

- [54] **COAL LIQUEFACTION PROCESS**
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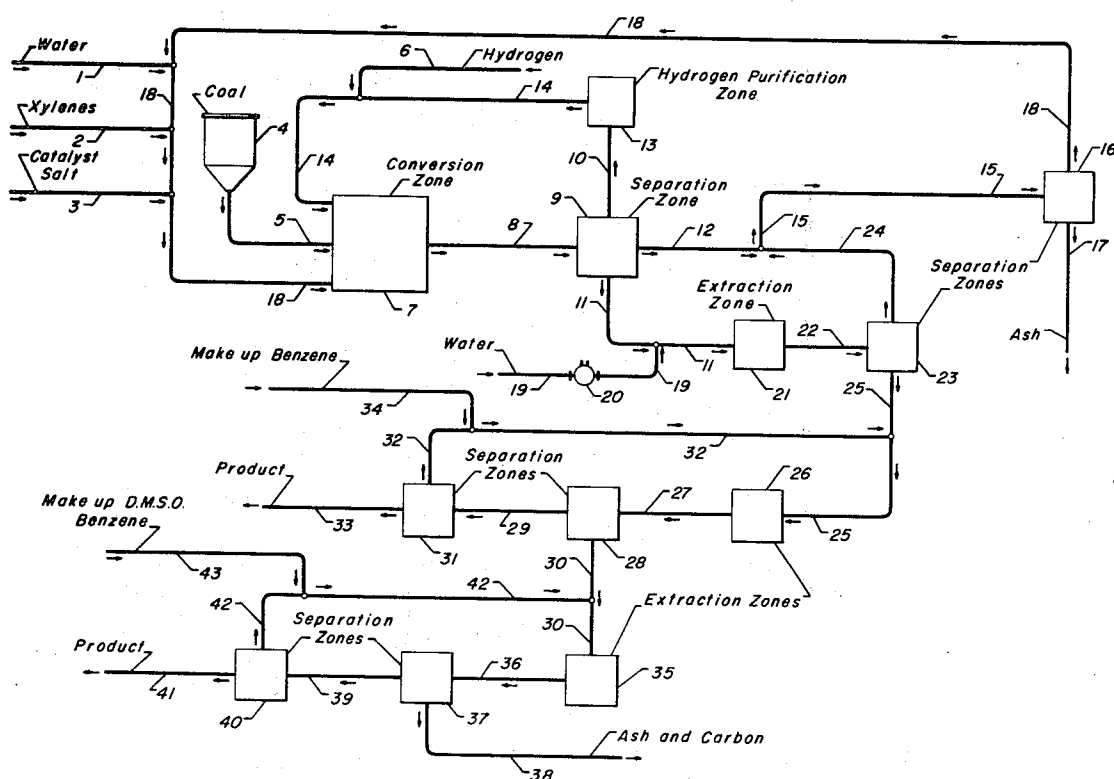
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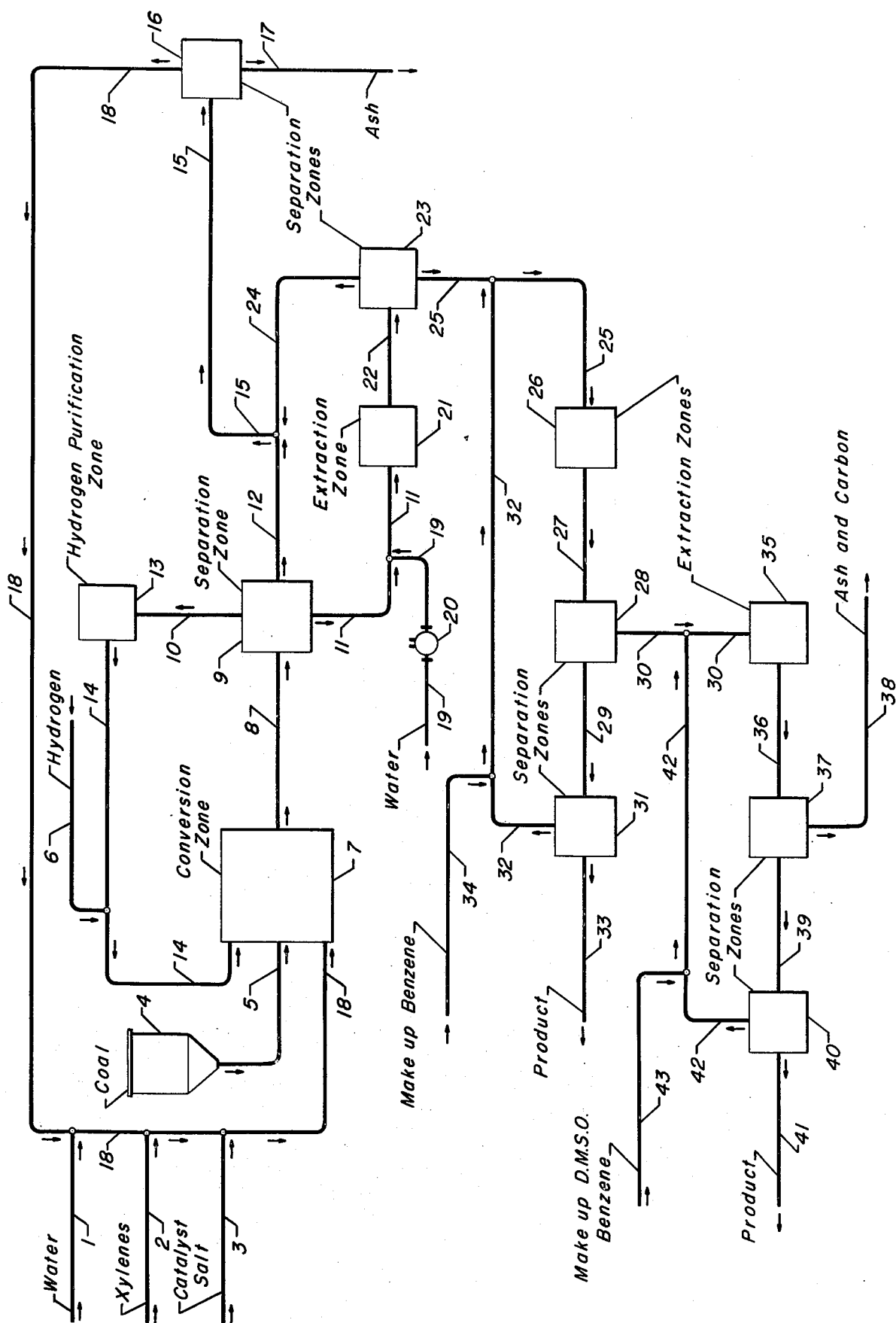
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[57] ABSTRACT

A process for producing hydrocarbonaceous products from coal which includes contacting coal with water, a reducing gas and a catalytic sulfur compound, separating the liquefied coal phase from an aqueous phase, contacting the liquefied coal phase with water to remove ash, extracting the resulting low ash coal liquids with an aromatic hydrocarbon solvent to recover a first, ash-free, hydrocarbonaceous product, and further extracting the raffinate from the aromatic extraction operation with a solvent mixture of a polar hydrocarbonaceous solvent and an aromatic solvent to recover a second, ash-free hydrocarbonaceous solvent and an aromatic solvent to recover a second, ash-free hydrocarbonaceous product.

7 Claims, 1 Drawing Figure





COAL LIQUEFACTION PROCESS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of my co-pending application Ser. No. 289,502, filed on Sept. 15, 1972, now U.S. Pat. No. 3,846,275, all the teachings of which are incorporated by specific reference.

BACKGROUND OF THE INVENTION

This invention relates to a process for converting coal to valuable hydrocarbonaceous products. In particular, the present invention relates to a process for producing ash-free, liquid, hydrocarbonaceous products from coal by liquefying the coal with water, a reducing gas, and a catalytic sulfur compound, whereby the coal ash is rendered hydrophilic, water washing the coal liquids to remove ash, and then extracting the coal liquids in two stages to provide the ash-free hydrocarbonaceous products.

Several methods for converting coal to more valuable liquids 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 the coal liquefaction art is the separation of liquefied hydrocarbonaceous products from solids, such as undissolved organic coal, ash, and other solid inorganic materials, e.g., metals, which are found in the raw coal. In typical prior art liquefaction systems, such solid materials are dispersed throughout the liquid solvent and liquefied coal during the liquefaction operation, and are thus present in the coal liquids when they are recovered after liquefaction. The solids are present in the liquefied materials in a finely divided, particulate state, making separation of the solids from the liquid extremely difficult. Techniques such as settling, centrifugation and filtration have been employed by the art as a means for deashing the liquefied materials.

The hydrocarbonaceous product which results from coal liquefaction typically requires further treatment, by techniques analogous to petroleum refining processes, in order to convert the coal liquefaction product into valuable liquid hydrocarbon products such as gasoline, as well as when it is desired to provide benzene and other relatively pure organic chemicals. Such further treatment by petroleum refining methods generally comprises catalytic hydrogenation and/or cracking of the hydrocarbonaceous tars which result from the primary coal liquefaction operation. It has been found that, in general, the particulate matter present in the coal liquids after liquefaction must be removed from the coal liquids before such further refining treatment can be effectively and economically undertaken. Consequently, the art has concentrated heavily on attempting to provide methods for economically separating ash and undissolved organic coal from the liquefaction products. The process of the present invention obviates the need for using such techniques for separating ash and filtration of the liquefaction product and provides a hydrocarbonaceous product which is very low in ash content. The ash which is present in the coal liquids after the primary liquefaction step in the present process can be removed by simple water washing of the coal liquids, settling, and decantation of the resulting water phase, because the ash which results from the li-

quefaction step in the present process is hydrophilic. The ash which results from prior art coal liquefaction processes, by way of contrast, is not hydrophilic, and is not particularly susceptible to removal by contacting the coal liquids with water.

A major drawback inherent in prior art coal liquefaction methods has been the requirement for large amounts of relatively pure hydrogen in such techniques as high pressure hydrogenation and solvent extraction. It has been suggested that the problem of providing hydrogen can be overcome by converting only a relatively small fraction of the coal which is inherently rich in hydrogen. It is obviously more desirable to convert a large fraction of the untreated coal to valuable hydrocarbonaceous products. A process which employs a low cost substitute for hydrogen, or which substantially reduces the requirement for relatively pure hydrogen, would be economically attractive and a desirable advance in the coal liquefaction art.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a novel process for the liquefaction of carbonaceous solids such as coal in order to produce valuable hydrocarbonaceous products.

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

A particular object of the present invention is to provide a process for producing hydrocarbonaceous products from coal using a particular method for liquefying the coal, in which the ash in the liquefied coal is rendered hydrophilic, with the hydrophilic ash present in the liquefied coal being removed by contacting the liquefied coal with, in turn, water, aromatic solvents, and polar hydrocarbonaceous solvents.

In an embodiment, the present invention relates to a process for producing hydrocarbonaceous liquid products from coal which comprises the steps of: contacting the coal, at coal liquefaction conditions with from about 100 weight percent to about 1000 weight percent of water, a reducing gas selected from the group consisting of hydrogen, carbon monoxide and mixtures thereof in an amount from about 0.5 to about 175 standard cubic feet per pound of carbon in the coal, and from about 0.01 weight percent to about 1000 weight percent of a catalyst comprising a catalytic sulfur compound selected from the group consisting of alkali metal and ammonium sulfite, sulfides and thiosulfate, and separating the resulting mixture to provide a first hydrocarbonaceous phase and a first aqueous phase, contacting the first hydrocarbonaceous phase with from about 10 weight percent to about 1000 weight percent of water at a temperature of about 10° to about 150°C., and a pressure of from about atmospheric to about 25 atmospheres, and separating the resulting mixture to provide a second hydrocarbonaceous phase and a second aqueous phase; admixing the second hydrocarbonaceous phase with from about 10 weight percent to about 1000 weight percent of a first solvent comprising an aromatic hydrocarbon at a temperature of from about 10° to about 150°C. and a pressure of from about atmospheric to about 25 atmospheres, separating the resulting mixture to provide a first, liquid solvent phase comprising the first solvent and a first hydrocarbonaceous product and a first raffinate phase,

and recovering the first hydrocarbonaceous product from the first solvent phase; and, admixing the first raffinate phase with from about 10 weight percent to about 1000 weight percent of a second solvent comprising a mixture of from about 50 weight percent to about 95 weight percent of an aromatic hydrocarbon and from about 5 weight percent to about 50 weight percent of a polar hydrocarbonaceous compound, at a temperature of from about 10° to about 150°C. and a pressure of from about atmospheric to about 25 atmospheres, separating the resulting mixture to provide a second, liquid solvent phase comprising the second solvent and a second hydrocarbonaceous product and a second raffinate phase, and recovering the second hydrocarbonaceous product from the second solvent phase.

I have found that coal and other similar carbonaceous solids 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. The ash content of the coal liquids produced by this liquefaction operation can be lowered very significantly by removal using liquid phase water, and the hydrocarbonaceous products can then be recovered by solvent extraction and may be further processed catalytically in a manner analogous to petroleum refining methods without the necessity of removing further ash and dissolved carbonaceous materials. The ash which remains in the liquefied coal after the primary liquefaction step, is rendered hydrophilic and can be removed by simple water washing of the liquefied coal, thus obviating the problem of ash removal which is encountered in prior art. As a substitute for relatively expensive, pure, hydrogen, which is employed in prior art liquefaction operations, the present process requires only carbon monoxide, or a mixture of carbon monoxide with hydrogen, in order to provide an effective reducing gas in the primary liquefaction step, permitting the use of low cost sources of reducing gas such as synthesis gas.

DESCRIPTION OF THE DRAWING

The attached drawing is a schematic illustration of one preferred embodiment of the process of the present invention. The scope of the present invention is not limited to the embodiment shown. Various other suitable embodiments will be apparent to those skilled in the art from the drawing and following description thereof and from the detailed description of the invention provided hereinafter.

Referring to the drawing, makeup water is introduced to the operation via conduit 1 and passed into conduit 18 which contains an aqueous recycle stream described hereinafter. A mixture of xylene isomers is passed into conduit 18 via conduit 2. Catalytic oxysulfur compounds may be introduced into conduit 18 from conduit 3, either in comminuted solid form or as a relatively concentrated aqueous solution. In the embodiment illustrated, the catalytic oxysulfur compound utilized is in the form of an aqueous solution of sodium thiosulfate. Comminuted bituminous coal is stored in hopper 4 and is passed through conduit 5 into conversion zone 6. The coal is comminuted to sufficiently small size to pass through a 200 mesh Tyler sieve, or finer, before being passed into conduit 5. Makeup hydrogen is introduced to the operation via conduit 6 and

is passed into conduit 14, which contains a stream of recycle hydrogen described hereinafter. The hydrogen charge stream in conduit 14 and the xylenes-water mixture, containing the catalytic oxysulfur compound, in conduit 18 are passed into conversion zone 7 and admixed therein with the comminuted coal introduced from conduit 5. The coal is admixed with the other components of the reaction mixture at a coal/water weight ratio of 1:1, a coal/xylenes weight ratio of 1:1 and a coal/sodium thiosulfate weight ratio of 1:1. Hydrogen is charged at the rate of 5–20 standard cubic feet (SCF) per pound of carbon in the coal to be treated. The mixture thus formed is subjected to a temperature of about 350°C. and a pressure of about 200 atmospheres for about 6 hours, with agitation by conventional stirring means in conversion zone 7. The treated mixture is then cooled to a temperature of about 50°C. and is passed out of conversion zone 7 through conduit 8 into separation zone 9. In separation zone 9 unconsumed hydrogen and any other gases present are separated from the liquid and solid material recovered from conversion zone 7 by flash separation. The gases thus separated are removed from separation zone 9 via conduit 10. The gaseous stream in conduit 10 is passed to conventional hydrogen purification zone 13. In purification zone 13, hydrogen is freed from inert contaminants formed in the conversion step, in order to provide a hydrogen recycle stream having a hydrogen partial pressure sufficiently high to maintain proper conditions in the primary liquefaction operation in conversion zone 7. A recycle hydrogen stream is removed from purification zone 13 and recycled to conversion zone 7 for further use as described above. Referring again to separation zone 9, the nongaseous components of the liquefied coal-water mixture are allowed to settle into immiscible aqueous and hydrocarbonaceous phases, which are separated by simple decantation. The aqueous phase thus separated in separation zone 9 contains a substantial fraction of the solid, unconverted portion of the treated coal, which comprise primarily inorganic ash materials. The liquid hydrocarbonaceous phase formed in separation zone 9, therefore, is relatively low in solids content, having only about 0.3–1.0 weight percent solid content. The high-ash aqueous phase is removed from separation zone 9 via conduit 12 and is passed through conduit 15 into separation zone 16. In separation zone 16, solid materials in the aqueous phase are removed therefrom by conventional means for removing solids from liquids, such as centrifugation, filtration, etc. The ash and any other solid materials, such as undissolved organic components of the coal, are withdrawn from separation zone 16 via conduit 17 and are passed out of the operation. Excess amounts of water which may be present in the operation, e.g., from water streams charged to the system via conduits 1 and 19, may also be removed from the operation by way of conduit 17. The aqueous phase, after it is freed from solids, is then withdrawn from separation zone 16 and is recycled through conduit 18 to conversion zone 7 for further use, as described above. Referring once more to separation zone 9, the relatively low-ash hydrocarbonaceous phase formed therein is removed and is passed into conduit 11. Water is introduced to the operation via conduit 19, heated to a temperature of 90°C. in heater 20 and passed through conduit 19 into conduit 11, wherein the heated water is mixed with the hydrocarbonaceous

stream. The mixture of heated water and hydrocarbonaceous materials in conduit 11 is passed into extraction zone 21 and the mixture is agitated therein at a temperature of about 90° and atmospheric pressure for about 5 minutes. The mixture in extraction, or washing, zone 21 contains about 10 parts of water per part of the hydrocarbonaceous materials, on a weight basis. In zone 21, the relatively small amount of hydrophilic ash contained in the hydrocarbonaceous phase charged thereto is extracted from the hydrocarbonaceous phase and absorbed into the aqueous phase. The mixture of aqueous phase and hydrocarbonaceous phase materials is then withdrawn from extraction zone 21 and passed through conduit 22 into separation zone 23. In separation zone 23, the mixture is settled in order to form an aqueous phase containing substantially all of the hydrophilic ash and other solids and to form an ash-free, hydrocarbonaceous phase. The aqueous phase and the hydrocarbonaceous phase are then separated by simple decantation. The separation operation by settling and decantation is preferably conducted at a temperature of about 90°C. The aqueous phase which is separated by decantation is removed from separation zone 23 via conduit 24, admixed in conduit 15 with the aqueous stream from conduit 12 and passed to separation zone 16 for treatment to remove solid materials, as described above. The hydrocarbonaceous phase which is separated from the aqueous phase in separation zone 23 is removed via conduit 25. Benzene solvent is introduced into conduit 25 from conduit 32, and the resulting mixture of hydrocarbonaceous materials and benzene is charged through conduit 25 into extraction zone 26 at a solvent/hydrocarbonaceous materials weight ratio of about 10:1. The mixture of hydrocarbonaceous materials and benzene solvent is agitated in extraction zone 26 at a temperature of about 75°C. and about atmospheric pressure for about 5 minutes, whereby the benzenesoluble components of the hydrocarbonaceous material charged thereto are extracted from the hydrocarbonaceous phase and taken into solution in the benzene solvent. This mixture is then withdrawn and passed through conduit 17 into separation zone 28. The mixture is settled in separation zone 28 to form a solvent phase, containing the benzene solvent and all the benzene soluble hydrocarbonaceous product components, and to form a raffinate phase containing all the benzene-insoluble hydrocarbonaceous components contained in the hydrocarbonaceous materials charged to extraction zone 26. The separation and decantation operation is preferably performed at a temperature of about 50°C. The benzene-insoluble raffinate phase formed in separation zone 28 may be either solid or liquid in form, depending upon the composition of the particular coal used in the operation. Generally, the raffinate phase is solid at a temperature of about 30°C. The solvent phase and hydrocarbonaceous raffinate phase are separated in separation zone 28 by simple decantation. The solvent phase is removed from separation zone 28 via conduit 29 and charged to separation zone 31. In separation zone 31, the benzene solvent is separated from the benzene soluble hydrocarbonaceous product by fractionation. The benzenesoluble hydrocarbonaceous product, which generally has an initial boiling point substantially higher than the boiling point of benzene, and is thus conveniently separated from the benzene solvent by fractionation, is removed from separation zone 31 and passed out of the

operation via conduit 33 for such use as further conventional refining, or as a fuel or petrochemical feedstock. The benzene solvent is removed from separation zone 31 and recycled via conduit 32 to conduit 25 for further use, as described above. Makeup benzene is introduced into conduit 32 via conduit 34 as needed. Referring again to separation zone 28, the benzene-insoluble raffinate phase is withdrawn and passed into conduit 30. A solvent mixture of 20 weight percent dimethylsulfoxide (DMSO) and 80 weight percent benzene is passed into conduit 30 from conduit 42. The resulting mixture of solvent and benzene insoluble hydrocarbonaceous raffinate is passed from conduit 30 into extraction zone 35. The mixture charge from conduit 30 is agitated in extraction zone 35 at a temperature of about 75° C. and atmospheric pressure for about 5 minutes, whereby the components of the hydrocarbonaceous raffinate which are soluble in the DMSO-benzene solvent are extracted from the raffinate phase and are taken into solution in the solvent. The mixture of solvent and raffinate is then withdrawn and passed through conduit 36 into separation zone 37. The mixture is settled therein to form a solvent phase containing the DMSO-benzene solvent and the solvent soluble hydrocarbonaceous products and an insoluble, solid raffinate phase containing primarily refractory carbon and carbonaceous material along with a small amount of inorganic ash. The solvent phase and the carbonaceous raffinate phase are separated by decantation. The carbonaceous, solid, raffinate phase is withdrawn from separation zone 37 via conduit 38 in the form of a concentrated slurry in a small amount of the solvent and is withdrawn from the process. This solvent raffinate may be burned for fuel value if desired. The solvent phase in separation zone 37 is removed therefrom via conduit 39 and is passed into separation zone 40. In separation zone 40, the DMSO-benzene solvent is separated from the hydrocarbonaceous product by fractionation. The hydrocarbonaceous materials which are soluble in the DMSO-benzene mixture have normal boiling points which are substantially higher than the boiling points of DMSO and benzene, so that separation of the product from the solvent by fractionation is comparatively simple. The hydrocarbonaceous product is removed from separation zone 40 and is passed out of the operation via conduit 41 for further conventional refining or for use as a fuel or petrochemical feedstock, as desired. The DMSO-benzene solvent mixture is withdrawn from separation zone 40 via conduit 42 for recycle to conduit 30, as described above. Makeup DMSO and benzene are introduced into conduit 42 from conduit 43, as needed.

DETAILED DESCRIPTION OF THE INVENTION

The carbonaceous, solid materials which can be treated in the present process include any sort of coal, e.g., bituminous coal, lignite, sub-bituminous coal, etc. Other solid carbonaceous materials such as peat, oil shale, tar sand and the like may also be utilized, but may not necessarily give equivalent results. The preferred carbonaceous solid is a bituminous coal. For example, an Illinois Bellville district stoker coal having a moisture and ash free (MAF) volatiles content of about 20 percent or higher is particularly suitable. Although not essential, it is preferred that the coal to be employed in the operation is first reduced to a particulate, comminuted form. Preferably, the coal is ground or

pulverized to provide particles sufficiently small to pass through a 100 mesh Tyler sieve or smaller. Coal which is ground sufficiently fine to pass through a 200 mesh Tyler sieve is particularly preferred for use.

The catalytic, sulfur-containing and alkali metal ion-containing or ammonium ion-containing compounds which are useful in converting the solid coal to liquid form are those capable of being catalytically reduced at the liquefaction conditions used in the primary coal liquefaction step described hereinafter. These catalytic materials 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 used in the liquefaction step 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 sulfides, cesium sulfides, etc.; however, sodium and potassium are particularly preferred alkali metals. Other sulfur-containing and alkali metal ion-containing compounds may be employed but not necessarily with results equivalent to use of the preferred compounds.

The reducing gas employed in the primary liquefaction step in the present process may be pure hydrogen or pure carbon monoxide. A mixture of any relative amounts of these two gases is also suitable. The reducing gas may be commingled with one or more gases or vapors which are relatively inert in the coal liquefaction reaction, including, for example, nitrogen, carbon dioxide, steam, etc. One convenient suitable source of the reducing gas utilized in the conversion step 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 suitable synthesis gas for use in the present process are well known in the art.

Liquefaction conditions employed in treating the solid coal in the primary liquefaction step in the present process include a broad temperature range of about 150° to about 375°C. and a pressure between about 10 atmospheres and about 400 atmospheres or more. Preferred conditions include a temperature of about 200° to about 375°C. and a pressure of about 10 atmospheres to about 300 atmospheres. Excellent results are obtained in the liquefaction step when at least a portion of the water employed in liquefying the coal is maintained in the liquid phase during treatment of the coal by appropriate relative adjustment of the temperature and pressure employed in the operation. Thus, preferred liquefaction conditions include a temperature of about 200° to about 375°C. and a pressure at least sufficient to provide a liquid water phase at the desired temperature. For example, when 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 atmospheres to about 220 atmospheres or more is maintained. Best results are achieved when a temperature of about 250° to about 350°C. is employed.

Liquefaction conditions used in treating the solid coal in the primary liquefaction step of the present process also preferably include the use of a normally liquid hydrocarbon in the liquefaction operation. In general, best results are achieved when such a hydrocarbon is utilized, in addition to the water, reducing gas and catalytic sulfur compound, in the primary conversion step. When a liquid hydrocarbon is utilized, it is provided in an amount of 1 weight percent to about 1000 weight percent of the coal which is to be liquefied. Hydrocarbons which may be utilized in the coal liquefaction step are well known to the art of coal liquefaction as solvents used in solvent extraction of coal. Among the hydrocarbon solvents preferred for use in the liquefaction step of the present process are benzene, lower alkyl benzenes such as toluene, xylenes, ethylbenzene, etc., naphthalene, and lower alkyl naphthalenes, etc., and similar aromatic hydrocarbons.

The amount of water which is to be contacted with the coal in the primary liquefaction step is between about 100 weight percent and about 1000 weight percent of the coal to be treated. Good results are obtained when the amount of water used is between about 100 weight percent and about 400 weight percent of the coal. The amount of the catalytic, sulfur-containing and alkali metal or ammonium ion-containing compound to be contacted with the coal is sufficient to provide a catalyst concentration between about 0.01 weight percent and 1000 weight percent of the coal. A catalyst concentration of about 0.1 weight percent to about 200 weight percent, based on the amount of coal to be treated, is preferred for use. The sulfur-containing catalytic compounds may conveniently be employed as an aqueous solution of, for example, ammonium sulfite or the like in the water component when the catalytic compound is soluble in water. When such an aqueous solution of the catalyst is employed, it is preferred to maintain a concentration of about 10 weight percent or more of the catalytic sulfur-containing compound in solution.

The super-atmospheric pressures employed in the primary solid coal conversion step in the present process may be wholly supplied by the reducing gas described hereinbefore, 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 percent of the total pressure in the coal conversion zone. The amount of reducing gas employed in the conversion step is between about 0.5 SCF and about 175 SCF per pound of carbon in the coal to be processed. Preferably, the amount of reducing gas utilized is from about 20 SCF to about 75 SCF per pound of carbon in the coal.

The primary coal liquefaction step in the present process may be performed in a batch type operation or a continuous type operation. When a batch operation is employed, fixed amounts of the coal, water, catalytic sulfur-containing compound, reducing gas, and hydrocarbon solvent, if employed, are charged to a suitable conventional coal 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. A suitable contact time in a batch type operation is from about 1 minute to about 600 minutes, preferably, from about 200 minutes to about 400 minutes. In a continuous type operation, the coal, water, catalytic, sulfur-containing compound, reducing gas, and hydrocarbon solvent, if employed, are continuously charged to a suitable conversion zone which may be of any type known in the art, and the reactants are contacted therein. The resulting mixture is continuously withdrawn from the reactor. A liquid hourly space velocity (LHSV) in a continuous type operation (defined as 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 a LHSV of about 0.25 to about 0.5 is particularly preferred.

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

The mixture recovered from the conversion zone after the primary, solid coal conversion step includes immiscible hydrocarbonaceous material and water. When the mixture is allowed to stand, i.e., settled, the water forms a distinct phase, separate from the hydrocarbonaceous, liquefied coal. Most of the solids contained in the mixture when it is withdrawn from the conversion zone (e.g., ash and unconverted organic coal components) are absorbed into the water phase when the water phase and hydrocarbonaceous phase are separated. Thus, the liquefied hydrocarbonaceous phase may conveniently be separated from a major portion of any residual solid material, such as ash, by simple mechanical separation, by decantation, of the water phase and hydrocarbonaceous phase which result from settling the effluent from the liquefaction reactor. The water phase thus recovered may be recycled to the primary solid coal conversion step after purification for further use, if desired. Similarly, reducing gas which is not consumed during the conversion step may be recovered during separation of the hydrocarbonaceous materials from water and may be recirculated to the solid coal conversion step after suitable purification, if desired. I have found that the primary coal conversion step in the present process actually does not consume either hydrogen or carbon monoxide, whichever is used, in particularly large amounts, so that only a small amount of reducing gas makeup is normally required in a continuous operation.

When the primary solid coal conversion step of the present process is utilized to treat the preferred bituminous coal, the hydrocarbonaceous phase recovered from the conversion step comprises a tarry material which is generally liquid at about 100°C. and which has an ash content and a sulfur content significantly lower than the inorganics content and the sulfur content, respectively, of the untreated bituminous coal. One of the major drawbacks encountered in prior art coal liquefaction operations has been the difficulty of separating ash from the liquid hydrocarbonaceous materials after

liquefaction. By using the hereinbefore described conversion step, the present process significantly reduces the amount of ash present in the liquefied hydrocarbonaceous phase recovered directly from the liquefaction of solid coal, since much of the solid residue present after liquefaction, such as inorganic ash, remains behind in the water phase after settling and decantation of the mixture resulting from conversion.

Liquefaction conditions utilized in the primary solid coal conversion step of the present process may include the use of various catalysts to further enhance the conversion of solid coal to a hydrocarbonaceous liquid phase. Suitable conventional catalysts include metals from Group VIII of the Periodic Table of the Elements, particularly the sulfides of these metals, and especially iron sulfide, nickel sulfide and cobalt sulfide. The above-noted metal sulfide catalysts may be utilized at a concentration of about 0.001 weight percent up to about 10 weight percent of the amount of coal to be treated. A preferred concentration for such conventional catalysts is from about 0.1 weight percent to about 2 weight percent of the coal. In general, a catalyst of this type may be employed by admixing it with the pulverized coal as a solid before contact with the water and any organic solvents utilized in the conversion step.

The hydrocarbonaceous phase recovered by settling and decantation of the mixture resulting from the primary solid coal conversion operation comprises a tarry material melting in the range from about 50° to about 200°, and usually melting at about 100°C. when bituminous coal is used. This hydrocarbonaceous phase comprises a mixture of various hydrocarbonaceous compounds containing about 80–85 weight percent carbon and about 6.5–8 weight percent hydrogen. This hydrocarbonaceous phase is further treated by the water contact and solvent extraction steps described herein after in order to recover the hydrocarbonaceous products of the present process.

The following example illustrates certain preferred embodiments and advantages of the primary conversion step in the present process, and contrasts this primary conversion step with prior art solid coal liquefaction methods. The example is not intended to limit the broad scope of the present process. Other advantages and embodiments of the solid coal conversion step of the present invention will be apparent to those skilled in the art from the description provided herein.

EXAMPLE

Run A

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. %
Ash	10.18
Total Nitrogen	1.32
Leco Sulfur	3.34
Total Oxygen	9.54
Frec 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 contrast to the coal conversion step employed in the process of this invention, no sulfur-containing catalytic compounds were employed in this run, in order to demonstrate the relatively low yield obtained when the catalytic sulfur compounds are not used. 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 300 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 was further examined and found to solidify at about 100°C. It was separated from the water phase by simple decantation and dried. The hydrocarbonaceous phase was then extracted with benzene at about 80°-85°C. to determine the extent of conversion of solid coal to liquids. It was found that the benzene soluble fraction of the hydrocarbonaceous phase contained 30 weight percent of the carbon in the original 100 grams of coal charged to the autoclave.

Run B

One hundred grams of the same pulverized coal in Run A was placed in the same autoclave used in Run A. In contrast to the coal conversion step of the present invention, no water and no sulfur-containing catalytic compounds were employed in this run, in order to demonstrate the relatively low yield obtained by prior art methods, even when using a hydrocarbonaceous solvent in the conversion step. 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 6 hours. The contents were then cooled and the excess pressure was released. After evaporation of the xylene solvent from the hydrocarbonaceous phase and drying of the hydrocarbonaceous phase, it was extracted with benzene in a manner identical to that used in Run A. It was found that 31 weight percent of the carbon in the original 100 grams of coal charged to the autoclave had been converted to benzene soluble hydrocarbonaceous materials.

Run C

Run C illustrates one preferred embodiment of the solid coal conversion step in the process of the present invention. In this run, 100 grams of the pulverized coal described in Run A was placed in the same 1850 cc. autoclave with 300 cc. of water, 100 grams of $(\text{NH}_4)_2\text{S}_2\text{O}_8$, 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 the temperature of 350°C. for 6 hours and then cooled to room temperature. Excess pressure was released and the mixture was

removed from the autoclave. A water phase containing a substantial amount of suspended solids was separated and removed from the mixture by decantation. The hydrocarbonaceous phase was recovered and examined. First, the hydrocarbonaceous phase was dried at 100°C. and then analyzed. The hydrocarbonaceous phase was then extracted with benzene in a manner identical to that used in Runs A and B, the hydrocarbonaceous phase recovered from Run C was found to contain 84 weight percent carbon, 7 weight percent hydrogen, 3.2 weight percent oxygen and 3.4 weight percent sulfur, with 2.4 weight percent ash and other materials. It was found that 61 weight percent of the carbon in the coal originally charged to the autoclave was contained in the benzene soluble fraction of the hydrocarbonaceous phase recovered from Run C. By comparing the results of Run C, performed according to a preferred embodiment of the conversion step of the present process, with the results from prior art Runs A and B, it is apparent that the primary conversion step in the process of the present invention provided a surprisingly greater amount of conversion. Where no sulfur-containing catalytic compound was used in the liquefaction step (Run A), only 30 percent conversion was obtained, and where a hydrocarbon solvent but no water and no catalytic sulfur containing compounds were used (Run B), only 31 weight percent conversion was obtained. By employing the conversion step according to the process of the present invention (Run C), 61 percent conversion was obtained at the same temperature, pressure reaction time and recovery conditions. Use of the primary conversion step according to the process of the present invention resulted in a conversion of substantially 100 percent greater than the conversion obtained when the catalytic sulfur containing compound was not used, with similar advantages over conversion using solely a hydrocarbon solvent.

Run D

Run D further illustrates a preferred embodiment of the primary conversion step of the present process. In this run, 100 grams of the pulverized coal described in Run A was charged to the same 1850 cc. autoclave. Also charged were 400 cc. water, 100 grams $\text{Na}_2\text{S}_2\text{O}_8$ 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 of the autoclave were removed. The water and the liquefied hydrocarbonaceous materials formed two separate phases upon settling of the mixture removed from the autoclave, and the two phases were separated by decantation. The hydrocarbonaceous phase was examined as follows. The hydrocarbonaceous phase was dried and extracted with benzene in a manner identical to that used in the previous run. It was found that 52 weight percent of the carbon in the original 100 grams of coal was present in the benzene soluble fraction. Thus, the conversion step employed in the process of the present invention provided a more than 70 percent greater conversion than the prior art conversions used in Runs A and B.

Run E

In order to demonstrate the necessity of employing a

reducing gas in the primary conversion step according to the present invention, a run was undertaken without the presence of a reducing gas, contrary to the process of this invention. In this run, 100 grams of coal, 400 cc. water, 100 grams of $\text{Na}_2\text{S}_2\text{O}_3$ and 7 grams of NH_4SH were placed in the same 1850 cc. autoclave as utilized in the previous runs. 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 settled, 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 run. It was found that essentially none of the coal had been converted to hydrocarbonaceous materials which could be extracted with benzene.

Run F

Run F illustrates a further preferred embodiment of the primary coal conversion step in the process of the present invention. In this run, 100 grams of the pulverized coal described in Run A, 400 cc. water, 100 grams of $\text{Na}_2\text{S}_2\text{O}_3$ and 100 cc. of 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 phase which formed when the contents removed from the autoclave were settled was separated by decantation and the hydrocarbonaceous phase was recovered. Before analysis, the hydrocarbonaceous phase was dried at 100°C. The hydrocarbonaceous phase was then extracted with benzene in the same analytical procedure as employed in the foregoing runs. The xylene solvent utilized in the conversion step was removed by evaporation during the drying operation. It was found that the benzene extractable hydrocarbonaceous materials contained 65 weight percent of the carbon in the original coal charged to the autoclave.

Run G

Run G illustrates another preferred embodiment of the primary coal conversion step in the process of the present invention. In this run, 100 grams of the pulverized coal described in Run A was placed in the 1850 cc. autoclave with 300 grams water, 100 grams of NaHSO_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 was released. The remaining contents of the autoclave were removed and settled and the water phase which resulted was separated by decantation. The hydrocarbonaceous phase was analyzed by drying and extraction with benzene in the identical procedure employed in the foregoing run. It was found that 73 weight percent of the carbon in the original coal charged to the autoclave was recovered in the benzene soluble hydrocarbonaceous materials.

Run H

Run H illustrates another preferred embodiment of

the primary coal conversion step in the process of the present invention. In this run, 100 grams of the coal described in Run A, 100 cc. water, 100 grams Na_2S and 100 cc. xylene were charged to the 1850 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 from the autoclave and settled, and the resulting water phase which formed was separated by decantation. The hydrocarbonaceous phase was examined as follows. The xylene solvent was removed by evaporation and the hydrocarbonaceous phase was 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 runs. It was found that 57 weight percent of the carbon in the original 100 gram charge coal was recovered in the benzene soluble extract fraction.

Run I

Run I illustrates another preferred embodiment of the primary coal conversion step in the process of the present invention. In this run, 100 grams of the pulverized coal described in Run A was placed in the 1850 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 of the autoclave were removed. After settling the mixture removed from the autoclave and decantation of the resulting water phase, the hydrocarbonaceous phase was examined by drying and extraction in a manner identical to that used in the previous runs. It was found that the benzene extractable fraction contained 53 weight percent of the carbon originally charged to the autoclave in the coal.

Run J

Run J illustrates a further preferred embodiment of the primary coal conversion step in the process of the present invention. In this run, 100 grams of the coal described in Run A was charged to the 1850 cc. autoclave with 100 cc. water, 50 grams NaHSO_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 of the autoclave were removed therefrom, and settled, and the resulting phase was separated by decantation. When the hydrocarbonaceous phase was examined by drying and extracting with benzene, it was found that the benzene extracted fraction of the hydrocarbonaceous phase contained 53 weight percent of the carbon in the original coal charged to the autoclave.

The foregoing example clearly illustrates the superior conversion achieved using the conditions and components according to the primary coal conversion step employed in the process of the present invention. The example illustrates a preferred mode of operation of the conversion step when a batch reaction scheme is

employed therefor. Modifications of the conversion step, for example, to a continuous type operation, will be apparent to those skilled in the art.

The hydrocarbonaceous phase which results from the conversion step is separated from the immiscible aqueous phase after the liquefaction operation by any conventional method for separating two immiscible phases, e.g., simple decantation, liquid centrifugation, or the like. The hydrocarbonaceous phase recovered therefrom is then contacted with liquid phase water to remove substantially all the remaining hydrophilic ash from the liquefied hydrocarbonaceous phase. The water utilized is admixed with the hydrocarbonaceous phase in an amount between about 10 weight percent and about 10,000 weight percent of the hydrocarbonaceous phase. Preferably, from about 1 part to about 20 parts of water, by weight, are used in the water washing step per part of the hydrocarbonaceous phase. The temperature and pressure maintained during the water contacting step are not critical, if the water employed is maintained in the liquid phase. Generally, good results are obtained when the water contacting step is performed at a temperature between about 10° and about 150°C. and a pressure between about atmospheric and about 25 atmospheres. A particularly preferred temperature range for conducting the water contacting step is between about 20° and about 100°C., and a particularly preferred pressure range for the water washing step is between about atmospheric and about 10 atmospheres. The water and hydrocarbonaceous phase are contacted for a time sufficient to allow substantially all the hydrophilic ash contained in the liquid hydrocarbonaceous phase to be removed therefrom and absorbed into the aqueous phase.

The water washing operation may be embodied in a batch type system or a continuous type system. In a batch operation, appropriate portions of water and the hydrocarbonaceous phase resulting from the conversion step are placed in a suitable vessel and contacted therein for a period of time sufficient to remove substantially all the hydrophilic ash from the hydrocarbonaceous material. Contact time is not critical, but best results are generally obtained in batch operations when a contact time between about 0.1 minute and about 100 minutes is utilized. A contact time between about 0.5 minute and about 10 minutes between the liquid water and the hydrocarbonaceous phase is particularly preferred. In a continuous type system, a water stream and a stream of the hydrocarbonaceous phase are continuously passed into a conventional vessel at appropriate weight ratios and admixed therein to remove hydrophilic ash from the hydrocarbonaceous stream. Suitable residence times are those generally maintained between about 0.1 minute and about 100 minutes.

The water-washing step may be performed in any conventional, container-type apparatus. Since the temperatures and pressures of operation of the water-washing step are not particularly severe, simple containers, preferably including some mixing or agitation means, are suitable for use.

After the hydrocarbonaceous phase provided from the solid coal conversion step and the water used in the washing step have been mixed and contacted for a suitable period, the resulting mixture is separated into two immiscible phases, an aqueous phase containing hydrophilic ash and a hydrocarbonaceous, substantially ash free phase. In most cases, the hydrocarbonaceous

phase recovered from the mixture will be a liquid material. The aqueous phase and hydrocarbonaceous phase in such cases are preferably separated by settling and decantation, but may also be separated by any similar known method for separating two immiscible liquid phases, such as centrifugation, use of a hydroclone, etc.

The aqueous phase separated from the hydrocarbonaceous phase after the water washing operation may simply be discarded or may be reused in the process after suitable purification for removal of inorganic solids, in particular, hydrophilic ash. After removal of such solids, this aqueous phase is suitable for use either in the primary, solid coal conversion step or in the water washing step.

EXAMPLE II

The following example illustrates a preferred embodiment of the water-washing step in the present process. One hundred grams of the same coal described in Run A of Example I was placed in a 1850 cc. rocking autoclave along with 100 cc. water, 100 grams of Na_2S and 100 cc. of xylene. The autoclave was sealed and pressurized to 50 atmospheres with hydrogen. The contents of the autoclave were heated to a temperature of 350°C. and agitated for 6 hours. The autoclave was then cooled and excess pressure was released. The mixture remaining in the autoclave was removed and settled, resulting in formation of an aqueous phase and a hydrocarbonaceous phase. The hydrocarbonaceous phase was separated from the aqueous phase by decantation and recovered. It was found to weigh 48.4 grams. The hydrocarbonaceous phase was then contacted with 500 grams of water in a stirred contactor at a temperature of 70°C. and a pressure of 1 atmosphere for a contact time of 5 minutes. The resulting mixture of immiscible hydrocarbonaceous and aqueous materials was then settled to form a hydrocarbonaceous phase and an aqueous phase. The hydrocarbonaceous phase and aqueous phase were separated by decantation. The aqueous phase was analyzed and found to contain 16.0 grams of ash material which was made up of 84 weight percent dry ash, 15 weight percent carbon and 1.7 weight percent hydrogen.

When the water-washing step has been completed and the hydrocarbonaceous phase recovered therefrom, the hydrocarbonaceous phase is then solvent extracted with an aromatic hydrocarbon solvent in order to recover a first hydrocarbonaceous product, one which is soluble in the aromatic solvent. Aromatic hydrocarbon solvents which are suitable for use in extracting the aromatic soluble product include benzene, lower alkylbenzenes, naphthalene, lower alkylnaphthalenes and hydroaromatics such as tetrahydronaphthalene and decahydronaphthalene. Examples of particular, suitable lower alkylbenzenes include toluene, xylenes, ethylbenzene, diethylbenzenes, cumene, sinene, methylisopropylbenzene, etc. In general, the suitable lower alkylbenzenes and lower alkylnaphthalenes are those having from one to six alkyl group substituents. The alkyl group substituents may each include carbon chains of from one to about five carbon atoms. There may be the same or different number of carbon atoms in each alkyl group substituent, where the alkylbenzene or alkylnaphthalene employed has plural alkyl group substituents. A mixture, in any proportion, of two or more of the suitable aromatic hydrocarbon solvents may be also utilized in the solvent ex-

traction operation. For example, a mixture of benzene with toluene, xylenes and ethylbenzene is a suitable solvent, as is a mixture of naphthalene and tetrahydronaphthalene, etc. The amount of the aromatic hydrocarbon solid which is utilized in the solvent extraction operation is generally between about 10 weight percent and about 10,000 weight percent of the hydrocarbonaceous phase recovered from the water-washing step. Preferably, the amount of the aromatic hydrocarbon employed in extracting the hydrocarbonaceous phase is between about one part and about 20 parts of the aromatic solvent, by way, per part of the hydrocarbonaceous phase to be extracted. The extraction step using the aromatic hydrocarbon solvent is performed at generally mild conditions of temperature and pressure. The temperature and pressure are not particularly critical to the performance of the extraction operation, as long as the aromatic solvent is maintained as a liquid during the operation, and in general, relatively lower temperatures and pressures are preferred because of ease of operation and lesser expenses. The extraction with the aromatic solvent may be performed in a broad range of conditions including a temperature of from about 10° to about 150°C. and a pressure of from about 21 atmospheres to about 25 atmospheres. Preferred extraction conditions in the extraction step using the aromatic solvent include a temperature between about 20° and about 100°C. and a pressure of from about 1 atmosphere to about 10 atmospheres.

Extraction of the hydrocarbonaceous phase with the aromatic solvent may be embodied in a batch type operation or a continuous type operation. In a batch type operation, a quantity of the relatively ash-free hydrocarbonaceous phase recovered from the water-washing step is contacted with the desired relative amount of the aromatic hydrocarbon solvent in a conventional, batch type solvent extraction system. Suitable conventional solvent extraction apparatus is well known in the art. For example, a conventional soxhlet extractor may be employed. The hydrocarbonaceous phase is extracted with the aromatic solvent for a time between about 0.1 minute and about 100 minutes. The components of the hydrocarbonaceous phase which are soluble in the aromatic hydrocarbon solvent are thereby taken into solution in the aromatic hydrocarbon, while the components of the hydrocarbonaceous phase which are insoluble in the aromatic solvent remain in a separate, raffinate phase. After the desired period of extraction time, the extraction mixture is removed from the extraction zone and separated into a solvent phase and a raffinate phase. The solvent and hydrocarbonaceous materials soluble therein may be separated from the insoluble hydrocarbonaceous raffinate by simple settling and decantation in most cases. The raffinate phase recovered after extraction with the aromatic hydrocarbon solvent is generally found to be in the form of a particular solid, so that the solvent phase can be separated from the solid raffinate by filtration, centrifugation, or other conventional means, if any of the raffinate remains in suspension in the solvent phase after settling of the extraction mixture. In a continuous type operation, a stream of the water-washed hydrocarbonaceous phase and a stream of the aromatic hydrocarbon solvent are passed continuously into a conventional, continuous type solvent extraction system at the desired relative rate, and the hydrocarbonaceous phase is extracted with the aromatic solvent for a residence

time between about 0.1 minute and about 100 minutes. Preferably, a residence time between about 0.5 minutes and about 10 minutes is utilized in a continuous type system, with the same time limitations being preferred in a batch type system.

The raffinate phase which remains after extraction of the water treated hydrocarbonaceous phase with the aromatic hydrocarbon solvent is a mixture of high molecular weight hydrocarbonaceous materials insoluble in aromatic hydrocarbons. The raffinate is generally solid at room temperature or at the generally mild conditions employed in the solvent extraction operations of the present process. The raffinate has a typical carbon content between about 75 weight percent and about 85 weight percent and a typical hydrogen content between about 6 weight percent and about 7 weight percent. This raffinate material is further extracted utilizing a solvent mixture of an aromatic hydrocarbon solvent and a polar hydrocarbonaceous solvent, as described hereinafter.

The aromatic solvent, containing the aromatic hydrocarbon soluble hydrocarbonaceous product, is further treated after separation from the raffinate in order to separate the hydrocarbonaceous product from the solvent. The boiling point of the aromatic solvent should be sufficiently below the initial boiling point of the hydrocarbonaceous product to insure that the product and solvent can be separated easily by fractionation, which is the preferred method for recovering the hydrocarbonaceous product from the solvent. The initial boiling point of the hydrocarbonaceous product is typically in the range from about 250° to about 400°C., so that separation from the preferred benzene or lower alkylbenzene solvents is not difficult. After fractionation or other conventional treatment to separate the aromatic hydrocarbon soluble product from the solvent, the solvent is preferably employed in further extraction of the water treated hydrocarbonaceous phase. Typically, the hydrocarbonaceous product recovered from the aromatic hydrocarbon extraction step has a carbon content of about 85–90 weight percent and a hydrogen content of about 7–8 weight percent. This aromatic soluble product can be utilized as a fuel, further refined by petroleum processing methods, or utilized as a petrochemical feedstock, etc.

The raffinate recovered from the first solvent extraction step is passed to a second solvent extraction step which employs a mixture of two distinct types of solvent. The solvent mixture utilized in the second extraction step is a mixture of about 50 weight percent to about 95 weight percent of an aromatic hydrocarbon and about 5 weight percent to about 50 weight percent of a polar hydrocarbonaceous component. The aromatic hydrocarbons which are suitable for use in the solvent mixture of the second extraction step include benzene, lower alkylbenzenes, naphthalene, lower alkyl naphthalenes and hydroaromatics such as tetrahydronaphthalene and decahydronaphthalene. Examples of particular suitable alkylbenzenes which may be utilized in a mixture include toluene, xylenes, ethylbenzene, diethylbenzenes, cumene, cymene, methylethylbenzene, methylisopropylbenzene, etc. In general, the suitable lower alkylbenzenes and lower alkyl naphthalenes are those having from one to six alkyl group substituents. The alkyl group substituents may each include carbon chains from one to about five carbon atoms. There may be the same or a different number of

carbon atoms in each alkyl group substituents, where the alkylbenzene or alkylnaphthalene employed in the solvent mixture has plural alkylgroup substituents. A mixture, in any proportions, of two or more of the suitable aromatic hydrocarbon compounds may also be utilized as the aromatic component of the solvent mixture. For example, a mixture of benzene with toluene, xylenes and ethylbenzene is a suitable aromatic component of the solvent mixture, as is a mixture of naphthalene and tetrahydronaphthalene. The polar hydrocarbonaceous component of the solvent mixture may be chosen from a wide range of hydrocarbonaceous compounds including lower alkyl sulfoxides, lower alkyl sulfones, pyridines, quinolines, phenol, lower alkylphenols, lower alkylamines, lower alkylformamides, lower alkylethers, of polyethyleneglycol and mixtures of two or more of the above listed types of compounds in any proportions. Those skilled in the art will recognize from the above listed examples of suitable hydrocarbonaceous components of the solvent that various other equivalent polar hydrocarbonaceous compounds may be selected for use in the solvent mixture; however, the exemplified hydrocarbonaceous compounds are preferred for use in the solvent mixture in the present process. As referred to above, the polar hydrocarbonaceous component of the solvent mixture utilized in a second extraction step may comprise from about 5 weight percent to about 50 weight percent of the solvent mixture. Preferably, the polar hydrocarbonaceous component of the solid mixture is from about 10 weight percent to about 30 weight percent of the solvent mixture.

The amount of the solvent mixture which is utilized in solvent extracting the raffinate from the first extraction step is between about 10 weight percent and about 10,000 weight percent of the hydrocarbonaceous phase recovered from the water-washing step. Preferably, the amount of the solvent mixture employed in extracting the raffinate is between about 1 part and about 20 parts of the solvent mixture, by weight, per part of the raffinate to be extracted in the second extraction step. The second extraction step utilizing the solvent mixture of an aromatic hydrocarbon and polar hydrocarbonaceous compound is performed at generally mild conditions of temperature and pressure. The temperature and pressure utilized in the extraction step are not particularly critical to successful operations, as long as the solvent mixture is maintained as a liquid during the operation, and, in general, relatively lower temperatures and pressures are preferred because of ease of operation and smaller expenses. The extraction with the solvent mixture may be performed in a broad range of conditions including a temperature of from about 10° to about 150°C. and a pressure of from about 1 atmosphere to about 25 atmospheres. Preferred extraction conditions in the extraction step using the mixture of an aromatic hydrocarbon and a polar hydrocarbonaceous material include a temperature between about 20° and about 100°C. and a pressure of from about 1 atmosphere to about 10 atmospheres.

Extraction of the raffinate from the previous extraction step with the solvent mixture of the aromatic component and polar hydrocarbonaceous component may be embodied in a batch type operation or continuous type operation. In a batch type operation a quantity of the raffinate from the previous extraction step is contacted with the desired relative amount of mixture of

the aromatic hydrocarbon component and polar hydrocarbonaceous component in a conventional, batch type solvent extraction system. Suitable conventional solvent extraction apparatus is well known in the art. For example, a conventional soxhlet extractor may be employed. The hydrocarbonaceous materials in the raffinate from the previous extraction step are extracted with the solvent mixture of the aromatic component and polar hydrocarbonaceous component for a time between about 0.1 minute and about 100 minutes. The components of the raffinate which are soluble in the mixture of the aromatic component and polar hydrocarbonaceous component are thereby taken into solution in the solvent, while the components of the raffinate which are insoluble in the solvent mixture remain in a separate, raffinate phase. After the desired period of extraction time, the extraction mixture is removed from the extraction zone and separated into a solvent phase and a second raffinate phase. In a continuous type operation, a stream of the raffinate from the previous extraction step and a stream of the solvent mixture of the aromatic hydrocarbon and polar hydrocarbonaceous compound are passed continuously into a conventional continuous type solvent extraction system at the desired relative rate, and the hydrocarbonaceous phase is extracted with the aromatic solvent for a residence time between about 0.1 minute and about 100 minutes. Preferably, a residence time between about 0.5 minute and about 10 minutes is utilized in a continuous type system, with the same time limitations being preferred in a batch type system. The solvent mixture and the hydrocarbonaceous materials which are soluble therein may be separated from the insoluble hydrocarbonaceous raffinate from the second extraction step by simple settling and decantation. The raffinate phase recovered from the second extraction step with the solvent mixture is typically in the form of a particulate solid, so that the solvent mixture and the hydrocarbonaceous product which is soluble therein can be separated from this solid raffinate by filtration, centrifugation, or other like conventional means if any of the solid raffinate materials remain in suspension in the solvent phase after settling and decantation of the extraction mixture.

The raffinate phase which remains after the second extraction step utilizing the solvent mixture of the aromatic hydrocarbon component and the polar hydrocarbonaceous component comprises a mixture of very high molecular weight hydrocarbonaceous materials, carbon, and a small amount of inorganic materials all of which are insoluble in the solvent mixture. The raffinate from the second extraction step is uniformly solid at room temperature and also at the generally mild extraction conditions employed in the second extraction step in the present process. The raffinate from the second extraction step has a typical carbon content between about 60 weight percent and about 80 weight percent and a typical hydrogen content between about 4.5 weight percent and about 6.5 weight percent. This second raffinate material may be utilized as a solid fuel similar to ordinary coal, if desired, or may be simply discarded.

The solvent mixture of the aromatic hydrocarbon component and polar hydrocarbonaceous component which contains the second hydrocarbonaceous product of the present process, is further treated after separation from the second raffinate in order to separate the

second hydrocarbonaceous product from the solvent mixture. The boiling point of the aromatic hydrocarbon component and the polar hydrocarbonaceous component of the solvent mixture utilized in the second extraction step should be chosen sufficiently below the initial boiling point of the second hydrocarbonaceous product to insure that the product and the solvent mixture can be separated easily by fractionation, which is the preferred method for recovering the second hydrocarbonaceous product from the solvent mixture. The initial boiling point of the second hydrocarbonaceous product produced by the second extraction operation is typically in the range from about 150° to about 400°C., so that separation from the preferred solvent mixture, comprising benzene and a polar hydrocarbonaceous component having a relatively low boiling point between about 80° and about 132°C. is not difficult. After fractionation or other conventional treatment to separate the solvent mixture from the second hydrocarbonaceous product soluble therein, the solvent mixture is preferably employed in further extraction of the raffinate from the first extraction step. Typically, the second hydrocarbonaceous product recovered from the second extraction step utilizing the solvent of the aromatic component and polar hydrocarbonaceous component has a carbon content of about 46 weight percent to about 60 weight percent and a hydrogen content of about 6 weight percent to about 8 weight percent. This second hydrocarbonaceous product may be utilized directly as a fuel, or preferably is further refined by petroleum processing methods such as hydrotreating, etc., in order that it may be upgraded to use in typical petroleum refining operations for producing gasoline and petrochemical feedstocks, etc.

The two products of the present process differ substantially in their properties and in their compositions. The product recovered from the first extraction operation, using an aromatic hydrocarbon solvent, is particularly suitable for catalytic treatment by methods such as those used in conventional petroleum refining operations. The primary utility of the product recovered from the first extraction is, thus, in providing hydrocarbon compounds for use, e.g., as motor fuel components. The product from the second extraction operation, using a solvent mixture of an aromatic hydrocarbon component and a polar hydrocarbonaceous component, is particularly suitable for treatment to recover various hydrocarbonaceous petrochemical compounds, such as those which are conventionally derived from coal in destructive distillation and like conventional conversion operations. The product from the second extraction step is particularly rich in oxygen-, nitrogen-, and sulfur-containing compounds, and may be treated, upon recovery from the present process, by fractionation or other known methods to recover the desired organic compounds.

I claim as my invention:

1. A process for producing hydrocarbonaceous liquid products from coal which comprises the steps of:

- a. contacting the coal, at a temperature of from about 150° to about 375°C. and a pressure of from about 10 to about 300 atmospheres for a contact time corresponding to from about 1 to about 600 minutes or a liquid hourly space velocity of from about 0.16 to about 1.0, with from about 100 weight percent to about 1000 weight 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 weight percent to about 1000 weight percent of a catalyst consisting essentially of a catalytic sulfur compound selected from the group consisting of alkali metal and ammonium sulfites, sulfides and thiosulfates, and separating the resulting mixture to provide a first hydrocarbonaceous phase and a first aqueous phase;

- b. contacting said first hydrocarbonaceous phase with from about 10 weight percent to about 1000 weight percent of water at a temperature of from about 10° to about 150°C. and a pressure of from about atmospheric to about 25 atmospheres for a contact time of from about 0.1 minute to about 100 minutes, and separating the resulting mixture to provide a second hydrocarbonaceous phase and a second aqueous phase;
 - c. admixing said second hydrocarbonaceous phase with from about 10 weight percent to about 1000 weight percent of a first solvent comprising an aromatic hydrocarbon at a temperature of from about 10° to about 150°C. and a pressure of from about atmospheric to about 25 atmospheres for a contact time of from about 0.1 minute to about 100 minutes, separating the resulting mixture to provide a first, liquid solvent phase comprising the first solvent and a first hydrocarbonaceous product and a first raffinate phase, and recovering the first hydrocarbonaceous product from the first solvent phase; and,
 - d. admixing said first raffinate phase with from about 10 weight percent to about 1000 weight percent of a second solvent comprising a mixture of from about 50 weight percent to about 95 weight percent of an aromatic hydrocarbon component and from about 5 weight percent to about 50 weight percent of a polar hydrocarbonaceous component at a temperature of from about 10° to about 150°C. and a pressure of from about atmospheric to about 25 atmospheres for a contact time of from about 0.1 minute to about 100 minutes, separating the resulting mixture to provide a second, liquid solvent phase comprising the second solvent and a second hydrocarbonaceous product and a second raffinate phase, and recovering the second hydrocarbonaceous product from the second solvent phase.
2. The process of claim 1 wherein said first solvent comprises a monocyclic aromatic hydrocarbon selected from the group consisting of benzene, lower alkylbenzenes, and mixtures thereof.
3. The process of claim 1 wherein said second solvent comprises a mixture of from about 50 weight percent to about 95 weight percent of a monocyclic aromatic hydrocarbon component selected from the group consisting of benzene, lower alkylbenzene, and mixtures thereof and from about 5 weight percent to about 50 weight percent of a polar hydrocarbonaceous component selected from the group consisting of lower alkylsulfoxides, lower alkylsulfones, pyridines, quinolines, phenol, lower alkylphenols, lower alkylamines, lower alkylformamides, lower alkylethers of polyethylene glycol, and mixtures thereof.
4. The process of claim 1 wherein said catalytic sulfur compound is an alkali metal sulfide.

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5. The process of claim 1 wherein said catalytic sulfur compound is an alkali metal sulfite.

6. The process of claim 1 wherein said catalytic sulfur compound is an alkali metal thiosulfate.

7. The process of claim 1 wherein said coal is contacted, in Step (a), with from about 1 weight percent

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to about 1000 weight percent of an aromatic hydrocarbon selected from benzene, lower alkylbenzenes, naphthalene, lower alkylnaphthalenes and mixtures thereof, in addition to said water, said reducing gas and said catalyst.

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