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COAL LIQUEFACTION PROCESS

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ABSTRACT OF THE DISCLOSURE

A process is disclosed for de-ashing and liquefying coal which comprises contacting comminuted coal with water, a reducing gas, and a compound containing a sulfur component and an alkali metal ion or ammonium ion component, at elevated temperatures and pressures.

BACKGROUND

This invention relates to a process for converting carbonaceous solids to more valuable hydrocarbonaceous products. More specifically, this invention relates to a process for de-ashing and converting coal to hydrocarbon products by contacting the coal with water, a compound containing sulfur and an alkali metal ion or ammonium ion, and a reducing gas, at particular liquefaction conditions to provide the hydrocarbon products.

Several methods for converting coal to more valuable liquid or liquefiable products are known to the art. One method employs destructive distillation of the coal. More recently, high pressure hydrogenation and solvent extraction techniques have been employed. One of the more onerous difficulties encountered in prior coal liquefaction art is the separation of the liquefied hydrocarbonaceous products from the unconverted coal, ash, and various solid inorganic materials found in the raw coal. Under typical prior art liquefaction conditions, the solids are dispersed in the liquefied material and in the organic solvent, if one is used, in a finely divided particulate state, rendering separation extremely difficult. Settling, centrifuging and filtration techniques have been employed with some success, but are economically unattractive as a means for de-ashing the liquefied materials.

The hydrocarbonaceous product of coal liquefaction typically requires further treatment by techniques analogous to petroleum refining methods in order to convert the liquefaction product into valuable liquid hydrocarbons such as gasoline, or to provide benzene and other organic chemicals. This further treatment generally comprises catalytic hydrogenation and cracking of the hydrocarbonaceous tars that result from liquefaction. It has been found that, in general, the particulate matter must be removed from the liquefaction product before such further treatment can effectively and economically be undertaken. Consequently, the prior art has concentrated on methods for economically separating ash from the liquefaction product. The process of this invention partially obviates the need for such separation techniques, by reducing the ash content of the liquefaction product to a low level. Further, the lesser amount of ash which does remain is hydrophilic, and can be removed from the liquefaction product by simple water washing and decantation, in contrast to the non-hydrophilic ash in prior art coal liquefaction processes, which is not susceptible to removal by water washing.

Another major drawback of prior art coal liquefaction methods has been the requirement for large amounts of hydrogen both in high pressure hydrogenation and in solvent extraction. It has been suggested that this problem can be overcome by converting only that small fraction of the coal which is relatively rich in hydrogen. It is obviously more desirable to convert as large a fraction

as possible of the coal to valuable products. A process which could employ a low cost substitute for hydrogen, or substantially reduce the amount of hydrogen needed, would be economically more attractive than prior art methods and would constitute a significant advancement.

SUMMARY

An object of the present invention is to provide a novel process for the liquefaction of carbonaceous solids to produce more valuable hydrocarbonaceous products.

A further object of the present invention is to provide an improved process for liquefying coal, utilizing liquid phase water and a readily available reducing gas, to produce valuable hydrocarbonaceous products.

A particular object of the present invention is to provide a process for liquefying coal in which the ash content of the product is reduced, resulting in a hydrocarbonaceous product of greater utility, while ash remaining in the product is hydrophilic.

In one embodiment, the present invention relates to a process for converting a solid carbonaceous material to a hydrocarbonaceous liquefaction product which comprises contacting said solid material with a reducing gas, water, and a catalytic compound containing a sulfur component and an alkali metal ion or ammonium ion component, at liquefaction conditions, and recovering said hydrocarbonaceous product from the resulting mixture.

In another, more limited embodiment, the present invention relates to a process for converting a solid carbonaceous material to a hydrocarbonaceous liquefaction product which comprises: contacting the solid material with a reducing gas, water, and a catalytic compound containing a sulfur component and an alkali metal ion or ammonium ion component at liquefaction conditions; separating the resulting mixture into an aqueous phase and a hydrocarbonaceous phase; extracting the hydrocarbonaceous phase with a hydrocarbonaceous solvent to provide an extract fraction and a solid residual fraction; and recovering the liquefaction product from the extract fraction.

I have discovered that coal and other carbonaceous solid materials can be liquefied to produce valuable hydrocarbonaceous products by treating the coal with a relatively large quantity of water, a reducing gas, and a compound containing a sulfur component and an alkali metal ion or ammonium ion component. I have found that the ash content of the coal can thereby be reduced significantly and that the hydrocarbonaceous product may, in some cases, be further processed catalytically, in a manner analogous to petroleum refining methods, without the necessity of removing further ash and undissolved carbonaceous materials from the liquefaction product. The ash which does remain in the liquefaction product, being hydrophilic, can be removed by simple water washing, thus obviating the problem of ash removal encountered in prior art. In place of relatively expensive hydrogen, employed in prior art liquefaction methods, carbon monoxide, or a mixture of carbon monoxide with hydrogen provides an effective reducing gas in the present process, permitting the use of low cost sources of reducing gas, e.g. synthesis gas.

PREFERRED EMBODIMENT

The carbonaceous solid materials which can be utilized in the present process to provide the hydrocarbonaceous product include any sort of coal, lignite, peat, oil shale, tar sand or similar substance. The preferred carbonaceous solid is a bituminous coal. For example, an Illinois Bellville District Stoker Coal having a moisture and ash free volatile content of about 20% or higher is suitable. Although not essential to the process, it is preferred that the carbonaceous solid to be employed in the process is first

reduced to a particulate, comminuted form. Preferably, the carbonaceous solid is ground or pulverized to provide particles sufficiently small to pass through a 100 mesh Tyler sieve or smaller. Coal ground sufficiently to pass through a 200 mesh sieve is particularly preferred.

The applicable sulfur-containing and alkali metal ion-containing or ammonium ion-containing catalytic compounds are those capable of being catalytically reduced at the liquefaction conditions hereinafter described. These include, for example, alkali metal sulfides, alkali metal sulfites, alkali metal thiosulfates, ammonium sulfide, ammonium sulfite, ammonium thiosulfate, etc. Particular compounds which are preferred for use as the sulfur-containing catalytic compound in the present process include sodium sulfide, potassium sulfide, sodium sulfite, potassium sulfite, sodium thiosulfate, potassium thiosulfate, sodium hydrosulfide, potassium hydrosulfide, sodium hydrogen sulfite, potassium hydrogen sulfite, sodium pyrosulfite, potassium pyrosulfite, the disulfides, trisulfides, tetrasulfides, and pentasulfides of sodium and potassium. Also preferred are the analogous ammonium compounds including ammonium sulfide, ammonium hydrosulfide, ammonium sulfite, ammonium hydrogen sulfite and ammonium thiosulfate. Other suitable compounds include lithium sulfide, lithium hydrosulfide, lithium sulfite, rubidium sulfide, cesium sulfides, etc.; however, sodium and potassium are particularly preferred alkali metals. Other sulfur-containing and alkali metal ion- or ammonium ion-containing compounds may be employed but not necessarily with equivalent results.

The reducing gas employed in the present process may be pure hydrogen or pure carbon monoxide. A mixture of these gases is also suitable. The reducing gas may be commingled with one or more gases or vapors which are relatively inert in the liquefaction reaction, including nitrogen, carbon dioxide, etc. One convenient, suitable source of the reducing gas is a synthesis gas produced by reaction of carbon or hydrocarbons with steam to produce carbon monoxide and hydrogen. A variety of methods for producing a synthesis gas suitable for use in the present process are known in the art.

Liquefaction conditions in the process of the present invention include a broad temperature range of about 150° C. to about 375° C. and a pressure of about 10 atmospheres to about 400 atmospheres or more. Preferred conditions include a temperature of about 200° C. to about 375° C. and a pressure of about 10 atmospheres to about 300 atmospheres. I have found that excellent results are obtained when at least a portion of the water employed in the liquefaction operation is maintained in the liquid phase by appropriate adjustment of the temperature and pressure employed in the operation. Thus, preferred liquefaction conditions include a temperature of about 200° C. to about 375° C. and a pressure at least sufficient to provide a liquid water phase at the desired temperature. For example, in an operation wherein it is desired to employ a temperature of about 200° C., a pressure of at least about 20 atmospheres is maintained. At higher temperature operations, e.g., 350–375° C., a pressure of about 135 amtospheres to about 220 atmospheres or more is maintained. Best results are achieved when a temperature of about 250° C. to about 350° C. is employed. Liquefaction conditions can also include the use of a hydrocarbonaceous solvent in the liquefaction operation, if desired. In general, better results are achieved when a solvent is employed. When such a solvent is utilized, it is provided at a concentration of about 1.0 wt. percent to about 1,000 wt. percent of the solid carbonaceous material. Particular hydrocarbonaeous solvents utilized in coal liquefaction are well known to the art. Among the solvents preferred in the present process are benzene, toluene, xylenes, ethylbenzene, and similar aromatic and alkylaromatic hydrocarbons.

The amount of water contacted with the solid carbonaceous material at liquefaction conditions is between about 100 wt. percent and about 1,000 wt. percent of the carbonaceous solid. Good results are obtained when the amount of water is between about 100 wt. percent and about 400 wt. percent of the carbonaceous solid. The amount of the sulfur-containing and alkali metal-containing or ammonium ion-containing compound contacted with the solid is sufficient to provide a concentration of about 0.01 wt. percent to about 1,000 wt. percent of the carbonaceous solid. A concentration of about 0.1 wt. percent to about 200 wt. percent based on the carbonaceous solid, is preferred. The sulfur-containing compound may conveniently be employed as an aqueous solution of, for example, sodium sulfite, etc., in the water component. When this method is employed, it is preferred to maintain a concentration of about 10 wt. percent or more of the sulfur-containing compound in solution. The superatmospheric pressures employed at liquefaction conditions in the present process may be wholly supplied by the reducing gas, or may be supplied in part, by inert gases, water vapor, etc. In any case, the partial pressure of the reducing gas is maintained as at least about 10% of the total pressure. The amount of the reducing gas employed is about 0.5 s.c.f. to about 175 s.c.f. per pound of carbon in the carbonaceous solid to be processed. Preferably, the amount of the reducing gas utilized is about 20 s.c.f. to about 75 s.c.f. per pound of carbon in the solid.

The process of the present invention may be employed in a batch type operation or a continuous type operation. When a batch operation is employed, fixed amounts of the carbonaceous solid, water, the catalytic sulfur-containing compound and the reducing gas are charged to a suitable liquefaction reactor, such as a rocking autoclave. The reactants are contacted in the liquefaction reactor for a period of time sufficient to produce the desired amount of conversion and then the resulting mixture is withdrawn from the liquefaction zone and the desired hydrocarbonaceous product is separated and recovered. A suitable contact time in a batch type operation is about 1 minute to about 600 minutes, preferably about 200 minutes to about 400 minutes. In a continuous operation, the carbonaceous solid, water, the sulfur-containing compound and the reducing gas are continuously charged to a suitable reaction zone and contacted therein. The resulting mixture is continuously withdrawn from the reactor and the desired hydrocarbonaceous product is separated and recovered. A suitable liquid hourly space velocity in a continuous type operation (volume of the reactor divided by the total volume of reactants charged per hour) of about 0.16 to about 1.0 may be employed, and about 0.25 to about 0.5 is particularly preferred.

The liquefaction zone or reactor utilized in the present process may be any suitable vessel or reactor which can maintain the reactants at sufficient temperature and pressure to provide the required liquefaction conditions. For example, a conventional rocking autoclave is a suitable reactor for use in a batch type operation. A variety of vessels suitable for use as the reactor are known in the art of coal liquefaction. Preferably, the liquefaction zone includes means for admixing the reactants by stirring or other agitation.

The mixture recovered after the liquefaction step, in addition to the desired hydrocarbonaceous product, will contain water, which is present as a phase separate from the product. Most of the solids remaining in the mixture will be found in the water phase. Thus, the hydrocarbonaceous product may conveniently be separated from the water and from at least a major portion of any remaining solid residual materials such as ash, by simple mechanical separation of the phases provided by settling the effluent from the liquefaction reactor. The water phase thus recovered may be recirculated to the reaction step for further use after purification, if desired. Similarly, reducing gas which is not consumed during the reaction, or liquefaction, step may be recovered and recirculated to the

liquefaction step. I have found that the present process actually does not consume hydrogen or carbon monoxide in substantial amounts, so that only a small amount of continuously supplied fresh reducing gas is normally required in a continuous operation. The hydrocarbonaceous product may be further processed, for example, by petroleum refining methods such as cracking, to provide hydrocarbon fuels, aromatic chemicals for petrochemical uses, etc. When the process herein disclosed is utilized to treat the preferred carbonaceous solid, bituminous coal, the hydrocarbonaceous product recovered comprises a tarry material which is liquid at about 100° C. and has an ash and sulfur content significantly lower than that of the raw bituminous coal. One of the major problems encountered in prior art coal liquefaction processes has been the separation of ash from the hydrocarbonaceous materials produced. The present process reduces the amount of ash in the hydrocarbonaceous liquefaction product sufficiently that further separation of solids may not be necessary, particularly since much of the solid residue remains in the water phase resulting from settling the liquefaction reactor effluent and is consequently very easily removed by decantation.

Liquefaction conditions may include the use of various catalysts to further enhance the liquefaction reactions in the present process. Suitable catalysts include metals from Group VIII of the Periodic Table of The Elements, particularly the sulfides of these metals, especially iron sulfide, nickel sulfide and cobalt sulfide. The above-noted metal sulfide catalysts may be utilized at a concentration of about 0.001 wt. percent to about 10 wt. percent of the amount of carbonaceous solid material to be treated. A preferred concentration for such catalysts is about 0.1 wt. percent to about 2 wt. percent of the carbonaceous solid. In general, a catalyst of this type may be employed by admixing it with the pulverized coal as a solid.

The hydrocarbonaceous liquefaction product recovered from the liquefaction step is a tarry material melting at about 50° C. to about 200° C., comprising a mixture of various hydrocarbonaceous compounds containing about 80–85 wt. percent carbon and about 6.5–8 wt. percent hydrogen. This liquefaction product is preferably further treated by conventional petroleum refining methods to provide hydrocarbon products. One particularly convenient method for recovering valuable components in the liquefaction product and simultaneously removing any remaining ash, carbonaceous solids, etc., is by extracting the hydrocarbonaceous product with an organic solvent. The solvents which may be employed are well known in the art. Examples of some suitable solvents which are particularly preferred include benzene, toluene, xylene, and similar C_6–C_{12} aromatics, hexane, heptane and similar C_6–C_{12} paraffins, ketones, C_6–C_{12} cycloparaffins and alkylcycloparaffins, etc. Extraction conditions generally include a temperature of about 30° C. to about 300° C. and preferably about 50° C. to about 150° C. Superatmospheric pressure is desirable but not essential. After a contact time of about 0.1 minute to about 1500 minutes, the solvent and the extract materials dissolved therein are decanted or otherwise mechanically separated from whatever solid residual materials remain at the extraction conditions employed. The extracted fraction is then recovered, e.g., by fractionation to separate the solvent, or by other conventional methods.

The following examples illustrate various embodiments and advantages of the process of the present invention. The examples are not intended to limit the broad scope of the present invention, and many other advantages and embodiments of the invention will be apparent to those skilled in the art from the description provided herein.

EXAMPLE I

A seam coal from Randolph Co., Bellville District, Illinois, was analyzed to determine its average composition, which was found to be as shown in Table I.

TABLE I

	Wt. percent
Ash	10.18
Total nitrogen	1.32
Leco sulfur	3.34
Total oxygen	9.54
Free water	4.00
Volatiles	39.72
Carbon	64.45
Hydrogen	5.25
Dry ash	10.70

The coal was pulverized to provide particles sufficiently small to pass through a 200 mesh Tyler screen. One hundred grams of the pulverized coal and 400 grams of water were placed in an 1850 cc. rocking autoclave. In this run, no sulfur-containing catalytic compounds were employed, in order to demonstrate the low yield obtained without their use. The autoclave was sealed and sufficient hydrogen was introduced to provide a pressure of 70 atmospheres. The contents of the autoclave were heated to a temperature of 350° C. and a pressure of 3.0 atmospheres in the autoclave was observed. The contents were agitated at 350° C. for 6 hours, and then the autoclave was cooled to room temperature. The pressure was observed to 62 atmospheres. The excess pressure was released and the remaining contents of the autoclave were removed. The effluent from the autoclave was observed to consist of a water phase and a hydrocarbonaceous phase. The hydrocarbonaceous phase, which solidified at about 100° C., was separated from the water phase by simple decantation and dried. The hydrocarbonaceous materials were then extracted with benzene at about 80–85° C. It was found that the benzene soluble fraction of the hydrocarbonaceous phase contained 30 wt. percent of the carbon in the original 100 grams of coal charged to the autoclave.

EXAMPLE II

One hundred grams of the same pulverized coal employed in Example I was placed in the same autoclave used in Example I. No water and no sulfur-containing catalytic compounds were employed in this run, in order to show the low yield obtained, even when using a hydrocarbonaceous solvent in the liquefaction operation. One hundred cc. of xylene was placed in the autoclave with the coal and the autoclave was sealed. Sufficient hydrogen was charged to the autoclave to produce a pressure of 70 atmospheres. The contents of the autoclave were agitated at a temperature of 350° C. for six hours. The contents were then cooled and the excess pressure was released. After evaporation of the xylene solvent from the hydrocarbonaceous product and drying, the product was extracted with benzene in a manner identical to that used in Example I. It was found that 31 wt. percent of the carbon in the original 100 grams charged to the autoclave had been converted to benzene soluble hydrocarbons.

EXAMPLE III

In this run, 100 grams of the pulverized coal described in Example I was placed in the same 1850 cc. autoclave with 300 cc. of water, 100 grams of $(NH_4)_2S_2O_3$, and 7 grams of NH_4SH. The autoclave was sealed and pressured to 70 atmospheres with hydrogen. The contents of the autoclave were heated to 350° C., and a pressure of 350 atmospheres was observed. The mixture in the autoclave was agitated at that temperature for 6 hours and then cooled to room temperature. Excess pressure was released and the mixture was removed from the autoclave. A water phase and suspended solids were separated and removed by decantation. The hydrocarbonaceous product phase was dried at 100° C. and analyzed. The hydrocarbonaceous product phase was then extracted with benzene in a manner identical to that used in Examples I and II. It was found to contain 84 wt. percent carbon, 7 wt. percent hydrogen, 3.2 wt. percent oxygen and 3.4 wt. percent

sulfur, with 2.4 wt. percent ash and other materials. It was found that 61 wt. percent of the carbon in the coal originally charged to the autoclave was contained in the benzene soluble fraction of the hydrocarbonaceous product.

By comparing the results of Example III with those of Examples I and II, it is apparent that the process of the present invention provided a suprisingly greater amount of conversion. Where no sulfur-containing salt was used in the liquefaction step, only 30% conversion was obtained, and where a hydrocarbon solvent, but no water and no sulfur-containing compounds were used (Example II), only 31 wt. percent conversion was obtained. By employing the process of the present invention, in Example III, 61% conversion was obtained at identical liquefaction conditions and product recovery conditions. Thus, the present process resulted in an increased conversion of substantially 100% over that obtained without using the catalytic sulfur-containing salt and also over that obtained using a hydrocarbon solvent.

EXAMPLE IV

In this run, 100 grams of the pulverized coal described in Example I was charged to the same 1850 cc. autoclave. Also charged were 400 cc. water, 100 grams $Na_2S_2O_3$ and 7 grams NH_4SH. The autoclave was sealed, and sufficient hydrogen was charged to provide a pressure of 70 atmospheres. The mixture in the autoclave was agitated at 350° C. for 6 hours and then cooled to room temperature. Excess pressure was released and the remaining contents were removed. The water and the hydrocarbonaceous product formed two separate phases, which were separated by decantation. The hydrocarbonaceous phase was dried and extracted with benzene in a manner identical to that used in the previous examples. It was found that 52 wt. percent of the carbon in the original 100 grams of coal was present in the benzene soluble fraction. Thus the method of the present invention provided a more than 70% greater conversion than the methods used in Examples I and II.

EXAMPLE V

In order to demonstrate the necessity of employing a reducing gas in the liquefaction step, a run was undertaken without using a reducing gas. In this run, 100 grams of coal, 400 cc. water, 100 grams of $Na_2S_2O_3$ and 7 grams of NH_4SH were placed in the same 1850 cc. autoclave as utilized in the previous examples. The autoclave was sealed, and sufficient nitrogen was charged to provide a pressure of 70 atmospheres. The mixture in the autoclave was agitated at 350° C. for 6 hours. The autoclave was then cooled to room temperature and the excess pressure was released. The mixture was removed from the autoclave and the resulting water phase was separated by decantation. The remaining materials were dried at 100° C. and extracted with benzene in a manner identical to that employed in the foregoing examples. It was found that essentially none of the coal had been converted to materials which could be extracted with benzene.

EXAMPLE VI

In this run, 100 grams of the puverized coal described in Example I, 400 cc. water, 100 grams of $Na_2S_2O_3$ and 100 cc. xylene were placed in the 1850 cc. autoclave. The autoclave was sealed and sufficient hydrogen was charged to increase the pressure to 70 atmospheres. The mixture was agitated at 350° C. for 6 hours and then cooled to room temperature. The excess pressure was released and the remaining contents were removed from the autoclave. The water was removed by decantation and the hydrocarbonaceous product was dried at 100° C. and extracted with benzene in the same procedure as employed in the foregoing examples. The xylene solvent was removed by evaporation during this drying operation. It was found that the benzene extracted hydrocarbons contained 65 wt. percent of the carbon in the original coal charged to the autoclave.

EXAMPLE VII

In this run, 100 grams of the pulverized coal of Example I was placed in the 1,850 cc. autoclave with 300 cc. water, 100 grams of $NaH\ SO_3$ and 100 cc. xylene. The autoclave was sealed and pressurized to 70 atmospheres with hydrogen. The contents of the autoclave were then agitated at 350° C. for 6 hours. The mixture in the autoclave was returned to room temperature and excess pressure released. The remaining contents were removed and the water was separated by decantation. The hydrocarbonaceous produce was dried and extracted with benzene in the identical procedure employed in the foregoing examples. It was found that 73 wt. percent of the carbon in the original coal charged to the autoclave was recovered in the benzene soluble hydrocarbons.

EXAMPLE VIII

In this run, 100 grams of the coal described in Example I, 100 cc. water, 100 grams Na_2S and 100 cc. xylene were charged to the 1,850 cc. autoclave. The autoclave was sealed and pressured to 50 atmospheres with hydrogen. The autoclave contents were heated to 350° C. and a pressure of 205 atmospheres was observed. The mixture in the autoclave was agitated at that temperature for 6 hours and then cooled to room temperature, and excess pressure was released. The mixture was removed and the water was separated by decantation. The xylene solvent was removed and the hydrocarbonaceous product dried at 100° C. The dried hydrocarbonaceous materials were extracted with benzene, the drying and extraction procedures being identical to those used in the foregoing examples. It was found that 57 wt. percent of the carbon in the original 100 gram charge was recovered in the benzene soluble extract fraction.

EXAMPLE IX

In this run, 100 grams of the pulverized coal of Example I was placed in the 1,850 cc. autoclave with 100 cc. water, 50 grams Na_2SO_4, 50 grams $NaHSO_3$ and 100 cc. xylene. The autoclave was sealed and sufficient hydrogen was introduced to provide 50 atmospheres pressure. The mixture in the autoclave was agitated at 350° C. for 6 hours and then cooled to room temperature. Excess pressure was released and the remaining contents were removed. After decantation of the water, drying and extraction of the hydrocarbonaceous products in a manner identical to that used in the previous examples, it was found that the benzene extracted fraction contained 53 wt percent of the carbon originally charged in the coal.

EXAMPLE X

In this run, 100 grams of the coal of Example I was charged to the 1,850 cc. autoclave with 100 cc. water, 50 grams $NaH\ SO_3$, 50 grams Na_2S and 100 cc. xylene. The autoclave was sealed and sufficient hydrogen was charged to provide a pressure of 50 atmospheres. After the mixture was agitated at 350° C. for 6 hours, it was cooled to room temperature and excess pressure was released. The remaining contents were removed from the autoclave and the water was separated by decantation. After drying and extracting the hydrocarbonaceous product with benzene, it was found that the benzene extracted fraction of the product contained 53 wt. percent of the carbon in the original charge to the autoclave.

The foregoing clearly demonstrates the superior conversion achieved using the processing conditions and components of the present invention, and indicates a preferred mode of operation of the present process when a batch reaction scheme is employed. Modification of the operation to a continuous type operation, etc., will be obvious to those skilled in the art.

I claim as my invention:

1. A process for the liquefaction of coal which comprises contacting the coal, at a temperature of from about 150° C. to about 375° C. and a pressure of from about 10 to about 300 atmospheres for a contact time corresponding to from 1 to 600 minutes or a liquid hourly spaced velocity of about 0.16 to about 1.0, with from about 100 wt. percent to about 1,000 wt. percent of water, a reducing gas selected from the group consisting of hydrogen, carbon monoxide and mixtures thereof in an amount of from about 0.5 to about 175 scf. per pound of carbon in the coal, and from about 0.01 wt. percent to about 1,000 wt. percent of a catalyst consisting essentially of a catalytic sulfur compound selected from the group consisting of alkali metal and ammonium sulfides, sulfites and thiosulfates.

2. The process of Claim 1 wherein said catalytic compound is an alkali metal sulfide.

3. The process of Claim 1 where said catalytic compound is an alkali metal sulfite.

4. The process of Claim 1 wherein said catalytic compound is an alkali metal thiosulfate.

5. The process of Claim 1 wherein said alkali metal is selected from sodium and potassium.

6. The process of Claim 1 wherein said catalytic compound is selected from ammonium sulfide, ammonium sulfite and ammonium thiosulfate.

7. The process of Claim 1 wherein said reducing gas comprises hydrogen.

8. The process of Claim 1 wherein said reducing gas comprises carbon monoxide.

9. The process of Claim 1 wherein at least a portion of said water is in the liquid phase, and the liquefaction conditions include a temperature of about 200° C. to about 375° C. and a pressure sufficient to maintain at least a portion of said water in the liquid phase.

10. The process of Claim 1 wherein the reaction mixture is separated into an aqueous phase and a hydrocarbonaceous phase, and liquid hydrocarbon product is recovered from the hydrocarbonaceous phase.

11. The process of Claim 10 wherein said hydrocarbonaceous phase is extracted with an aromatic or paraffinic hydrocarbon solvent to provide an extract fraction and an insoluble fraction, and said product is recovered from the extract fraction.

12. The process of Claim 1 wherein said solvent is a monocyclic aromatic hydrocarbon.

13. The process of Claim 1 wherein said coal is also contacted with about 1.0 wt. percent to about 1,000 wt. percent of a hydrocarbon solvent selected from benzene, toluene, xylene and ethylbenzene.

References Cited

UNITED STATES PATENTS

1,959,175	5/1934	Pier et al.	208—10
3,642,607	2/1972	Seitzer	208—10
3,687,838	8/1972	Seitzer	208—10
1,852,988	4/1932	Varga	208—10
1,894,926	1/1933	Varga	208—10
2,123,623	7/1938	Brown	208—10
2,039,259	4/1936	Pier et al	208—10

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