

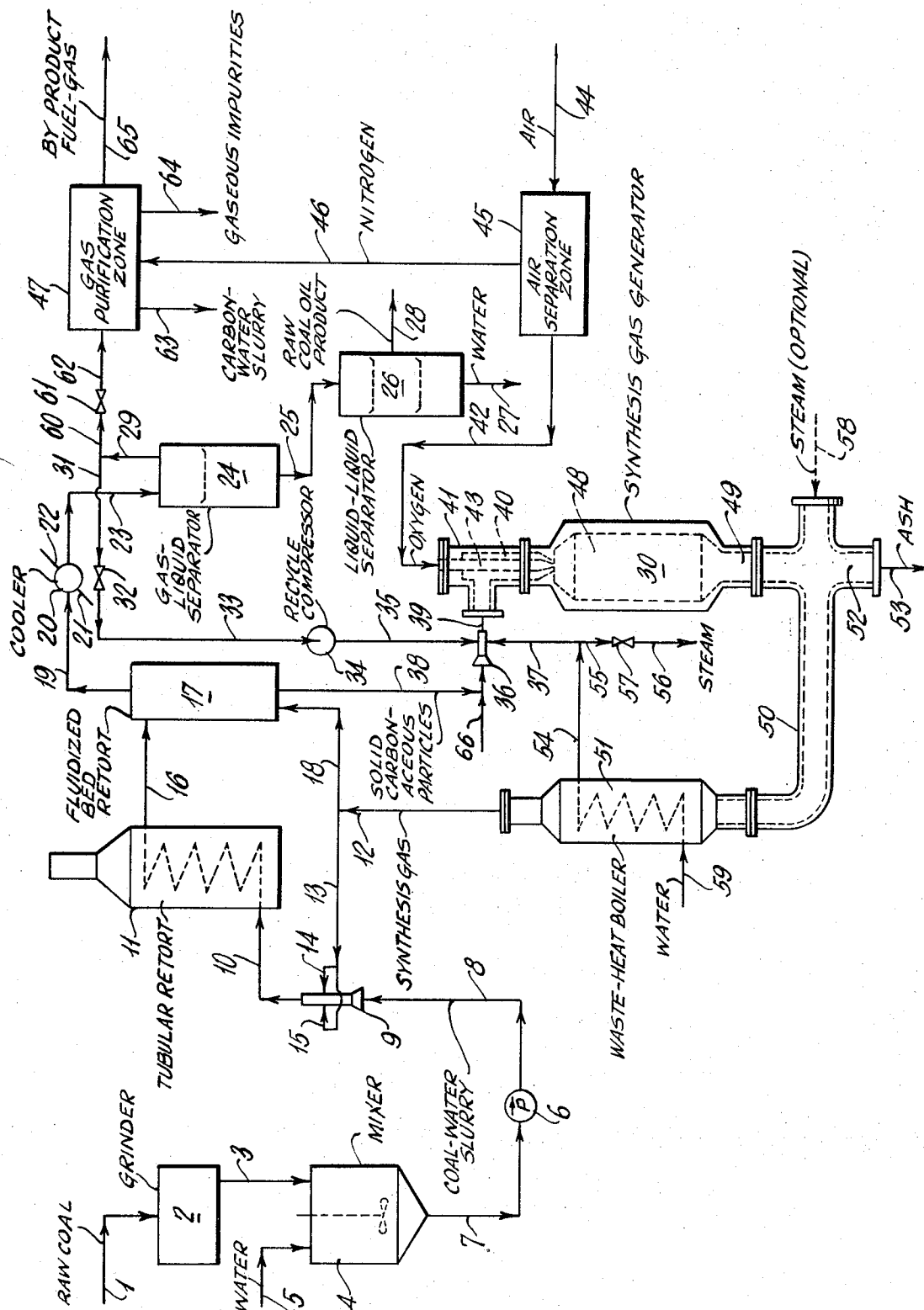
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# MULTI-HYDROTORTING OF COAL

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## MULTI-HYDROTORTING OF COAL

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### ABSTRACT OF THE DISCLOSURE

A noncatalytic multi-hydrotorting process for maximizing the conversion of coal into coal oil. A pumpable coal-water slurry in admixture with a stream of synthesis gas is passed through a tubular retort where it is heated to a temperature in the range of about 600 to 950° F. in the absence of air. The solid coal particles are fragmented and carbonized in the tubular retort, the volatile constituents in said slurry are volatilized and simultaneously hydrogenation of the process stream takes place. The effluent from the tubular retort is then introduced into a fluidized bed retort along with a second stream of synthesis gas. Thermal decomposition of the carbonaceous materials takes place in the absence of air and the process stream is hydrogenated for a second time. The process stream leaving the fluidized bed retort is cooled to condense out and separate water and raw coal-oil in a gas-liquid separation zone. A portion of the off-gas from the gas-liquid separator may be scrubbed and purified to produce nonpolluting fuel gas having a high heating value. Spent carbonaceous particles leaving the fluidized bed retort and optionally a portion of the off-gas from the gas-liquid separator are introduced into a free-flow noncatalytic gas generator for conversion into preferably hydrogen-rich synthesis gas by partial oxidation for use in the aforesaid two hydrotorting stages.

### BACKGROUND OF THE INVENTION

#### Field of the invention

This invention relates to the production of oil from coal and other solid carbonaceous fuels. More specifically it relates to the hydroconversion of coal with synthesis gas in the absence of a catalyst to produce coal oil.

#### Description of the prior art

The liquid phase catalytic hydrogenation of mixtures of ground coal, oil, and catalyst are known to the art. By this means heavy coal oil is produced which requires extensive processing to rid the oil of catalyst and to fractionate it into usable liquid products. Off-gas from these processes contain substantial amounts of H<sub>2</sub>S and other acid gas constituents which pollute the environment. Further, such prior art processes are not too practical because of the deposition of asphalt and high polymers which foul and plug apparatus and rapidly deactivate the catalyst.

Batch hydrotorting of coal is uneconomical because of the slow heating time required to pass through the softening temperature point of the coal, the fusion of the coal to the retort wall, the poor rate of heat transfer into the lump coal, and the comparatively increased hydrogen consumption.

Other contemporary coal hydrogenation processes are unsatisfactory because of one or more of the following reasons: they utilize extensive purification processes to make pure hydrogen for use in hydrogenation, they require expensive fine grinding of the coal and pretreatment by oxidation to overcome agglomerating tendencies of raw coal, they produce an excess amount of waste

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products, the coal oil has a high sulfur and nitrogen content, and a large amount of heat from an external source must be supplied to the system.

The present invention overcomes the difficulties inherent in the above-described prior art processes. Further, there are achieved important economies in the production of a gas rich in hydrogen for hydrogenating the coal.

### SUMMARY

This is a continuous process for the production of coal oil from coal. It is also applicable for converting other solid carbonaceous fuels such as oil shale, tar sands, and petroleum coke into liquid fuels. The process involves multi-hydrotorting of the carbonaceous fuel using synthesis gas produced subsequently in the process by partial oxidation of residue from the hydrotorting steps, producing a high quality liquid fuel. Coal oil may be produced by the subject process in quantities in excess of the Fischer Assay and having a reduced amount of sulfur and nitrogen. The crude oil may be upgraded, for example to gasoline, by conventional refinery operations.

In a preferred embodiment, raw coal is ground to a size in the range of about 1/2 to 1/4 inch diameter and mixed with water to form a pumpable slurry having a solids content in the range of about 25–55 weight percent, and higher. The coal-water slurry is dispersed in a stream of synthesis gas and is then introduced into a tubular retort in the absence of air under conditions of turbulent flow and at a pressure in the range of 1 to 400 atmospheres and at a temperature in the range of about 600 to 950° F. The solid coal particles are fragmented and carbonized in the tubular retort, the volatile constituents in the slurry are vaporized, and a dispersion of solid carbonaceous particles and volatilized coal products in a mixture of steam and synthesis gas is formed. Simultaneously hydrogenation of said dispersion is effected by the hydrogen in said synthesis gas.

The effluent from the tubular retort is introduced into the top of a fluidized-bed. Fluidizing is effected by a second stream of said synthesis gas entering at the bottom of said fluidized-bed. By this means, intimate contacting and a second hydrogenation of the process stream is effected in the fluidized bed in the absence of air at a temperature in the range of about 700 to 950° F. and a pressure in the range of about 1 to 400 atmospheres, and preferably from about 100 to 375 atmospheres.

The process stream leaving from the top of the fluidized bed retort is cooled to condense out and separate any normally nonvolatile materials such as water and coal oil in a gas-liquid separation zone. Off-gas from the gas-liquid separator comprises spent synthesis gas, particulate carbon, and a comparatively minor amount of impurities e.g. N<sub>2</sub>, H<sub>2</sub>S, A, COS, and NH<sub>3</sub>. Optionally, this gas stream may be recycled to a synthesis gas generator, to be further described; or, it may be purified in a gas purification zone and used as fuel gas or both.

Solid carbonaceous matter from the bottom of the fluidized-bed hydrotort is introduced into a free-flow noncatalytic synthesis gas generator and reacted by partial oxidation at a temperature in the range of 1200 to 3000° F. and a pressure in the range of about 1 to 400 atmospheres with an oxygen-rich gas and steam to produce the synthesis gas for use in the aforesaid two hydrotorting steps. Preferably, the synthesis gas is produced having a hydrogen content in the range of about 25 to 80 mole percent. This may be done by reacting the raw effluent synthesis gas with supplemental steam by the noncatalytic thermal shift reaction at a temperature in the range of about preferably 2600 to 1650° F. and a pressure in the range of about preferably 100 to 375 atmospheres. Preferably, all steps in the multi-hydrotorting process are op-

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erated at the same pressure, less ordinary line drop. The operating conditions of the process are such so as to produce from coal oil having a reduced amount of sulfur and nitrogen. Further, greater quantities of coal oil are produced than can be obtained by the Fischer Assay. Since all of the carbon containing by-products, i.e. solid carbonaceous particles and off-gas may be utilized in the production of synthesis gas, there is substantially no waste of the carbon values in the coal.

It is therefore a principal object of the present invention to provide a continuous process for economically and efficiently producing a crude oil having a reduced sulfur and nitrogen content from a solid carbonaceous fuel.

Another object is to produce a maximum amount of desulfurized and denitrogenated coal oil from coal, while utilizing substantially all of the carbon in the coal.

One further object of the invention is to produce from coal crude oil that may be used as refinery feedstock.

### DESCRIPTION OF THE INVENTION

The present invention involves a noncatalytic continuous process for making principally fuel oil and refinery feedstock of improved product quality and quantity from a solid carbonaceous fuel.

The process of the present invention is especially useful for the conversion of coal and similar fuels containing volatilizable constituents. Various grades of coal may be treated including bituminous, subbituminous, and anthracite coals. Waste coals, such as slack coal and the like, cokes made from coal, and lignite are also suitable for use in the present process. Further, the process is also applicable to the treatment of oil shale, tar sands, petroleum coke, asphalt, and pitch.

Sulfur levels in coal range from 0.2% or less to about 7 weight percent on a dry basis. In the manufacture of coal oil and fuel gas from coal most of the sulfur and nitrogen in the coal are gasified. Prevention of air pollution demands that the sulfur level in fuel gas be reduced to about less than 500 parts per million. This may be accomplished by the process of our invention. Similarly, the sulfur and nitrogen levels in coal oil may be reduced to a maximum level of 0.3 wt. percent sulfur and 0.4 wt. percent nitrogen. Further, the quantity of coal oil produced may be 400% of that produced by the Fischer Assay. Approximately 95 percent by weight of the moisture- and ash-free coal is converted.

The particle size of the raw coal, or other solid carbonaceous fuel fed to the subject process is not of particular importance. This is an important economic advantage; for, by our process it is not necessary to resort to costly fine grinding or pulverization of the coal in the preparation of the feed. In comparison, conventional hydrogenation processes ordinarily require large expenditures of power to pulverize the coal to the size of powder.

In our process, coal may be crushed mechanically to a particle size of about 1/2 inch to 1/4 inch in average diameter or smaller with a relatively small expenditure of power and in conventional coarse grinding equipment. Further reduction in size of the coal particles and fragmentation occurs subsequently in the process, while simultaneously being hydrogenated in a tubular retort to be further described.

The coarse ground coal particles are mixed with a suitable carrier such as oil or water. Preferably, water is mixed with the particles of coal so as to form a pumpable coal-water slurry containing about 25 to 55 weight percent of solids at ambient temperature. The coal-water slurry is then mixed with synthesis gas. For example, mixing may be done by pumping the slurry through the axial passage of an orifice-type mixer, e.g. venturi or nozzle mixer such as shown in the drawing or in Perry's Chemical Engineers' Handbook, fourth edition, McGraw-Hill, 1963, pages 18-54 to 56.

Hot raw synthesis gas, a gaseous mixture substantially comprising  $H_2$  and CO and preferably rich in hydro-

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gen, is produced subsequently in the process. This synthesis gas is injected into the coal-water slurry accelerating through the throat of the nozzle mixer to form a dispersion. The synthesis gas is supplied at a temperature in the range of about 1200-3000° F., a pressure in the range of about 1 to 400 atmospheres, and in an amount sufficient to provide about 1500 to 6500 standard cubic feet (s.c.f.) of hydrogen per ton of coal feed (dry basis).

The dispersion of coal,  $H_2O$ , and synthesis gas at the inlet to the tubular retort is at a velocity in the range of about 5 to 50 feet per second and suitably about 10 feet per second. The velocity of the gaseous dispersion of particles of solid carbonaceous matter and vapor at the outlet of the coil is within the range of from about 25 to about 500 feet per second, and suitably about 60 feet per second. The tubular retort is an elongated tubular reactor of relatively great length in comparison with its cross-sectional area, e.g. about 1 to 8 inches inside diameter and larger and about 500 to 4,000 feet long. It is more fully described in U.S. Pat. 2,989,461 issued to Du Bois Eastman and W. G. Schlinger. Advantageously, by our process substantially all of the heat required for retorting may be supplied by the synthesis gas. However, if, desired only a portion of the necessary heat may be provided by the sensible heat of the synthesis gas since the tubular retort may be externally heated if necessary. The temperature at the outlet of the tubular retort may range from about 600 to 950° F., and preferably within the range of about 850 to 925° F. The extent of pyrolysis and carbonization, i.e. thermal decomposition of the coal in the absence of air with distillation of volatilizable constituents in the coal may be controlled by control of the temperature. The distillation of volatilizable materials is also dependent to a limited extent of the amount of water in the coal-water slurry feed. Further, steam reacts with carbon and carbon monoxide to form hydrogen and carbon oxides. This later reaction reduces the amount of synthesis gas required at a great economic savings. Expansion of the water in the coal upon being converted into steam helps to rupture the coal particles. The particles of solid carbonaceous matter produced by devolatilization of the coal comprises principally carbon with a small amount of ash and relatively minor amounts of hydrogen, oxygen, nitrogen, and sulfur. Reactions between hydrogen and sulfur to produce hydrogen sulfide and hydrogen and nitrogen to produce ammonia take place.

The residence time in the tubular retort is long enough to permit the coal to fragmentize and carbonize, the volatile materials to volatilize, and for hydrogenation to commence. Thus, the residence time is maintained in the range of about 1/4 minute to 5 minutes while at the previously mentioned conditions of temperature, pressure and feed composition.

The volume and velocity of the dispersion flowing within the tubular retort are such as to ensure highly turbulent flow conditions, which combined with heat and pressure therein promotes the attrition and disintegration of the coal and the dispersal of fine carbonaceous solid particles in a fluidized dispersion with steam and synthesis gas. The turbulence level, as defined by the ratio of

$$\frac{\bar{\epsilon}_m}{\nu}$$

where  $\bar{\epsilon}_m$  is the average apparent viscosity and  $\nu$  is the kinematic viscosity, is maintained in the range of about 25 to 100,000, and preferably at least 500. Suitably, pressure in the tubular retort is about 100 p.s.i.g. less than the reaction pressure in the synthesis gas generator to be further described, due to normal pressure drop in the lines related to resistance to flow.

The effluent stream leaving the tubular retort is introduced into the upper end of a fluidized-bed retort where

second-stage hydrotorting of the solid carbonaceous particules and the volatilized products in the effluent stream from the tubular retort takes place in the absence of air. Suitably, the fluidized-bed retort comprises a vertical steel pressure vessel. A second and separate portion of synthesis gas produced subsequently in the process is introduced at the bottom of the retort at a temperature in the range of about 700 to 950° F., and preferably in the range of about 850 to 925° F. The pressure in the fluidized-bed retort is in the range of about 1 to 400 atm. and preferably in the range of about 100 to 375 atm. Suitably, the pressure is substantially that of the synthesis gas generator, to be further described, less ordinary line drop. The synthesis gas is passed upwardly through the hydrogenation zone in contact with the fluidized bed of solid carbonaceous particles.

The evolved vapor and the up-flowing synthesis gas provide the fluidizing medium for agitation of the bed of fine carbonaceous particles. Sufficient synthesis gas is supplied so as to provide from about 1500 to 6500 s.c.f. of hydrogen per ton of solid carbonaceous particles (dry basis). The velocity of the synthesis gas should be sufficient to fluidize, that is to suspend but not to entrain the mass of carbonaceous particles in the upflowing stream of gases.

Hydrogenation of the solid carbonaceous particles and the volatile products in the process gas stream takes place in the fluidized-bed retort. Further, steam reacts with carbon and carbon monoxide to form hydrogen and carbon oxides. This later reaction reduces the amount of synthesis gas required at a great economic savings. Sulfur and nitrogen impurities react with hydrogen to produce hydrogen sulfide and ammonia. The particles of solid carbonaceous matter are reacted in the fluidized-bed until preferably about 40 to 95 weight percent of the carbon in the feed is gasified. Thus, the residence time in the fluidized-bed retort may range from about 5 to 55 minutes, and preferably about 30 minutes.

The process gas stream leaving from the top of the fluidized-bed retort is cooled to a temperature below the dewpoint by indirect heat exchange with water. Steam for use in the process may be produced thereby. Vaporized crude oil in the process stream is condensed out along with water containing water soluble compounds such as ammonium salts. Separation of the cooled process stream into a gaseous mixture and a liquid mixture may be effected in a conventional gas-liquid separator. The liquid mixture may be further separated into crude oil and water by gravity separation in a conventional liquid-liquid separator. Water soluble ammonium salts may be recovered from the water. The water may be then recycled and mixed with ground solid carbonaceous fuel to produce the aforesaid slurry feed. For example, a water yield in the range of about 200 to 300 lbs. of water may be produced per ton of coal processed; and generally, the water yield varies directly with pressure and temperature in the hydrotort. The crude oil may be upgraded by conventional refinery processes to gasoline and other liquid fuels. For example an oil yield in the range of about 1.6 to 4.0 barrels of oil per ton of coal may be produced over a pressure in the range of about 800 to 8500 p.s.i.a. and a hydrotort temperature in the range of about 855 to 910° F. Generally, the oil yield varies with temperature and pressure in the hydrotort. Further, up to about 1200 p.s.i.g., the percent sulfur in the coal remaining in the product oil decreases and the residue yield of solid carbonaceous particles decreases as hydrotort pressure increases to about 5500 p.s.i.g. and above, the net hydrogen uptake in standard cubic feet per barrel of coal oil produced increases from about 1500 to 6500.

Crude product coal oil has a gravity in the range of about 12 to 21° API, and a distillation end point in the range of about 740 to 760° F. Maximum sulfur content is about 0.37 weight percent, and maximum nitrogen content is about 0.47 weight percent.

The dry process gas stream from the gas-liquid separator has the analysis as shown in Table I. It may also contain about .5 to 5 weight percent (basis carbon in feed) of particulate carbon added during the manufacture of the synthesis gas. The particulate carbon is removed along with gaseous impurities such as H<sub>2</sub>S, COS, and CO<sub>2</sub> in the gas purification zone. The composition of the purified product fuel gas from the gas purification zone is shown in Table I. The nonpolluting product gas has a gross heating value in the range of about 500 to 800 B.t.u. per standard cubic foot.

For example, in the gas purification zone particulate carbon and other solid impurities may be removed by scrubbing with water or oil by standard gas scrubbing procedure. For example, the process stream is accelerated through the center passage of an orifice-type scrubber, such as a venturi, jet, or nozzle type scrubber and clear water is injected into the process stream at the throat of the nozzle scrubber. A mixture comprising the process gas stream and the scrubbing water is then passed into a separation zone where by conventional means, solids-free process gas is separated from the rest of the mixture. For example, the separation zone may include a gravity separator from which a solids-free process gas stream is drawn off and separated from a mixture of water and particulate carbon. The later mixture is then introduced into a separation vessel from which clear water is drawn off and recycled to the nozzle scrubber for additional gas scrubbing. The residue consisting of a concentrated carbonaceous slurry comprising about to 20 weight percent solids may be used in the production of the aforesaid synthesis gas to be described later. CO<sub>2</sub> and acid gases, e.g. H<sub>2</sub>S and COS, may be removed from the solids-free process gas stream leaving the gas-scrubbing unit in an acid-gas separation zone by suitable conventional processes involving refrigeration and physical or chemical absorption with solvents, such as n-methylpyrrolidone, triethanolamine, propylene carbonate, or alternately with hot potassium carbonate. Methane should be substantially insoluble in the solvent selected. Most of the CO<sub>2</sub> absorbed in the solvent can be released by simple flashing, the rest being removed by stripping. This may be done most economically with nitrogen that is available free of cost from the air-separation unit used to provide oxygen for the gasification step. The stream of CO<sub>2</sub> has a purity of more than 98.5% and may therefore be used for organic synthesis. The regenerated solvent is then recycled to the absorption column for reuse. When necessary, final cleanup may be accomplished by passing the process gas through iron oxide, zinc oxide, or activated carbon to remove residual traces of H<sub>2</sub>S or organic sulfide. Similarly H<sub>2</sub>S and COS are then converted into sulfur by a suitable process; for example, the Claus process for producing elemental sulfur from H<sub>2</sub>S is described in Kirk-Othmer Encyclopedia of Chemical Technology, second edition, volume 19, John Wiley, 1969, page 352. Excess SO<sub>2</sub> may be removed and discarded in chemical combination with limestone, or by means of a suitable commercial extraction process.

TABLE I.—GAS COMPOSITION (MOLE PERCENT)  
[Dry basis]

|                                     | Synthesis gas | Off-gas from gas-liquid separator | By-product fuel-gas |
|-------------------------------------|---------------|-----------------------------------|---------------------|
| H <sub>2</sub> .....                | 59.70-23.5    | 20-10                             | 5-20                |
| CO.....                             | 36.20-30.0    | 30-42                             | 75-35               |
| CH <sub>4</sub> .....               | .50-15.0      | 10-33                             | 25-40               |
| CO <sub>2</sub> .....               | 3.32-30.5     | 35-5                              | 10-25               |
| C <sub>2</sub> H <sub>6</sub> ..... | 0-0           | 1-4                               | 4.0-4.8             |
| A.....                              | .08-10        | .05-10                            | .08-1               |
| N <sub>2</sub> .....                | .11-0.5       | .3-1                              | .32-10              |
| H <sub>2</sub> S.....               | .08-0.37      | .3-1                              | 10-25               |
| COS.....                            | .01-03        | .05-.01                           | .....               |
| NH <sub>3</sub> .....               | .....         | .35-.79                           | .....               |

<sup>1</sup> P.p.m.

The spent solid carbonaceous particles from the bottom of the fluidized-bed retort and concentrated carbon slurry from the gas purification are introduced into a conven-

tional free-flow synthesis gas generator as feed. Optionally, at least a portion of the off-gas from the gas-liquid separator may be included in the feed to the gas generator. The synthesis gas generator is a vertical, cylindrical shaped refractory lined steel pressure vessel that is free from packing, catalyst, or any other obstruction to flow of the gases therethrough. The feed is introduced into the reaction zone by means of an axially aligned burner at one end of the gas generator. The hot raw synthesis gas produced in the reaction zone is discharged from an axially aligned exit port located at the end of the gas generator opposite to the inlet.

Suitably, the aforesaid feed mixture may be dispersed in steam and then introduced into the reaction zone of the gas generator by way of the annulus of an annulus-type burner. For example, a suitable burner is shown in coassigned U.S. Pat. No. 2,928,460 issued to Du Bois Eastman, Charles P. Marion, and William L. Slater. An oxygen-rich gas, i.e. air, oxygen enriched air (22 mole percent  $O_2$  and higher), and preferably substantially pure oxygen (95 mole percent  $O_2$  and more) in order to avoid subsequent removal of the impurities found in air is also passed into the refractory lined reaction zone by way of the center passage of the burner. The atomic ratio of free (uncombined) oxygen to carbon in the feed (O/C ratio) is maintained in the range of about 0.60 to 1.2, and preferably below 1.0.

The feed streams leaving the burner impinge against each other in the reaction zone of the gas generator and are atomized. Partial oxidation of the carbonaceous fuel then takes place at an autogenous temperature in the range of about 1200 to 3000° F. and at a pressure in the range of about 1 to 400 atmospheres. Residence time in the gas generator is about 5 to 35 seconds. The weight ratio of  $H_2O$  to carbonaceous fuel is in the range of about 0.5 to 5, that is, 0.5 to 5 parts by weight of  $H_2O$  for each part by weight of carbonaceous fuel. The  $H_2O$  may be supplied to the generator in liquid or gaseous phase. It will react with the CO and carbonaceous fuel, and moderate the temperature in the reaction zone. Optionally, the  $H_2O$  may be introduced in admixture with the oxygen-rich gas or with the solid or gaseous carbonaceous fuel.

The hot raw synthesis gas discharged from the reaction zone of the synthesis gas generator has an analysis as shown in Table I. About .5 to 5 weight percent of particulate carbon (basis weight of carbon in the feed to the gas generator) are entrained in the stream of raw synthesis gas. The hot gas is passed through a refractory lined connector which joins the synthesis gas generator to a waste heat boiler. On the way to the waste heat boiler, solid ash drops out and is separated from the synthesis gas. The ash is collected, for example in a water-cooled ash chamber and periodically removed from the system. Ash is the residue resulting from the partial oxidation reaction. It consists principally of silica, alumina, ferric oxide, lime, unconverted particulate carbon, together with smaller amounts of magnesia, titanium oxide, alkali compounds and sulfur compounds. These compounds are derived largely from the clay.

Optionally, it may be desirable to increase the amount of hydrogen in the synthesis gas to a value in the range of about 66 to 86 mole percent (dry basis). Advantageously, the yield of solid carbonaceous particles as a percent of the coal charged decreases as the retort pressure and concentration of hydrogen in the synthesis gas increases. Further the sulfur and nitrogen content in the product crude oil is reduced.

While the well known water-gas shift reaction over a conventional iron oxide-chromium oxide catalyst may be employed to increase the sydgrogen concentration in the synthesis gas, preferably and advantageously, the subject invention employs high temperature thermal water-gas shift in an insulated line free from catalyst or packing. Thus the effluent process gas may be shifted while passing

from the synthesis gas generator to a waste heat boiler and there is no costly shift catalyst to contend with. For example, the raw effluent synthesis gas from the gas generator is introduced into a joining refractory lined free-flow conduit where it is mixed with supplemental steam. About 0.1 to 2.5 moles of supplemental steam, such as produced subsequently in the process at a temperature in the range of about 500 to 1500° F., and preferably in the range of about 500 to 1000° F., are mixed with each mole of effluent process gas (dry basis) from the synthesis gas generator. The process gas is at substantially the same conditions of temperature and pressure as in the synthesis gas generator, less ordinary line drop. By noncatalytic adiabatic water-gas direct shift reaction, CO and  $H_2O$  in the process gas stream react at a temperature in the range of 1525 to 3000° F. and preferably in the range of 1700 to 2600° F. and at a pressure in the range of 1 to 400 atmospheres to produce additional  $H_2$  and  $CO_2$ .

Whether or not the effluent gas from the gas generator after noncatalytic thermal shift is cooled in a waste-heat boiler depends on material and heat balances. Such factors are considered as the desired operating temperature in each retort, the temperature of the effluent gas from the gas generator, and the quantities and compositions of the various streams. However, by noncontact heat exchange between water and the shifted process gas stream, steam may be produced for example in a waste heat boiler. This steam may be introduced to the synthesis gas generator, as described previously, at a substantial economic gain.

#### DESCRIPTION OF THE DRAWING AND EXAMPLE

A more complete understanding of the invention may be had by reference to the accompanying schematic drawing which shows the previously described process in detail. Although the drawing illustrates a preferred embodiment of the process of this invention, it is not intended to limit the continuous process illustrated to the particular apparatus or materials described. Quantities have been assigned to the various streams so that the description may also serve as an example.

On an hourly basis, with reference to the drawing about 2000 pounds of raw bituminous lump coal in line 1 are introduced into grinder 2 having the following proximate analysis in weight percent, as received: moisture 4.8, volatile matter 42.8, fixed carbon 46.0 and ash 6.59. The coal has a heating value of 13,500 B.t.u. per pound and an ash softening temperature of 2300° F.

Coal reduced in size from 6" lumps to a size range of about  $\frac{1}{4}$  to  $\frac{1}{2}$  inch average diameter by means of a conventional grinder 2, are passed through line 3 into mixer 4. 2000 pounds of water from line 5 are added to the mixer and a coal-water slurry is produced. At ambient temperature by means of pump 6, the slurry is pumped through lines 7 and 8, nozzle-mixer 9, and line 10 into tubular hydrotort 11 where fragmentizing and pyrolysis of the coal, volatilizing of the volatilizable materials in the slurry, and preliminary hydrogenation of the process stream is effected. 17,100 standard cubic feet per hour (s.c.f.h.) of hydrogen-rich synthesis gas at a temperature of about 1000° F. and a pressure at about 5550 p.s.i.g. in lines 12 and 13, as produced subsequently in the process, are passed through lines 14 and 15 at the throat of nozzle mixer 9 and mixed with the coal-water slurry axially passing and accelerating through the throat of nozzle mixer 9.

Thus, about 4000 pounds per hour of coal-water slurry dispersed in synthesis gas in line 10 at a temperature of about 300° F. are introduced at a velocity of about 9.0 ft./sec. into noncatalytic tubular retort 11 consisting of a 1 inch Schedule 80 pipe x 530 feet long. Conditions in tubular retort 11 include: pressure 5500 p.s.i.g., retorting period 30 seconds, turbulence level 810, exit temperature 925° F., and hydrogen consumption 4000 s.c.f. per ton of raw coal feed in line 1. The effluent process

stream from the tubular retort is passed through line 16 into fluidized bed retort 17 where second-stage thermal decomposition and hydrotorting takes place in the absence of air. About 5700 s.c.f. of hydrogen-rich synthesis gas is introduced through line 18 at the bottom of fluidized-bed retort 17 to fluidize but not to entrain the down moving solids. The synthesis gas is produced subsequently in the process and will be further described later.

The overhead effluent gas stream leaving fluidized-bed hydrotort 17 by way of line 19 is cooled below the dew-point in heat exchanger 20 by indirect heat exchange with water entering by way of line 21 and leaving as steam by way of line 22. The process stream is passed through line 23 into gas-liquid separator 24. A mixture of liquids is passed through line 25 into liquid-liquid separator 26. About 2460 lbs. of water containing dissolved ammonium salts are drawn off by way of line 27 at the bottom of gravity separator 26. The ammonium salts are recovered by standard procedures and the clear water is recycled to mixer 4 as a portion of the water used to slurry the ground raw coal. Recycling of water in this manner is an economic advantage.

About 1035 lbs. of raw coal oil product is drawn off through line 28. The coal oil is suitable for refinery feed and has the following characteristics: gravity 20° API, viscosity 48 SUS, pour point 80° F., and ASTM Distillation end point 745° F. The yield is 3 barrels of coal oil per ton of coal (dry basis). In comparison, coal oil produced by the standard Fischer Assay Test has a yield of about 1.04 barrels (42 gallons per barrel) of oil per ton of coal and the following properties: gravity 14.2° API, viscosity SUS at 100° F. 267, nitrogen .55 wt. percent, sulfur .32 wt. percent, pour point 95° F., ASTM Distillation at 50%—620° F. and 60%-cracked. 2264 s.c.f. of the gas from line 29 at a temperature of about 130° F. is recycled to synthesis gas generator 30 as a portion of the feed. This gas stream is passed through line 31, valve 32, line 33, recycle compressor 34, line 35 and then into the throat of nozzle mixer 36. There it is mixed with 354 lbs. of steam which is introduced into the throat of nozzle mixer 36 by way of line 37 at a temperature of about 600° F., and 320 lbs. of solid carbonaceous particles leaving fluidized bed retort 17 at a temperature of about 925° F., by way of line 38. The mixture is accelerated through the axial passage of nozzle mixer 36. The solid carbonaceous particles comprise about 16 wt. percent of the raw coal feed (dry basis) and have the following ultimate analysis in wt. percent: C, 82.09; H, 4.0; O, 1.53; N, 1.53; S, .50; ash, 10.53.

The effluent mixture of fuel gas, solid carbonaceous particles, and steam leaving nozzle mixer 36 is passed through line 39 into annulus passage 40 of annulus type burner 41 located in the upper end of vertical, refractory lined, free-flow synthesis gas generator 30 which is free from catalyst or packing.

About 8850 s.c.f.h. of oxygen (99.5 mole percent O<sub>2</sub>) at a temperature of 130° F. from line 42 are passed through the center passage 43 of burner 41 at a velocity of 400 feet per second providing an O/C mole ratio of about .953. The oxygen in line 42 is preferably made by passing air from line 44 into conventional air separation zone 45. Advantageously, by-product liquid nitrogen may be obtained from air separation zone 45 and by way of line 46 introduced into gas purification zone 47 as part of the gas purification process, to be further described. Optionally, the aforesaid steam may be mixed with the oxygen for introduction into the gas generator.

Upon impact within reaction zone 48 of gas generator 30, atomization of the feed streams takes place and by partial oxidation at an autogenous temperature of about 1835° F. and at a pressure of about 378 atmospheres, synthesis gas is produced having the composition shown in Table II. The hot effluent synthesis gas leaves gas generator 30 by way of axially aligned exit port 49 and passes through refractory lined connector 50 to waste-heat boiler

51. On the way, about 132 lbs./hr. of ash drop out of the process gas stream by gravity. Periodically, ash is removed from the system by way of leg 52, of connector 50, and line 53 which leads to a water-cooled ash chamber and lock-hopper unit not shown.

About 248 lbs. per hr. of steam produced elsewhere in the process, as for example leaving waste-heat boiler 51 by way of lines 54, 55, 56, and valve 57 are introduced into connector 50 by way of line 58 at a temperature of 980° F. The steam mixes with the synthesis gas and at a temperature of 1950° F. and at a pressure of 5500 p.s.i.g., i.e. at substantially the same as in the gas generator less ordinary line drop, H<sub>2</sub>O and CO react adiabatically in free-flow unpacked conduit 50. By the water-gas thermal shift reaction without a catalyst, additional H<sub>2</sub> and CO<sub>2</sub> are thereby produced. The shifted synthesis gas flows through waste-heat boiler 51 and is cooled to an exit temperature of 1000° F. by noncontact heat exchange with water, entering by way of line 59 and leaving as steam by way of line 54. Excess steam may be drawn off by way of lines 54, 55, 56 and valve 57 for use elsewhere in the system e.g. operation of grinder 2, or air separation unit 45. The analysis of the hydrogen-rich synthesis gas leaving waste-heat boiler 51 by way of line 12 is shown in Table II.

About 22,200 s.c.f.h. of off-gas from gas-liquid separator 24 are passed through line 60, valve 61, and line 62 into a conventional gas purification zone 47, as previously described. About 40 lbs. per hour of particulate carbon are removed from the gas stream by scrubbing with water and leave the gas purification zone by way of line 63. Optionally, the carbon-water slurry in line 63 may be recycled to gas generator 30 by way of line 66, as a portion of the feed. Gaseous impurities such as CO<sub>2</sub>, H<sub>2</sub>S and COS are removed by previously described conventional gas purification procedures and leave by way of line 64. Valuable by-product sulfur and CO<sub>2</sub> are recovered. Finally about 19,800 s.c.f.h. of nonpolluting fuel gas having a gross heating value of 715 B.t.u. per s.c.f. and an analysis as shown in Table II are produced by the aforesaid process and leave by way of line 65.

TABLE II.—GAS ANALYSIS, MOLE PERCENT

|                                     | [Dry basis]   |         | Off-gas from gas-liquid separator, line 29 | Nonpolluting fuel gas product, line 65 |
|-------------------------------------|---------------|---------|--------------------------------------------|----------------------------------------|
|                                     | Synthesis gas |         |                                            |                                        |
|                                     | Line 12       | Port 49 |                                            |                                        |
| H <sub>2</sub> .....                | 28.86         | 52.15   | 13.55                                      | 15.02                                  |
| CO.....                             | 37.01         | 12.00   | 34.27                                      | 38.40                                  |
| CH <sub>4</sub> .....               | 9.87          | 1.60    | 31.53                                      | 35.40                                  |
| C <sub>2</sub> H <sub>6</sub> ..... | .....         | .....   | 9.54                                       | 10.70                                  |
| CO <sub>2</sub> .....               | 23.62         | 33.69   | 10.16                                      | .....                                  |
| COS.....                            | .01           | .01     | .13                                        | .....                                  |
| H <sub>2</sub> S.....               | .13           | .10     | .37                                        | <.5                                    |
| A, N <sub>2</sub> .....             | .50           | .45     | .45                                        | .30                                    |

<sup>1</sup> P.p.m.

The compositions and process of the invention have been described generally and by example with reference to particular compositions for purposes of clarity and illustration only. It will be apparent to those skilled in the art from the foregoing that various modifications of the process and the compositions disclosed herein can be made without departure from the spirit of the invention.

We claim:

1. A process for producing oil and nonpolluting fuel gas from a solid carbonaceous fuel comprising

(1) preparing a pumpable solid carbonaceous fuel-water slurry and introducing same in admixture with a first stream of synthesis gas into a tubular retort where at a pressure in the range of 1 to 400 atmospheres said mixture is fragmented, pyrolyzed, and hydrogenated with said synthesis gas, producing a dispersion of solid carbonaceous fuel particles and the volatilized products thereof in steam and a gaseous mixture comprising hydrogen, carbon oxides, methane and acid gases at an exit temperature in the range of about 600 to 950° F.;

- (2) introducing the dispersion from (1) into a fluidized-bed retort where at a temperature in the range of about 600 to 950° F. and a pressure in the range of 1 to 400 atmospheres said dispersion is fluidized, pyrolyzed, and hydrogenated with a second stream of synthesis gas, producing an effluent process gas stream mixture comprising volatilized oil, steam, hydrogen, carbon oxides, methane and acid gases and a separate stream of particles of solid carbonaceous fuel residue;
- (3) cooling the effluent process gas stream from (2) below the dewpoint, condensing out and separating product oil and water from each other and from uncondensed gases;
- (4) purifying the uncondensed gases from (3) by removing said acid gases and CO<sub>2</sub>, yielding a by-product stream of nonpolluting fuel gas; and
- (5) introducing a fuel selected from the group consisting of at least a portion of the residue carbonaceous solids from (2), at least a portion of the uncondensed gases from (3), and mixtures thereof into the reaction zone of a free flow synthesis gas generator where in the absence of packing and catalyst and by the partial oxidation reaction with an oxygen-rich gas and steam at an autogenous temperature in the range of 1200 to 3000° F. and a pressure in the range of about 1 to 400 atmospheres a stream of synthesis gas is produced for use in (1) and (2).

2. The process of claim 1 further provided with the steps of increasing the hydrogen content in the synthesis gas produced in step (5) by mixing the stream of synthesis gas leaving step (5) with supplemental steam in the amount of .1 to 2.5 moles of steam per mole of synthesis gas (dry basis), and reacting CO and H<sub>2</sub>O in the synthesis gas at a temperature in the range of about 1525 to 3000° F. and at a pressure in the range of 1 to 400 atmospheres in a free-flow adiabatic water-gas shift conversion zone free from catalyst or packing.

3. The process of claim 1 further provided with the steps of preparing the pumpable solid carbonaceous fuel-water slurry in step (1) by grinding coal to a particle size of ½ to ¼ inch diameter and mixing same with water to produce a coal-water slurring having a solids content of 25-55 weight percent.

4. The process of claim 1 wherein said solid carbonaceous fuel is selected from the group consisting of bituminous coal, anthracite coal, cokes made from coal, oil shale, tar sands, petroleum coke, asphalt, pitch and lignite.

5. The process of claim 1 further provided with the step of passing the mixture of synthesis gas and solid carbonaceous fuel-water slurry through the tubular retort in step (1) at a turbulence level

$$\frac{\bar{\epsilon}_m}{\nu}$$

in the range of 25 to 100,000 where  $\bar{\epsilon}_m$  is the average apparent viscosity and  $\nu$  is the kinematic viscosity.

6. The process of claim 1 wherein each of the separate streams of synthesis gas introduced into the tubular retort in step (1) and into the fluidized bed in step (2) is introduced in an amount to provide 1500 to 6500 standard cubic feet of hydrogen per ton of solid carbonaceous fuel (dry basis).

7. In a process for producing coal oil by the hydrotorting of coal, the improvement comprising

- (1) grinding the coal to a ½" diameter or smaller and mixing with water to produce a pumpable slurry containing about 25 to 55 weight percent solids;
- (2) mixing the slurry of (1) with hydrogen enriched synthesis gas produced subsequently in the process at a temperature in the range of about 1200 to 3000° F. and in an amount to provide about 1500 to 6500

standard cubic feet of hydrogen per ton of dry coal feed;

- (3) passing the synthesis gas and slurry mixture of (2) through a tubular retort at a pressure in the range of about 1 to 400 atmospheres and at a temperature in the range of about 600 to 950° F. under turbulent conditions to fragmentize and pyrolyze said coal particles, volatilize the volatile constituents in said slurry and simultaneously hydrogenate the process stream;
- (4) introducing the effluent process stream from the tubular retort in (3) in admixture with a separate stream of hydrogen-enriched synthesis gas being produced subsequently in the process and supplied at a temperature in the range of about 1200 to 3000° F. and in an amount to provide about 1500 to 6500 s.c.f. of hydrogen per ton of dry coal feed into a fluidized bed retort where at a pressure in the range of about 1 to 400 atmospheres and at a temperature in the range of about 600 to 950° F. thermal decomposition and hydrogenation take place;
- (5) withdrawing an overhead process stream from the fluidized-bed retort of (4), cooling said process stream to below the dewpoint, and separating a mixture of coal oil and water from uncondensed gases;
- (6) withdrawing spent particles of solid carbonaceous fuel from the fluidized-bed retort of (4), introducing a fuel selected from the group consisting of said spent particles of solid carbonaceous fuel, at least a portion of the uncondensed gases from (5), and mixtures thereof into the reaction zone of a free-flow, non-catalytic synthesis gas generator where by the partial oxidation reaction with steam and substantially pure oxygen at an autogenous temperature in the range of about 1200 to 3000° F. and at a pressure in the range of about 1 to 400 atmospheres, a stream of synthesis gas is produced;
- (7) introducing the stream of synthesis gas from (6) into a free-flow water-gas shift conversion zone free from catalyst or packing in admixture with supplemental steam supplied in the amount of .1 to 2.5 moles of steam per mole of synthesis gas (dry basis), reacting CO and H<sub>2</sub>O in the gas stream at a temperature in the range of about 1525 to 3000° F. and at a pressure in the range of 1 to 400 atmospheres to produce a stream of hydrogen-enriched synthesis gas, and providing separate streams of said hydrogen-enriched synthesis gas to (2) and (4) as previously described;
- (8) purifying any remaining uncondensed gases from (5) to produce a by-product stream of nonpolluting fuel gas; and
- (9) separating product coal oil from the mixture of coal oil and water in (5).
8. The process of claim 7 further provided with the step of passing the hydrogen-enriched synthesis gas produced in step (7) in indirect heat exchange with water thereby cooling said synthesis gas while simultaneously producing steam for use in step (6) in the generation of said synthesis gas.

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