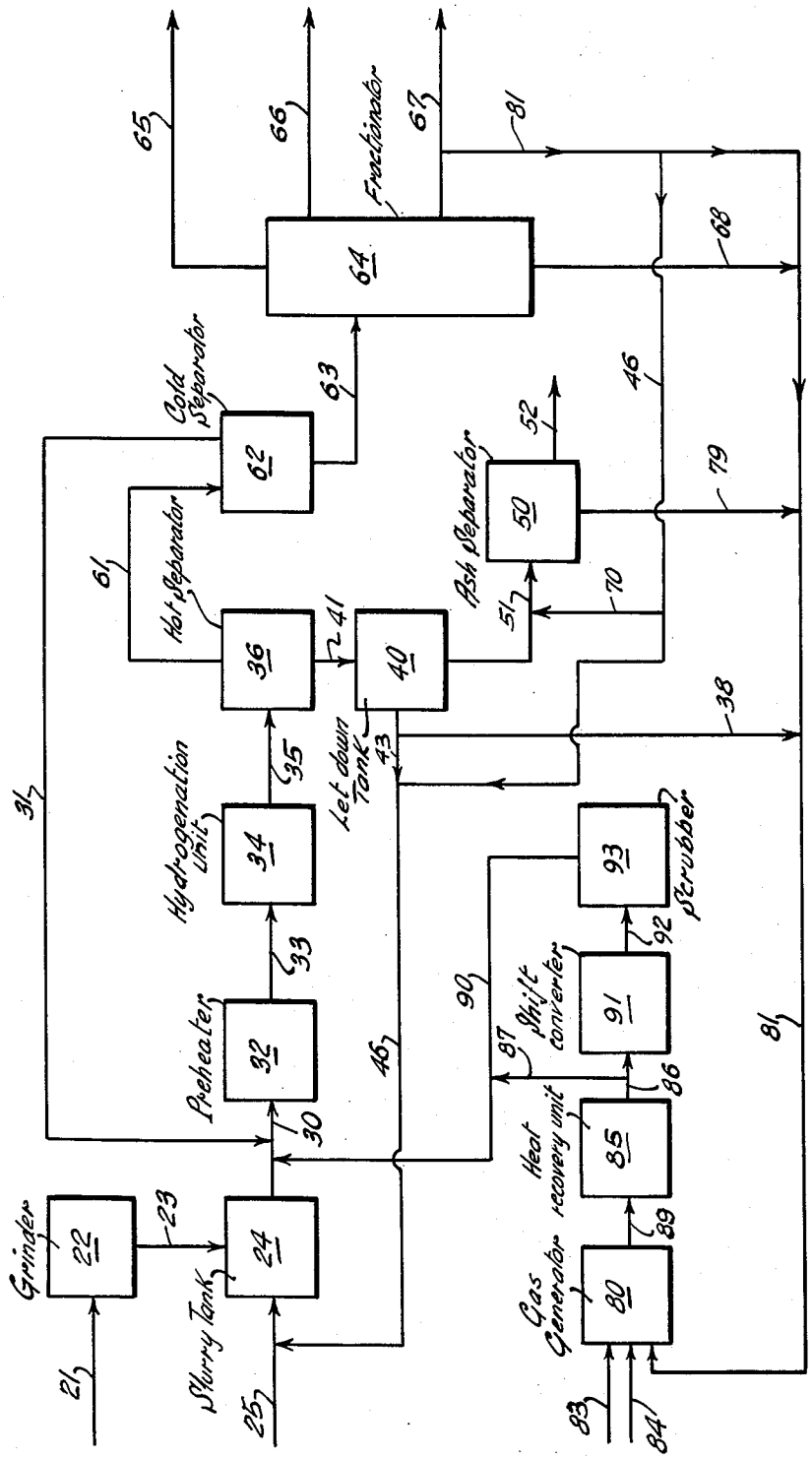
Jan. 29, 1963 DU BOIS EASTMAN ET AL 3,075,912

HYDROCONVERSION OF SOLID CARBONACEOUS MATERIALS

Filed Sept. 18, 1958



United States Patent Office 3,075,912
Patented Jan. 29, 1963

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HYDROCONVERSION OF SOLID CARBONACEOUS MATERIALS

Du Bois Eastman, Whittier, and Warren G. Schlinger, Pasadena, Calif., assignors to Texaco Inc., a corporation of Delaware

Filed Sept. 18, 1958, Ser. No. 761,772
3 Claims. (Cl. 208—8)

This invention relates to the hydroconversion of solid carbonaceous materials. The process of the present invention is particularly applicable to the treatment of coal and may be applied to the hydrogenation of anthracite, bituminous coal or lignite. In its more specific aspects, this invention relates to the production of valuable liquids such as fuels for internal combustion engines.

Prior attempts to convert solid carbonaceous materials such as coal into valuable liquid products by hydrogenation have not proven satisfactory. Because of the high pressures which are required and the long reaction times, the equipment necessary for carrying out the reaction has been expensive and cumbersome, e.g. a commercial reactor large enough to allow a reaction time of 3–4 hours would have an internal diameter of 32 inches and a wall thickness of about 8 inches. In addition, the use of a catalyst has presented several problems. Fixed bed catalysts have proven impractical because of the nature of the material being treated. The use of a finely divided catalyst suspended in the reaction medium has proven costly because of the inefficiency of the known hydrogenation methods. The catalyst rapidly became deactivated by being coated with asphalt and after one pass through the reaction zone had to be discarded. Also, because of the inefficiency of known methods, it was necessary, for the production of lighter hydrocarbon liquids to hydrogenate the coal in one reactor using a finely divided catalyst, separate the heavy liquid product from the ash and contaminated catalyst, add fresh catalyst to the heavy liquid product and then subject it to additional hydrogenation in a second reactor to produce a liquid boiling in the gasoline range.

It is an object of the present invention to provide an improved process for the hydrogenation of a solid carbonaceous material.

Another object of the present invention is to provide an improved process for the production of valuable liquids from coal by reaction of the powdered coal with hydrogen.

Still another object is to provide an improved process for the production of motor fuels from coal by a non-catalytic hydrogenation process.

In accordance with the process of the present invention the solid carbonaceous material such as coal is finely divided, slurried in a liquid medium such as water or oil and passed in contact with hydrogen through a reactor under conditions of highly turbulent flow to produce valuable liquid products.

Any solid carbonaceous material may be suitably treated by the process of the present invention. Such materials as anthracite, anthracite silt, bituminous coal, lignite, peat, sawdust and the like are satisfactory feed stocks. The solid carbonaceous material which will be referred to as coal in the following general description of the invention is pulverized to an average particle size of about —60 mesh and is then slurried with a suitable liquid medium which is inert or only slightly reactive under reaction conditions such as water or an oil which may serve as a hydrogen donor. Preferably, the slurrying medium used in forming the suspension is a hydrogenated aromatic or an oil mixture comprising hydroaromatics which act as hydrogen transfer agents. Hydroaromatics

which are suitable for use in the process include tetralin and decalin. The heavy oil or middle distillate which are obtained from the hydrogenation of the coal are especially suited for the preparation of the feed mixture and contain hydroaromatics. If desired, a fraction separated from the heavy oil product or a suitable fraction of oil from another source may be used in the preparation of the feed slurry. The slurry will usually contain at least about 35% by weight of liquid. To maintain the liquid particles in suspension, the liquid slurry should be maintained at a velocity of about 1 to 10 feet per second depending on the slurry medium and on the average particle size.

The reaction in which the coal is hydrogenated is carried out in a tubular reactor having a length of at least 100 and preferably at least 150 times the maximum cross sectional dimension of the reactor.

The hydrogen used in the process of the present invention may be derived from any suitable source. Electrolytic hydrogen or hydrogen obtained by the partial combustion of carbonaceous materials has proven satisfactory. Materials suitable for feed stock to a partial combustion gas generator are powdered solid carbonaceous materials, liquid hydrocarbons or gaseous hydrocarbons. Heavy liquid hydrocarbons and hydrocarbon gases which are produced by the hydrogenation of solid carbonaceous materials are particularly desirable. When solid carbonaceous materials containing volatile substances are used as feed stock to the gas generator, the materials volatilized during the preheating of the solid carbonaceous material may be removed and, if desired, included in the feed to the hydrogenation unit. When materials containing large amounts of moisture such as lignite are used as feed stock for the gas generation, after preheating, a portion of the steam should be removed prior to the introduction of the feed into the generator to prevent the introduction of excessive amounts of steam into the gas generator. The hydrogen used in the hydrogenation step may be in relatively pure form or may be used in concentrations as low as 25 volume percent. Synthesis gas, i.e. a mixture of carbon monoxide and hydrogen such as that obtained by the methods disclosed in U.S. Patents 2,582,938 and 2,669,509 may be used satisfactorily.

Reaction times may range from 1 second to 2 hours but reaction times of 20 to 300 seconds are preferred. Temperatures of 700 to 1500° F., preferably between about 900 and 1100° F. may be employed. Superatmospheric pressures ranging from 500 to 20,000 p.s.i.g. and higher may be used although pressures of 1500 to 10,000 p.s.i.g. are preferred. Hydrogen rates may range from 1000 to 100,000 standard cubic feet per barrel of slurry feed, rates of 2000 to 50,000 standard cubic feet per barrel of slurry feed being preferred.

For the hydrogenation of the coal to be effective the reaction mixture must be maintained, during the reaction, under conditions of high turbulence. The slurry feed rate, hydrogen recycle rate, reaction coil diameter and operating conditions of temperature and pressure all tend to affect the velocity of flow and the turbulence. It has been found convenient to express turbulence in terms of the ratio of the average apparent viscosity of the flowing stream, $\bar{\epsilon}_m$, to the molecular or kinematic viscosity ν, viz.

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

Hereinafter, we shall refer to this ratio

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

as turbulence level. The apparent viscosity of the flowing stream, ϵ_m, equals the sum of the eddy viscosity, ϵ_m, and the kinematic viscosity ν which may be shown in the expression $\epsilon_m = \epsilon_m + \nu$. Under conditions of turbulence, ϵ_m, has a finite value and it is apparent that if the magnitude of the apparent viscosity exceeds the kinematic viscosity at the point in question, that the ratio of

$$\frac{\epsilon_m}{\nu}$$

exceeds unity. For a given system, it follows that the average value of the ratio, as expressed by

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

exceeds unity. The average apparent viscosity, $\bar{\epsilon}_m$, as employed herein is defined by the equation

$$\bar{\epsilon}_m = \frac{1}{r_0}\int_0^{r_0} \epsilon_m dr$$

where r_0 is the radius of the conduit. By substitution and integration, employing the parameters described by Corcoran et al., Industrial and Engineering Chemistry, 44, 410 (1952), this expression

$$\bar{\epsilon}_m = \frac{1}{r_0}\int_0^{r_0} \epsilon_m dr$$

may be rewritten

$$\bar{\epsilon}_m = \frac{r_0}{15}\sqrt{\frac{r_0 g}{2\sigma}\frac{dp}{dx}}$$

The latter equation is in terms which may be readily determined for a given system; r_0 being the conduit radius, σ the specific weight of the flowing fluid, g the acceleration of gravity and

$$\frac{dp}{dx}$$

the pressure drop per unit of conduit length. In the process of this invention, turbulence levels of 25 and higher may be employed but turbulence levels of 50 to 1000 are preferable. At turbulence levels below 25, a heavy tar-like material is formed at the expense of the desired products. This tar-like material also causes fouling and plugging of the apparatus requiring frequent shut-downs.

In the foregoing paragraph, the various symbols used in the formulas are defined as follows:

d=differential
g=acceleration of gravity, feet per second
p=pressure, pounds per square foot
r=radial distance from center of conduit, feet
r_0=radius of conduit, feet
x=distance, feet
ϵ_m=eddy viscosity, square feet per second
ϵ_m=apparent viscosity, square feet per second
$\bar{\epsilon}_m$=average apparent viscosity, square feet per second
ν=kinematic viscosity, square feet per second
σ=specific weight, pounds per cubic foot.

The invention may be better understood by referring to the accompanying drawing which represents diagrammatically a flow scheme for the practice of the present invention.

Coal is introduced through line **21** to grinding mechanism **22** where it is pulverized to an average particle size of below about −60 mesh. The powder is transferred through line **23** to mixing chamber **24** wherein it is mixed with oil introduced through line **25**. The coal oil slurry is then transferred through line **30** and with hydrogen from line **31** is introduced into preheater **32** where the temperature is raised to about 500–600° F.

The heated slurry and hydrogen are then passed through line **33** to hydrogenation unit **34** where they are subjected to highly turbulent flow. The hydrogenation product is removed from hydrogenation unit **34** through line **35** and introduced into hot separator **36** where gaseous material is separated from the liquid product. The liquid product is transferred to let down tank **40** through line **41**. In let down tank **40**, the pressure is reduced and a separation is effected between the heavy oil and the oil saturated residue. The heavy oil is removed from let down tank **40** through line **43** and may be returned to slurry tank **24** through lines **46** and **25** or sent to gas generator **80** by means of lines **43**, **38** and **81**. The heavy oil saturated ash is sent to ash separator **50** through line **51** where the heavy oil is separated to a large extent from the ash which is removed from ash separator **50** through line **52**, the oil being withdrawn through line **79**. Ash separator **50** may be either in the form of a centrifuge or in the form of a separating tank containing a lower layer of water. In either case, dilution of the heavy oil with a lighter oil is preferred in the first case to facilitate the removal of the ash and in the second case to minimize the possibility of the formation of oil-water emulsions. The overhead from hot separator **36** is withdrawn through line **61** and after cooling in a heat exchanger (not shown) is sent to cold separator **62** from which hydrogen is withdrawn through line **31** and returned to preheater **32** through line **30**. The liquid hydrogenation product is removed from cold separator **62** through line **63** and introduced into fractionator **64** wherein a separation is made of light hydrocarbon gases withdrawn through line **65**, a motor fuel fraction withdrawn through line **66**, a middle distillate fraction withdrawn through line **67** and a residual fraction withdrawn through line **68**. When a portion of the middle distillate is used to dilute the heavy residue withdrawn from let down tank **40** through line **51** it is sent through lines **67**, **81**, **46**, **70** and **51** to ash separator **50** where it facilitates the separation of the heavy oil from the ash. If desired, a portion of the middle distillate from fractionator **64** may be used to form a slurry of the coal feed, in which case it is sent to mixing chamber **24** through lines **67**, **81**, **46** and **25**.

Hydrogen for the process is preferably supplied by partial combustion of the heavy liquid products resulting from the hydrogenation of the coal. Heavy oil from ash separator **50** for the bottoms from fractionator **64** or a portion of the middle distillate from fractionator **64** may be sent to generator **80** through lines **79** and **81**, **68** and **81** or **67** and **81** respectively or a mixture thereof may be used as feed to gas generator **80**. Steam from line **84** and oxygen from line **85** are also introduced into gas generator **80** where the oil is subjected to partial combustion. The products are removed from generator **80** through line **89** and partially cooled in heat recovery unit **85**, which may be, for example, a heat exchanger in which the hot gaseous products are passed in indirect heat exchange with water. The resulting steam may be used as a source of power for the grinding operation. The product gases then may be sent through to preheater **32** by means of lines **86**, **87**, **90** and **30** or if a high concentration of hyodrogen is desired, may be subjected to a water gas shift in shift reactor **91** where the partial combustion products are contacted with an iron oxide catalyst in the presence of steam, the carbon monoxide reacting with steam to produce carbon dioxide and additional hydrogen. The shifted gas is transferred through line **92** to scrubber **93** wherein the gas is contacted with an amine solution for the removal of CO_2 and a gas containing about 95% hydrogen is removed and sent to preheater **32** through lines **90** and **30**.

The following example is given for illustrative purposes only and it should be understood that the invention is not limited thereto.

A slurry composed of 10 parts by weight of bitumin-

ous coal pulverized to a particle size of −60 mesh and 11 parts by weight of a middle distillate, the source of which will be explained later, is mixed with 10,000 cubic feet of a gas containing 80% hydrogen per barrel of slurry. The mixture is passed through a tubular reactor at a temperature of 950° F., a pressure of 5000 p.s.i.g., a reaction time of 50 seconds and at a turbulence level of 450. The hydrogen containing gas is made up of 7640 standard cubic feet of recycle gas and 2360 standard cubic feet of make-up hydrogen having a purity of 95%. After hot and cold separation, let down, centrifuging and fractionating, the products obtained per 100 lb. of coal feed are as follows:

	Lbs.
Ash and unconverted coal	8.0
H_2S, CO, CO_2	2.5
H_2O	6.0
NH_3	2.0
C_1–C_4 hydrocarbon gases	12.0
C_5–400° F. end point gasoline	37.0
Middle distillate (including 110 lbs. in slurry)	130
Heavy oil	20.5

Hydrogen consumption amounts to 1400 standard cubic feet per 100 lb. coal feed.

Of the 130 pounds of middle distillate, 110 pounds is recycled per 100 lb. of coal feed to make up additional slurry, 10 pounds is withdrawn to storage and the remaining 10 pounds together with 20.5 pounds of heavy oil are charged with 15.2 pounds of steam and 31.5 pounds of oxygen to a synthesis gas generator. The gas generator is operated at 290 p.s.i.g. and 2400° F. After quenching, the effluent gases are passed to a shift converter and then contacted with an amine scrubber. The product gas amounts to 1400 standard cubic feet of 98% purity hydrogen which is used as make up for the hydrogenation unit. The gasoline produced has the following characteristics.

Gravity, ° API	59.3
Distillation range, ° F.:	
IBP	92
10%	124
50%	252
90%	360
EP	402

This gasoline may be upgraded, by catalytic reforming, to produce a motor fuel having a leaded octane number of about 100.

Obviously, many other modifications and variations of the invention as hereinbefore set forth may be made

without departing from the spirit and scope thereof and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A process for the hydroconversion of a solid carbonaceous material which comprises forming a slurry of said solid carbonaceous material with a hydrocarbon liquid boiling in the middle distillate range, passing said slurry as a confined stream through a hydrogenation zone maintained at a temperature between about 700 and 1500° F., a pressure between about 1500 and 10,000 p.s.i.g. and a turbulence level of between about 50 and 1000 in the presence of hydrogen, separating the effluent from said hydrogenation zone into a gas containing hydrogen, a fraction containing hydrocarbon gases, a fraction boiling in the motor fuel range, a fraction boiling in the middle distillate range and a heavy oil, recycling said gas containing hydrogen to the hydrogenation zone, recycling at least a portion of said fraction boiling in the middle distillate range to form additional slurry, forming a second slurry of finely-divided solid carbonaceous material with at least a portion of said heavy oil, subjecting said second slurry to partial combustion to produce a gas containing hydrogen and carbon monoxide, blending a portion of said gas containing hydrogen and carbon monoxide with said fraction containing hydrocarbon gases to produce a gas suitable for use as a heating gas, subjecting the balance of said gas containing hydrogen and carbon monoxide to a water gas shift reaction to produce a hydrogen rich gas and introducing said hydrogen rich gas into the hydrogenation zone as make-up hydrogen.

2. The process of claim 1 in which the temperature is 900–1100° F.

3. The process of claim 1 in which the solid carbonaceous material comprises coal.

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