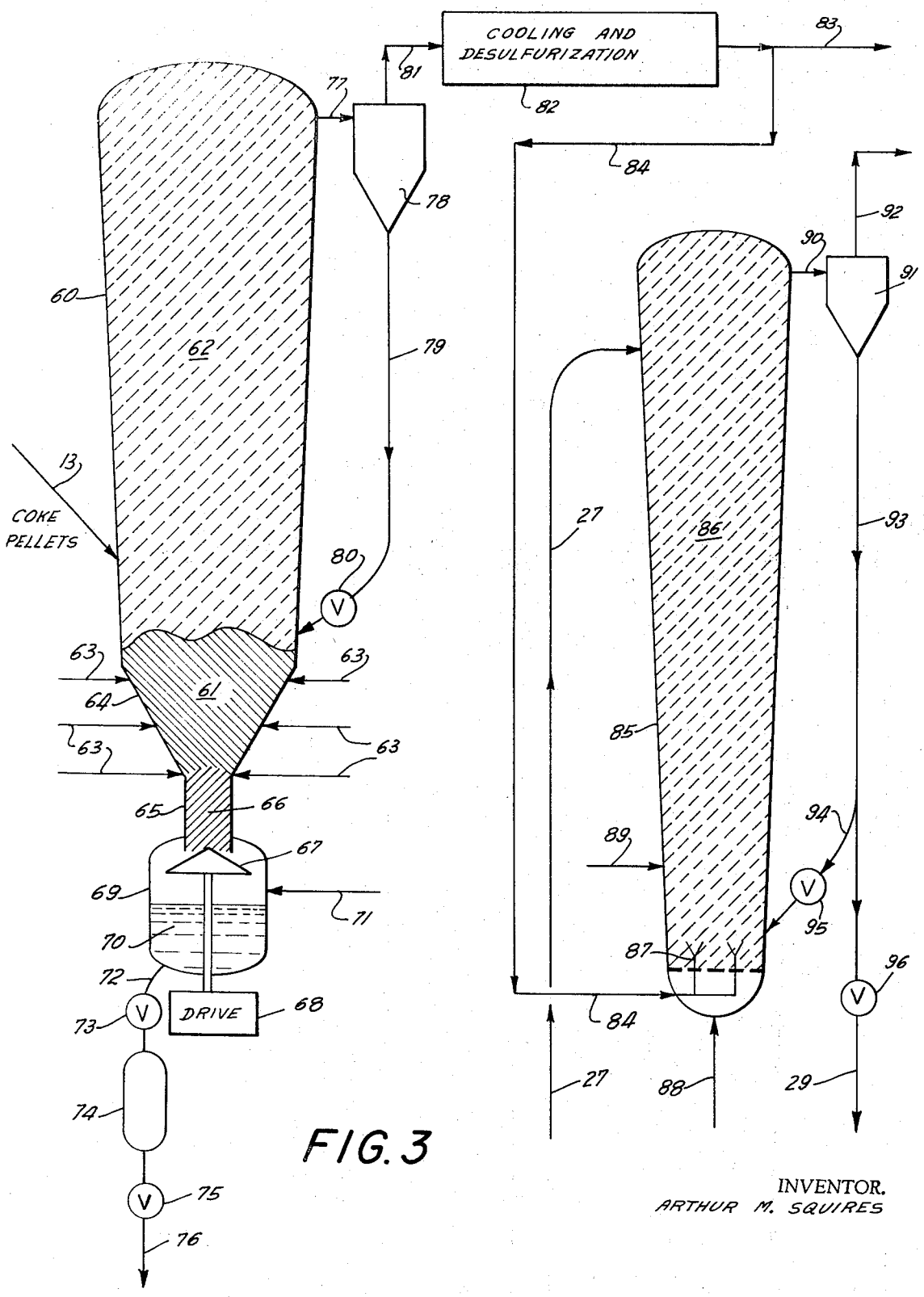


FIG. 3

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HYDROPYROLYSIS OF HYDROCARBONACEOUS FUEL AT SHORT REACTION TIMES

This is a continuation of application Ser. No. 167,686, filed July 30, 1971 and now abandoned, which application is a continuation-in-part of my copending application Ser. No. 812,786, filed Apr. 2, 1969, and to issue as U.S. Pat. No. 3,597,327, on Aug. 3, 1971.

BACKGROUND OF THE INVENTION

My U.S. Pat. No. 3,437,561 discloses a technique for hydrocarbonizing coal in an agglomerating fluidized bed, to form pellets of coke and a gas rich in methane.

U.S. Pat. No. 3,030,297 teaches the hydrogenation of coal in absence of an added oil and of catalyst at a temperature between about 600° and 1,000°C, at a pressure of about 500 to 3,000 pounds per square inch gauge, at a total time of reaction for the coal-hydrogen mixture above 300°C of less than 2 minutes, and at a time of reaction above 600°C of less than one minute. The time of reaction above 600°C is preferably between about 2 and 20 seconds. In an example, this patent teaches the heating of a mixture of coal and hydrogen in a tubular preheater to 600°C in about 1 minute. Reaction is initiated in the preheater. The mixture passes from the preheater to a reactor provided with a jacket for temperature control. As a result of formation of methane in the reactor, the temperature of the mixture rises about 150° to 200°C. Retention time in the reactor is also less than about 1 minute. Products were rapidly quenched by spraying water into the stream to reduce the temperature to around 250°C. Yield of a light aromatic liquid was 50 percent by weight of the coal fed (on a moisture- and ash-free basis), conversion of hydrogen was 55 percent, and yield of hydrocarbon gas was 6 standard cubic feet per pound of coal fed.

The technique disclosed in my U.S. Pat. No. 3,437,561 can be advantageously employed to conduct substantially the process of the above-described example from U.S. Pat. No. 3,030,297. To do this, the total reaction time prior to quench of hydrogenation products would be suitably limited, and the total heat content of hydrogen and coal fed to the agglomerating bed of U.S. Pat. No. 3,437,561 would be adjusted to match the heat added to the mixture of hydrogen and coal in the preheater of the example from U.S. Pat. No. 3,030,297. Better control of the operation is afforded using the technique of U.S. Pat. No. 3,437,561. In the example from U.S. Pat. No. 3,030,297, there is risk in practical operation that too little heat will be added in the preheater, with the effect that insufficient reaction will occur in the reactor and the desired temperature at the reactor outlet will not be attained. On the other hand, there is also risk that too much heat will be added in the preheater, and the reaction in the reactor will be so vigorous that the desired temperature will be greatly exceeded and the reactor endangered. These dangers do not arise in operation of the agglomerating bed of U.S. Pat. No. 3,437,561. Also, by the technique of 3,437,561, there is no necessity to provide tubular surface for transfer of heat to and from a mixture of coal and hydrogen; not only is such surface expensive, but also it is subject to risk of fouling by deposits of coke which would mar its performance.

However, the range of operability of the technique disclosed in my U.S. Pat. No. 3,437,561 is narrow because the agglomerating bed was to be operated adiabatically. The range of suitable variables such as hydrogen pressure, temperature, and coal feed rate was relatively narrow. I have found that operation outside of this relatively narrow range of variables is frequently desirable to attain the full benefit of the superior yields of gas and liquid which short reaction times can afford. Sometimes, in order to sustain the temperature of the agglomerating bed at the desired level, more heat must be added than can conveniently be introduced in form of sensible heat in the fluidizing gas. This is often the case when conditions are selected for maximum production of a liquid product. If a large production of methane is achieved, sometimes heat must be withdrawn from the agglomerating bed.

My aforementioned application, to become U.S. Pat. No. 3,597,327, teaches a procedure for supplying heat to or removing heat from an agglomerating fluidized-bed zone of the type disclosed in my U.S. Pat. No. 3,437,561. A superposed, contiguous fluidized-bed zone is provided comprising a solid smaller in particle size than the coke pellets of the agglomerating-bed zone. The fluidizing-gas velocity in the superposed fluidized-bed zone is appreciably less than the velocity in the agglomerating zone. Heat can be supplied to or removed from the agglomerating zone by allowing heat to flow by conduction between this zone and the superposed fluidized-bed zone.

If a short reaction time is desired, the procedure of U.S. Pat. No. 3,597,327 has the drawback that the gas residence time in the superposed fluidized-bed zone of fine solid is necessarily rather long, because the fluidizing-gas velocity appropriate for the "stationary" fluidization of a fine solid is relatively low.

SUMMARY OF THE INVENTION

The invention relates to an improved method for hydropyrolyzing coal or residual oil under conditions which are agglomerating with respect to the coke product and which give maximum yield of gas or liquid.

An object of the invention is to provide an improved process for converting caking coals or residual oils into gaseous and liquid products and coke.

Another object is to provide processes to produce liquid fuels from coal or lighter liquids from heavy residual oils.

Another object is to provide processes yielding a methanerich gas and coke starting from coal, including bituminous and subbituminous coals and lignites, many of which are not ordinarily considered to be caking coals, or from fluid hydrocarbonaceous fuel such as residual oil, bitumen, pitch, tar, kerogen, and the like.

Another object is to provide processes to produce a synthetic fuel gas of pipeline grade according to U.S. standards for such a gas.

More specifically, the invention relates to an improved method for supplying heat to (or removing heat from) a fluidized-bed zone in which coal or oil undergoes pyrolysis in presence of hydrogen, under conditions which are agglomerating with respect to the coke product, and at short residence times for the gaseous products of the hydropyrolysis.

According to the invention, there is provided a process for hydropyrolyzing a solid or liquid hydrocarbonaceous fuel at short reaction times. A fluidized bed at

a temperature between about 1100° and 1800°F is provided, the bed comprising coke pellets larger than about one sixty-fourth inch in size and displaying a range of diameters. The bed is fluidized with a gas containing hydrogen, preferably at a pressure greater than 20 atmospheres. Solid or liquid hydrocarbonaceous fuel is charged to the fluidized bed, and the solid product of the hydropyrolysis occurring within the bed accretes upon the coke pellets. A space is provided above the fluidized bed to receive gaseous products of the hydropyrolysis including unreacted hydrogen, and the dimensions of the fluidized bed and the superposed space is such that the residence time of the gaseous products is less than about 20 seconds. A fine solid, preferably between about 50 and 100 microns in size and displaying a range of diameters, is supplied to the space, preferably near the upper level of the fluidized bed, at a temperature and rate of flow to maintain the temperature of the fluidized bed substantially constant. Gaseous products and fine solid are removed from the top of the superposed space, and coke pellets are withdrawn from the fluidized bed.

I have been surprised to discover that there is an effective transfer of heat between the fine solid introduced into the superposed space and the fluidized bed of coke pellets, even though the gas velocity in the space be too high for the establishment therein of a "stationary" fluidized bed. I do not fully understand the relative importance of several mechanisms of heat transfer which appear to occur. Some fine solid falls onto the upper surface of the bed of coke pellets. This solid exchanges heat with the coke, and then is reentrained by gas and carried back into the superposed space. Coke pellets are ejected from the agglomerating fluidized bed into the superposed space, and the pellets exchange heat with gas and fine solid in this space while the pellets fall back into the bed. Downward currents of gas occur in the space, and such currents exchange heat with the upper surface of the bed of coke pellets. By whatever mechanisms, the exchange of heat is effective in preventing the development of a large temperature difference between the bed of coke pellets and the superposed space. Addition of a fine solid hotter than the bed of coke pellets serves to provide heat to the bed, and addition of a cooler solid serves to withdraw heat. By maintaining a relatively high gas velocity in the superposed space, the residence time of gaseous products including unreacted hydrogen can be kept low. The velocity of fluidizing gas in the agglomerating bed is advantageously between about 5 and 25 feet per second, and the gas velocity in the superposed space is advantageously between about 4 and 15 feet per second.

The term "solid or liquid hydrocarbonaceous fuel" as here used embraces, as a first category, solid fuels which when heated either exhibit a softening temperature or begin to decompose with deformation and, as a second category, fuels normally liquid at room temperature and solid fuels which when heated exhibit a melting temperature and can thereafter be pumped.

Suitable fuels of the first category for practice of the invention are to be found among bituminous and subbituminous coals and lignites, including many coals ordinarily considered non-caking when viewed in light of conventional atmospheric-pressure coal-carbonization procedures. To use some of the non-caking coals or lignites successfully, one must operate the process of the invention at a high pressure and provide for presence of a high partial pressure of hydrogen. It is to be understood that bituminous and subbituminous coals and lignites may be altered by a partial carbonization or a partial oxidation or a reduction in the intrinsic moisture (as, for example, in the drying of lignites by the Fleissner Process). Suitable fuels of the first category are also to be found among such altered coals and lignites, provided the altered material does not contain more than 91 weight percent carbon on a moisture-and-ash-free basis and display a hydrogen-to-carbon ratio below 0.6.

Coal or other solid fuel for treatment by the process of the invention is advantageously ground to a fineness substantially smaller than 100-mesh (U.S. Standard) before it is charged to the agglomerating fluidized bed.

Fuels of the second category include petroleum fractions from the gas-oil range and heavier, but the greater practical interest lies in application of the instant invention to treatment of fuels of the second category which are generally characterized by high specific gravity, low hydrogen content, a significant aromatic content, and a Conradson carbon greater than about 1 percent, usually greater than 2 percent. Examples of the latter fuels are residual fuel oils, cracked residua, asphalts, asphalt fractions prepared from residua by solvent extraction, heavy coker tars, coal tars, pitches, bitumens, carbonaceous matter from tar sands, Gilsonite, kerogens, carbonaceous matter from oil shales, and the like. An artificial heavy oil may be prepared by hydrogenating coal at high pressure and at a temperature in the vicinity of 800° to 900°F, either catalytically or non-catalytically, and filtering the product from coal ash; such an artificial oil is also suitable as a fuel of the second category.

The importance of a short reaction time for maximizing yields of methane and useful liquid products is readily understood. If the reaction time is too long, particularly at higher temperatures, hydrogenation and crackng of the liquid products diminish their quantity and increase the yield of coke and to some degree of methane. At lower temperatures, the light molecules produced by the initial disruption of the feed tend to be chemically active toward reactions which polymerize these species to form a heavy, non-distillable liquid tar having little if any greater value than the feed. This is particularly the case for a coal feed. The molecular weight of individual chemical species in raw coal typically averages in the neighborhood of 3,000 to 5,000; the molecular weight of the largest species in the coal may be no more than 10 times greater than the average. Deelder (Ph.D. thesis, Tech. Hogeschool, Eindhoven, Netherlands, 1966, NASA Accession No. N66-26774) has shown that the intitial step in the rapid pyrolysis of coal is a depolymerization leading to formation of free radicals of relatively low molecular weight. Subsequently, heavy tar of an oligomerous character forms by virtue of the polymerization of the monomeric units, the heavy tar often containing species of molecular weight greatly exceeding that of any species present in the initial coal. Generalized characteristics of the coke residue (index of aromaticity, mean number of condensed rings, ratio of oxygen to carbon) resemble those of separated hydrocarbons, suggesting that much of the coke is a secondary product of polymerization reactions. Liquid yield from a pyrolysis of coal can be maxi-

mized if the free radicals initially formed can be directed into reaction paths leading to relatively stable light species and away from paths leading to heavy tar species and coke. In general, the former paths are favored by higher temperature and higher partial pressure of hydrogen. However, the higher the temperature the greater the risk that cracking reactions will increase the yield of coke at expense of yield of liquid, and so it is important that the reaction time be short if liquid is desired. On the other hand, if a lower reaction temperature should be preferred, for example because of a preference for an aliphatic liquid product versus the aromatic product provided at higher temperatures, it is important that reaction time be short to prevent polymerization reactions from occurring which would alter the liquid product to a heavy, non-distillable tar of relatively low value.

The instant invention may be practiced over a wide range of temperature and pressure and over a range of reaction time preferably smaller than 20 seconds. in general, higher temperature favors production of methane and a light aromatic liquid. Lower temperature favors production of a paraffinic liquid. Higher pressure favors production of lighter liquids. Shorter times tend to give greater relative yield of liquid, and longer times tend to give relatively more methane and more coke.

In the operation of the instant invention at higher pressures, the volume of gaseous products of hydropyrolysis may be relatively small. In such a case, the quantity of fine solid introduced into the space above the agglomerating fluidized bed of coke pellets may amount to several pounds of fine solid per cubic foot of the gaseous products. In this circumstance, the fine solid may form what I prefer to call a "fast fluidized bed" in the aforementioned space. This is in distinction from the "stationary" fluidized bed of conventional fluidization art. I will now explain this distinction.

In a stationary fluidized bed, the fluidized solid remains in place, the bed displays a distinct upper surface, and the bed is characterized by a relatively continuous solid "phase" and a relatively discontinuous gas "phase." The solid mainly occupies the so-called "dense phase", and the gas passes through the bed primarily in form of "bubbles." For a fine solid, having a mean particle size between about 50 and 100 microns, the fluidization velocity appropriate for stationary fluidization is generally below about 2 feet per second.

If the fluidization velocity to a stationary fluidized bed is gradually increased, the density of the fluidized bed decreases, but the rate of decrease in density with increase in velocity is not marked. Ultimately, however, a critical velocity is abruptly reached at which the density of the bed drops sharply; the bed appears suddenly to "thin out." Unless the space containing the bed is extremely tall, the gas will convey most of the bed overhead and away from the space. This critical velocity may be termed the "dilute-phase transition velocity for zero transport."

If now the space be supplied at the bottom with gas at a velocity somewhat greater than this transition velocity, and if particulate solid be supplied to the bottom of the vessel at a definite rate, the solid will in general be conveyed upward through the vessel and out at the top in dilute-phase transport. However, if the rate of supply of particulate solid be gradually increased, at a critical rate of supply the inventory of solid in the space will sharply increase. Dense-phase regions appear, the solid in these regions tending to stream downward at a high velocity.

If the gas velocity is further increased, a critical velocity is again reached at which the inventory of solid drops, and the solid supplied to the space is again conveyed upward in dilute-phase transport. This critical velocity may be termed the "dilute-phase transition velocity for transport" at the rate of supply of solid to the space.

For a given rate of supply of solid to the bottom of a space, the "fast-fluidized state" is a convenient term to denote the condition in the space when the prevailing gas velocity is greater than the dilute-phase transition velocity for zero transport and less than the dilute-phase transition velocity for transport at the given rate of supply.

The "fast fluidized bed" is in commercial use for the calcining of aluminum hydroxide to produce cell-grade alumina (see L. Reh, "Fluidized Bed Processing", *Chem. Eng. Progr.*, vol. 68, p. 58, February 1971; see also U.S. Pat. No. 3,565,408). In this application, the supply of solid to the bottom of the reaction space is established by separating solid from gas leaving the top of the space and returning the separated solid to the bottom. An inventory of 5 to 10 pounds of solid per cubic foot of reaction space can be achieved for alumina of 50 to 100 microns fluidized at about 10 feet per second.

No scientific study of the fast fluidized bed is yet available, but some facts already appear clear. In contrast to the stationary fluidized bed, the fast fluidized bed exhibits no upper surface but substantially fills the space available. There is a marked gradient in solid density between the bottom and top of the space, the density being greater at the bottom. The aforementioned inventory of 5 to 10 pounds per cubic foot is an average. The solid phase in the fast fluidized bed appears on the whole to be the discontinuous phase, and the gas phase appears to be on the whole continuous. The solid phase appears generally to take the form of falling streamers and ribbons, while the gas appears to flow upward inbetween. The gas conveys solid upward, and much "refluxing" of the solid occurs in the fast fluidized bed.

Heat interchange between the space receiving gaseous products of hydropyrolysis and the agglomerating fluidized bed of coke pellets is enhanced if the instant invention be operated to provide for existence of a fast fluidized bed in the aforementioned space. As mentioned earlier, the quantity of fine solid introduced into this space may be sufficient to establish the fast-fluidized state therein. If not, a recirculation of solid separated from gas leaving this space may advantageously be provided, to increase the rate of supply of solid to the bottom of the space.

If the temperatures of the bed of coke pellets and the superposed space differ too greatly, they may be brought closer together by providing means to circulate coke pellets from the bed into the space. For example, a vertical pipe or riser could be provided extending from near the top of the bed of coke pellets well into the space, transport gas being supplied to the bottom of the pipe to convey coke pellets upward therein.

Seed particles should be added to the bed of coke pellets to provide new particles on which coke may accrete.

Successful operation of the process of the invention depends upon commencing the operation with a suitable "starter" bed of solid, which should comproise a "starter solid" displaying a range of particle sizes, preferably at least five-fold, and with a smallest particle larger than about one sixty-fourth inch. The starter bed need not be carbonaceous, a solid suitable for use at high temperature and having a density between about 80 and 150 pounds per cubic foot being generally satisfactory.

Quenching of the gaseous products of hydropyrolysis may be practiced by any of several known techniques, such as injecting water or scrubbing with a tar maintained at an appropriate temperature.

An advantageous procedure for quenching the products is to establish a fast fluidized bed of the same fine solid above the superposed space, this additional bed operating at a suitable temperature, for example about 600° to 900°F, and receiving the products. A restriction in area for gas flow would be provided between the superposed space and the additional bed to hinder backflow of gas or solid. This arrangement allows for a particularly short reaction time, for example less than 5 seconds.

The coke product of the invention may advantageously be gasified by reaction with oxygen and steam, air and steam, air and combustion products or flue gas, air and carbon dioxide, or other such gasification media. An advantageous gasification procedure would combine a stationary fluidized bed of coke pellets and a superposed fast fluidized bed, operating at substantially the same velocity, to consume coke fines produced as the coke pellets waste away and disintegrate. By operating at a temperature between about 1900° and 2100°F, one may advantageously exploit the discovery of Godel (see my article in *Science*, vol. 169, p. 821, Aug. 28, 1970) that ash matter from substantially all coals becomes sticky in this temperature range. As ash matter is released from the wasting away of the coke pellets, ash sticks to ash and forms loose, friable agglomerates. As the agglomerates grow, they reach a size too large to be buoyed in the fluidized bed of coke pellets, and they sink to the bottom of this bed. This bottom is advantageously provided in frustoconical form exhibiting an included angle of 60°, with the smaller area at the bottom, this area leading into a vertical pipe for conducting ash agglomerates away from the fluidized bed. A rotating grate may advantageously be provided at the bottom of the pipe to discharge ash agglomerates therefrom.

If operation of the invention calls for providing fine solid at a temperature greater than the temperature of the agglomerating fluidized bed of coke pellets, the fine solid may advantageously be heated in a fast fluidized bed by combustion of a fuel gas, sometimes advantageously fuel gas produced by the aforementioned gasification of coke product.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention including various novel features will be more fully understood by reference to the accompanying drawings and the following description of the operation of the alternatives illustrated therein:

FIG. 1 is schematic diagram of an embodiment of the invention for treating coal.

FIG. 2 is a schematic diagram of an alternative embodiment generally capable of affording an especially short time of reaction.

FIG. 3 is a schematic diagram illustrating how coke pellets resulting from the process of the invention may be gasified to produce a fuel gas or a synthesis gas. FIG. 3 also illustrates how this fuel gas, or another fuel gas, may advantageously be used to heat a fine soid which serves to carry heat to the hydropyrolysis step in FIG. 1 or FIG. 2.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Reference is now made to the schematic diagram of FIG. 1. Grinding means 2 grinds bituminous coal from line 1, preferably to a fineness such that substantially all of the coal will pass through a 100-mesh screen (U.S. Standard) and such that about 70 percent will pass through a 200-mesh screen. Line 3 conveys the ground coal to drying-and-heating means 4. Line 5 carries dried and heated coal from means 4 to lock system 6, which is supplied with a gas rich in hydrogen from line 7. Lock system 6 preferably has the form disclosed in my co-pending application, filed simultaneously herewith, entitled "Method and Apparatus for Transferring a Comminuted Solid from a Low Pressure into a Space Occupied by Gas at High Pressure." Coal passes via a multiplicity of lines 8 and nozzles 9 into vessel 10. For simplicity of the drawing, only one line 8 and one nozzle 9 are shown. Vessel 10 houses agglomerating fluidized bed 11. Bed 11 comprises coke pellets larger than about one sixty-fourth inch in diameter and preferably displaying at least a five-fold range in size. Bed 11 is, in general, preferably at a pressure greater than about 20 atmospheres and at a temperature between about 1100° and 1800°F. Fluidizing gas rich in hydrogen is supplied to bed 11 via line 12. Coal entering bed 11 via nozzle 9 is heated almost instantaneously to substantially the bed temperature, and hydropyrolysis of the coal is initiated practically instantaneously. Almost at once, the coal is split into a gaseous fraction and a sticky, semi-fluid residue. The latter is "captured" by a coke pellet, sticking thereto to form a "smear" upon the surface of the pellet. Bed 11 serves as a "dust trap" for the sticky initial pyrolysis residue. Further reactions with hdyrogen convert the gaseous fraction into lighter products and transform the sticky smear into dry coke with evolution of additional gases and vapors. The solid residue of the hydropyrolysis of the coal remains sticky for a time only on the order of a second. Coke pellets are discharged from bed 11 via pipe 13, to keep the inventory of coke pellets in bed 11 substantially constant. Gases and vapors from bed 11 pass into zone 14. A fine pulverulent solid, preferably between about 50 and 100 microns in average particle size, is introduced into zone 14 via line 29. Line 29 preferably enters vessel 10 approximately at the elevation of the upper surface of bed 11. The fine solid entering via line 29 is at a higher temperature than bed 11 if the overall chemical process which occurs in bed 11 is endothermic. Alternatively, the fine solid is at a lower temperature than bed 11 if the process in bed 11 is exothermic. The temperature and quantity of fine solid passing through line 29 are variables providing a control on the temperature of bed 11. Fine solid entering zone 14 from line 29 quickly exchanges heat with gases and solids in zone 14. The solids in zone 14 com-

prise the fine solid, being conveyed upward, and also, in the lower elevations of zone **14**, some coke pellets which have been ejected upward into zone **14** from bed **11** and are falling back into bed **11**. There is effective heat interchange between bed **11** and zone **14**, and no substantial temperature gradient exists throughout vessel **10**. Fine solid and gases and vapors leave vessel **10** at the top via line **15**, and solid and gas are separated in cyclone separator **16**. Gases and vapors pass from separator **16** via line **17** to quench means **18**, where these materials are quickly reduced in temperature. Means **18** may take any of several known forms; e.g., a scrubbing column may be provided, with supply of a scrubbing oil entering the column at a temperature below the temperature desired for the quench. Quenched gases and vapors may advantageously pass directly from quench means **18** via line **19** to a treating operation **20**, in which the materials are hydrotreated without prior cooling and condensation of the vapors, as suggested for example in U.S. Pat. Nos. 3,231,486 and 3,244,615. The treated products are delivered via line **21**. Fine solid separated from gases and vapors in cyclone **16** passes downward through standpipe **22** through solid-flow-control valve **25** and into riser **27**, which is supplied with conveying gas from line **26**. The solid is conveyed upward in riser **27** into means **28** for heating or cooling the fine solid. The heated or cooled solid is returned from means **28** to vessel **10** via line **29**, already mentioned. It will be understood that if the overall chemical process in bed **11** is exothermic, means **28** will cool the solid; alternatively, if the process in bed **11** is endothermic, means **28** will heat the solid. A supply of seed particles of coke is furnished to bed **11** from line **52** via valve **53**. The supply of seed should be at a particle-number rate substantially equal to the particle-number rate of withdrawal of coke product from bed **11** via pipe **13**. Make-up of fine solid may also be added as required from line **52** via valve **53**.

It is desirable that the fine solid move upward through space **14** in the "fast-fluidized state", as hereinbefore described. Sometimes the rate of supply of solid from line **29** to space **14** is sufficient to establish the fast-fluidized state in space **14**. If not, line **23** and valve **24** are desirably furnished to circulate additional solid from standpipe **22** into space **14** near its bottom. The advantage of providing for attainment of the fast-fluidized state in space **14** is that heat exchange between this space and bed **11** is more effective, and the temperatures throughout bed **11** and zone **14** are more uniform.

The fine solid is suitably a fine size of coke or a sand or an alumina or an alumina-silicate or any of a wide range of other solids.

EXAMPLE

I give now an example of the invention based upon FIG. **1**. Bituminous coal is supplied through line **1** in an amount comprising 100,000 pounds per hour of moisture-free coal, having the following analysis (expressed in weight percent):

69.7	carbon
5.3	hydrogen
3.8	sulfur
9.9	oxygen
1.3	nitrogen
10.0	ash

The higher heating value of the coal is 12,700 British thermal units per pound (dry basis). The coal is dried and heated to 300°F in means **4**. Gas supplied in lines **7** and **12** is substantially pure hydrogen at an average temperature of 1,000°F, and the total flow of hydrogen amounts to 4,088.3 pound-moles per hour. Bed **11** operates at 1600°F and 100 atmospheres. Coke pellets in pipe **13** comprise 22,500 pounds per hour of coke and 10,000 pounds per hour of ash. Gas and vapor in line **19** comprise 31,500 pounds per hour of a light, distillable aromatic tar and 1,510 pound-moles per hour of methane, along with 1,520 pound-moles per hour of unreacted hydrogen and minor amounts of CO_2, CO, H_2O, H_2S, and NH_3.

The coke pellets in bed **11** suitably range from about one-twelfth inch to about one-half inch in diameter, and the fluidizing-gas velocity is suitably 20 feet per second at the bottom of bed **11** and **15** at the top. The height of bed **11** is suitably 40 feet, to provide a gas residence time on the order of 2.5 seconds. The gas velocity in zone **14** is suitably 7 feet per second. The height of zone **14** is also suitably 40 feet, to provide a gas residence time on the order of 6 seconds. The total gas residence time in vessel **10** and cyclone **16**, prior to quench **18**, in less than 10 seconds.

The fine solid is alumina having a mean particle size of about 50 microns and displaying an eight-fold range in size. Means **28** heats the alumina from 1600°F to 2200°F. The quantity of alumina flowing in riser **27** and line **29** is 170,000 pounds per hour. This amounts to about 2.7 pounds per actual cubic foot of gaseous products of hydropyrolysis entering zone **14** from bed **11**, and is sufficient to establish the fast-fluidized state in zone **14**.

Residual fuel oil or other solid or liquid hydrocarbonaceous fuel of types hereinbefore described could be substituted for the coal supplied to vessel **10** via lines **8** and nozzles **9**.

Turning now to FIG. **2**, I describe an alternative embodiment capable of providing a shorter gas residence time. Coal or residual oil is charged via a multiplicity of lines **8** and nozzles **9** into vessel **10** housing agglomerating bed **11**. The operation of bed **11** is substantially as described earlier in connection with FIG. **1**. A hydrogen-rich gas is supplied to bed **11** via line **12**. Coke pellets are discharged from bed **11** via pipe **13**. Gases and vapors from bed **11** pass into zone **31**. If the overall chemical process occurring in bed **11** is exothermic, a relatively colder fine solid is admitted to zone **31** from line **44** via valve **45**. If the process in bed **11** is endothermic, a relatively hotter fine solid is admitted to zone **31** from line **51**. Zone **31** and bed **11** operate at substantially the same temperature, the fine solid entering zone **31** from line **44** or line **51** quickly exchanging heat with matter in zone **31** and approaching this matter in temperature. The solid entering zone **31** is conveyed by gases and vapors through grid plate **32** and into zone **33**, which operates at a temperature preferably between about 600° and 900°F and which serves to quench the gases and vapors rising from zone **31**. Zone **33** preferably operates as a fast fluidized bed. Fine solid accompanies gases and vapors leaving zone **33** in line **34**, and the solid is separated therefrom by cyclone separator **35**. Gases and vapors pass to treating means **20** and leave the system via line **21**. Solid from cyclone **35** passes downward in standpipe **36** via valve **39** into riser **41**. Riser **41** is supplied with conveying gas from line

40, and solid from valve 39 is conveyed in riser 41 into cooling means 42, where the solid is cooled to a temperature preferably about 100° below the temperature of zone 33. Solid is returned from cooling means 42 to zone 33 via line 43. If the process in bed 11 is exothermic, solid at substantially the temperature of zone 33 is passed from standpipe 36 into zone 31 via line 44 and valve 45. If the process in bed 11 is endothermic, line 46 is provided to convey solid via valve 47 into riser 49. Riser 49 is supplied with conveying gas from line 48, and solid from valve 47 is conveyed in riser 49 into heating means 50. Solid heated to a temperature greater than that in bed 11 is returned from means 50 to zone 31 via line 51. If the flow fo fine solid from zone 31 and line 43 is insufficient to establish the fast-fluidized state in zone 33, line 37 and valve 38 are advantageously provided to recirculate additional fine solid from standpipe 36 into zone 33. Line 52 and valve 53 are provided for supply of seed particles of coke.

The embodiment of FIG. 2 is advantageous if an especially short gas residence time is desired. For example, suppose the height of bed 11 is 30 feet, with velocities of 20 feet per second at bottom and 15 at top, to provide a gas residence time on the order of 1.7 seconds. Zone 31 might be 20 feet in height with a velocity of 7 feet per second, to provide a gas residence time on the order of 3 seconds. The overall gas residence time is thus less than 5 seconds.

FIG. 3 depicts schematically an advantageous arrangement for heating fine solid. The arrangement may be used for means 28 in FIG. 1, when means 28 is intended for heating of fine solid.

Coke pellets made from coal by the process of FIG. 1 are introduced from pipe 13 into vessel 60, which operates at substantially the same pressure as vessel 10 of FIG. 1. The coke pellets fall to the bottom of vessel 60 to form fluidized bed 61. Gasification medium is introduced into bed 61 from a multiplicity of substantially horizontal inlet pipes 63 penetrating frusto-conical segment 64 of the walls of vessel 60. The included angle of segment 64 is preferably about 60°. The gasification medium may be steam and oxygen, if a gas comprising primarily hydrogen and carbon monoxide is desired. The gasification medium may be steam and air (or recycled combustion products and air) if a fuel gas is desired. The temperature and composition of the gasification medium are preferably adjusted so that the temperature of bed 61 is between about 1900° and 2100°F. The coke pellets react with the gasification medium to form a mixture of CH_4, H_2, CO, H_2O, and CO_2, together with N_2 if the gasification medium includes air. The H_2, CO, and H_2O can stand to one another in substantially the equilibrium relationship for reaction of steam with carbon if vessel 60 is made adequate in size. As coke is consumed from the coke pellets, ash matter is released. At the specified temperature, ash matter of substantially all coals is sticky. Ash sticks to ash, not to coke; and as ash matter is released, ash agglomerates form. when an agglomerate grows too large to be fluidized at the velocity prevailing in bed 61 (suitably about 10 feet per second), the agglomerate sinks to the bottom of bed 61 and enters zone 66 in the straight-sided section 65 of vessel 60. Zone 66 is a gravitating bed of ash agglomerates, the discharge of agglomerates from zone 66 being governed by rotating grate 67, which is provided with a suitable drive 68. Ash agglomerates drop into water pool 70 housed in chamber 69. Water is furnished to pool 70 from line 71. Ash and water are let down to the atmosphere through line 72, valves 73 and 75, lock chamber 74, and line 76. As coke pellets are consumed in bed 61, coke dust is generated which enters zone 62 along with gasification products. Zone 62 is a fast fluidized bed, established by the circulation of coke dust through line 77 into cyclone separator 78, and thence into standpipe 79 and through valve 80 back into the bottom of zone 62. Fuel gas from cyclone 81 is cooled and desulfurized in means 82, preferably according to the teachings of my U.S. Pat. No. 3,402,998 for use of half-calcined dolomite, [$CaCO_3$+MgO], to absorb H_2S from the fuel gas at a temperature slightly below the temperature at which $CaCO_3$ has an equilibrium decomposition temperature equal to the partial pressure of CO_2 in the fuel gas. The desulfurized gas is delivered via line 83. If more gas is desired than can be produced from the available coke pellets, raw coal may also be fed along with the coke pellets to vessel 60. The raw coal may suitably be crushed to smaller than three-fourths inch.

A portion of the desulfurized gas is used in FIG. 3 as a fuel in vessel 85 to heat fine solid from line 27 of FIG. 1. Vessel 85 houses fast fluidized bed 86 and operates at substantially the same pressure as vessel 10 of FIG. 1. Fine solid is supplied to bed 86 from line 27. Fuel gas is supplied from line 84 via nozzles 87. (Alternatively, if preferred, another fuel gas might be used, including a fuel gas recovered from products in line 21 of FIG. 1.) Combustion air is supplied at the bottom of bed 86 from line 88 in an amount insufficient for complete combustion of the fuel, and additional air, sufficient to complete the combustion, is added from line 89 at an elevation on the order of 10 feet above the bottom of bed 86. Combustion products and solid leave vessel 86 via line 90 and are separated in cyclone separator 91. Combustion products leave via line 92, and solid moves downward in standpipe 93. A portion of the sold is returned to vessel 10 of FIG. 1 via valve 96 and line 29. Another portion of the solid is returned near the bottom of bed 86 via line 94 and valve 95.

Vessel 85 may advantageously work in cooperation with a gas-turbine power plant (not shown in FIG. 3). Air to lines 88 and 89 may be supplied from the air compressor of the gas turbine, or from another air compressor of the axial-flow type commonly used in large industrial gas turbines. Combustion products from line 92 may be expanded in the expansion turbine of the gas-turbine power plant.

If air is used in the gasifcation medium supplied in lines 63 to vessel 60, the fuel gas in line 83 may advantageously be used to fire a gas-turbine power plant (not shown in FIG. 3). If oxygen is used in the gasification medium, gases in line 83 may advantageously be used to prepare hydrogen for supply in lines 7 and 12 to vessel 10 of FIG. 1. Hydrogen for lines 7 and 12 may also be manufactured by reforming methane in products in line 21 of FIG. 1.

I do not wish my invention to be limited to the particular embodiments illustrated in the drawings and described above in detail. It will be understood that grid plate 32 of FIG. 2 may be replaced by other means providing for a restriction in area for gas flow to hinder the backflow of gas or solid from zone 33 to zone 31. Heating step 28 of FIG. 1 might be used to calcine dolomite, and the pressure and temperature in vessel 10 might be chosen so that calcined dolomite supplied via line 29 to

a fast fluidized bed occupying zone **14** will recarbonate with production of heat in zone **14**, either by absorbing CO_2 from gaseous products of hydropyrolysis entering zone **14** from bed **11**, or by absorbing CO_2 from a gas containing CO_2 or CO and H_2O introduced into zone **14** from line **52** via valve **53**. Other arrangements will be recognized by those skilled in the art, as well as other purposes which the invention can advantageously serve.

I claim:

1. A process for hydropyrolyzing a solid or liquid hydrocarbonaceous fuel at short reaction times, comprising:

providing a fluidized bed at a temperature between about 1100° and 1800° F and at a pressure greater than about 20 atmospheres, said fluidized bed comprising coke pellets larger than about one sixty-fourth inch and displaying at least a substantially five-fold range in diameter;

supplying fluidizing gas to said bed at a superficial velocity greater than about 5 feet per second, said gas containing hydrogen;

charging a solid or liquid hydrocarbonaceous fuel to said fluidized bed, the solid product of the hydropyrolysis of said fuel within said bed accreting upon said coke pellets;

providing a space situated above said fluidized bed to receive gaseous products of said hydropyrolysis including unreacted hydrogen, the dimension of said bed and said space being such that the residence of said gaseous products in said bed and said space is less than about 10 seconds, the diameter of said space being such that the superficial velocity of said gaseous products in said space is greater than about 4 feet per second;

supplying solid particles substantially smaller than 100 microns to said space at a temperature and rate of flow to maintain said temperature of said fluidized bed substantially constant, said rate of flow being sufficient to establish the fast-fluidized state in said space;

withdrawing said gaseous products and said solid particles from the top of said space; and,

withdrawing coke pellets from said fluidized bed.

2. The process of claim **1** including the following additional steps:

providing a second space situated above said first space situated above said fluidized bed, said gaseous products and said solid particles supplied to said first space being allowed to pass from said first space into said second space, a restriction in area for flow being interposed between said two spaces to hinder backflow of gas or solid from said second space to said first space; and,

withdrawing gas and solid at the top of said second space, separating solid from said gas by a syclone, cooling at least a portion of said separated solid and returning said portion to said second space to maintain a temperature in said second space between about 600° and 900° F.

3. The process of claim **2** in which said dimensions are such that said residence time is less than about 5 seconds.

4. The process of claim **1** in which at least a portion of the carbon contained in at least a portion of said coke pellets withdrawn from said fluidized bed is gasified by a gasification medium selected from the group consisting of oxygen, air, steam, carbon dioxide, and flue gas in a second fluidized bed of said coke pellets operating at about 1900° to 2100° F, fine particles containing carbon being produced in said second fluidized bed by the wastage of said coke pellets undergoing gasification, and including the step of establishing a fast fluidized bed of said fine particles containing carbon in a zone above said second fluidized bed by separating said fine particles from gaseous products of gasification leaving the top of said zone and recirculating said separated fine particles to substantially the bottom of said zone.

5. A process for hydropyrolyzing a solid or liquid hydrocarbonaceous fuel at short reaction times, comprising:

providing a fluidized bed at a temperature between about 1100° and 1800° F and at a pressure greater than about 20 atmospheres, said fluidized bed comprising coke pellets larger than about one sixty-fourth inch and displaying at least a substantially five-fold range in diameter;

supplying fluidizing gas to said bed at a superficial velocity greater than about 5 feet per second, said gas containing hydrogen;

charging a solid or liquid hydrocarbonaceous fuel to said fluidized bed, the solid product of the hydropyrolysis of said fuel within said bed accreting upon said coke pellets;

providing a space situated above said fluidized bed to receive gaseous products of said hydropyrolysis including unreacted hydrogen, the dimensions of said bed and said space being such that the residence time of said gaseous products in said bed and said space is less than about 10 seconds, the diameter of said space being such that the superficial velocity of said gaseous products in said space is greater than about 4 feet per second;

supplying solid particles substantially smaller than 100 microns to said space at a temperature greater than said temperature of said fluidized bed and at a rate of flow to maintain said temperature of said fluidized bed substantially constant, said rate of flow being sufficient to establish the fast-fluidized state in said space;

withdrawing said gaseous products and said solid particles from the top of said space; and,

withdrawing coke pellets from said fluidized bed.

6. The process of claim **5** including the following additional steps:

providing a second space situated above said first space situated above said fluidized bed, said gaseous products and said solid particles supplied to said first space being allowed to pass from said first space into said second space, a restriction in area for flow being interposed between said two spaces to hinder backflow of gas or solid from said second space to said first space; and,

withdrawing gas and solid at the top of said second space, separating solid from said gas by a cyclone, cooling at least a portion of said separated solid and returning said portion to said second space to maintain a temperature in said second space between about 600° and 900° F.

7. The process of claim **6** in which said dimensions are such that said residence time is less than about 5 seconds.

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