COAL LIQUEFACTION PROCESS BY THREE-
STAGE SOLVENT EXTRACTION

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ABSTRACT OF THE DISCLOSURE

Coal is converted into valuable liquid products utilizing a three-stage solvent extraction process. The coal is first contacted with a conventional coal solvent such as tetrahydrophthalene, with the resulting liquid coal extract separated with a first aliphatic solvent to produce an asphaltene-free extract to the resultant residue being treated with a light aromatic solvent to further produce a second coal extract. Each of the extract materials are separately refined, and produced are coal products free of solid material without the utilization of intricate filtration principles.

BACKGROUND OF THE INVENTION

This invention relates to a process for converting coal to liquid products. In particular, this invention relates to a process for converting coal to liquid products through the use of three stages of solvent separation, with each stage involving a different solvent.

Coal represents a valuable source of energy to the world, particularly since it appears that known coal and lignite deposits are an order of magnitude greater than those of known petroleum reserves. As these petroleum reserves are depleting and the need for liquid hydrocarbons increases, it becomes imperative that methods for converting coal to liquid products be developed.

Several methods of converting coal to more valuable liquid products are known in the art. One of these methods employs gasification techniques such as destructive distillation to effect the conversion of coal to liquid products. Another recently developed technique involves a high pressure hydrogenation technique. Still another recently developed technique involves solvent extraction of the liquid hydrocarbons from the coal, a technique which involves recovery from the solid coal extract to the liquid coal extract and conversion to a liquid extract to liquid products.

In the prior art solvent extraction processes, crushed, rather finely divided particulate coal, is contacted with a select solvent mixture which serves, to at least in part, as a hydrogen donor as well as a solvent for the conversion of the hydrogen deficient coal to liquid products. Following this extraction step, the prior art completely filters out the undissolved solid particles, recovering therefrom a solid-free, liquid coal extract-solvent mixture. The liquid coal extract is then recovered, typically by fractionalization, and is further processed by conventional hydrocarbon processing techniques including coking, cracking, hydrogenation, etc., to convert the liquid coal extract into a more valuable and useful liquid coal products.

One of the main difficulties encountered in the prior art solvent extraction processes is in the separation of the liquid coal extract from the undissolved coal, ash, and other solid inorganic particulate matter typically contained in raw coal. Under the conditions utilized in the extraction step, the solid coal dispersed in the liquid phase is in a very finely divided physical state which, because of its fine particle size and the physical properties of the solvent-liquid coal extract, renders physical separation difficult, if not impossible. The extremely fine solid particles are also not readily removed by settling or centrifuging techniques and as a result cause problems in further catalytic processing of the extracted coal product. These fine particles are capable of almost complete removal by intricate filtration techniques but, unfortunately, these techniques are not completely satisfactory in a practical economic sense since the paper, fabric, or cake used for the complete filtration and solids removal is readily obstructed and requires continuous replacement.

Another problem confronting the prior art in the production of liquid coal products from coal is the selectivity associated with the solvent extraction since the solvents typically heretofore utilized, accomplished essentially total solution of the coal without regard to selectivity for the higher value, higher hydrogen content liquid coal components or the lower value lower hydrogen content coal components. In essence, the solvents typically utilized in coal extraction indiscriminately produce a coal extract containing both high hydrogen content and low hydrogen content components. Both of these high hydrogen and low hydrogen content components require further processing but under different refining conditions to efficiently convert the coal to valuable liquid products such as gasoline.

Accordingly, a further problem encountered in the art is the separation and the refining of these differing hydrogen content liquid coal components.

SUMMARY OF THE INVENTION

Accordingly, it is an object of this invention to produce an efficient method of converting coal to liquid products by utilizing a three stage solvent extraction technique. It is a particular object of this invention to provide a solvent extraction process wherein undissolved coal, ash and inorganic materials present at the termination of the coal extraction reaction, in intimate admixture with the liquid coal products and excess solvent are readily removed from the liquid coal products without the need for intricate separation and filtration techniques and wherein further, the higher value high hydrogen components present in the liquid coal extract are readily separable from the lower value, low hydrogen content components, with each of these components being recovered and further processed to produce an upgraded liquid coal product in an efficient novel manner.

It has now been discovered that the dissolved coal components extracted from the coal in conventional solvent extraction processes utilizing conventional coal solvents such as tetrahydrophthalene, which is a relatively high hydrogen component (trade trademark, Tetralin) and present in admixture with unconverted coal, ash and excess solvent is readily separated from such material into distinct hydrocarbon fractions in a manner which allows complete conversion of the extract coal, materials, in an efficient processing manner to liquid products. This coal extract present after conventional solvent extraction operations contains hydrocarbons of varying hydrogen to carbon atomic ratios with these hydrocarbons existing in relatively distinct hydrogen to carbon atomic ratio ranges. There exists a hydrogen rich segment which has a hydrogen to carbon atomic ratio of from about 1.1:1 to about 1.3:1 and referred to herein as the hydrogen rich components. There also exists hydrogen lean asphaltene components which have a hydrogen to carbon atomic ratio of about 0.6:1 to about 1.0:1. Within this range of hydrogen-lean asphaltene components, the hydrogen to carbon atomic ratio segment having a hydrogen to carbon atomic ratio of about 0.8:1 to about 1.0:1. Thus the term relatively high or low hydrogen to carbon atomic ratio refers to those identified components within the hydrogen-lean asphaltene segment which are separate and distinct from the identified high hydrogen-rich components. Therefore, the terminology "relatively high" and "rela-
Highly low refers to the relative hydrogen to carbon atomic ratios in the hydrogen lean asphaltene range only. Thus, it is seen that there are three distinct classes of hydrocarbons with varying hydrogen to carbon atomic ratios existing in the coal extract, in addition to the undissolved coal material. These distinct components are separated from each other and the undissolved coal and ash by treating the coal extraction product with a selective light aliphatic solvent such as heptane. This solvent selectively removes the high hydrogen content components including the first coal solvent from the hydrogen lean asphaltene components and undissolved coal and ash for further refining and processing. If desired, although not necessary, at least a portion and even all of the first coal solvent may be removed say fractional distillate before treating the liquid coal products with the aliphatic solvent to lower the amount of material to be so treated. Thus, it is within the scope of the present invention to extract either the total liquefaction product or a portion produced by removal of the first coal solvent. Therefore, the "coal extraction product" includes the liquid coal products whether in admixture with the first coal solvent or not. From the resultant hydrogen lean asphaltene residue, the components having a relatively high hydrogen to carbon atomic ratio are separated from the relatively lower hydrogen to carbon atomic ratio material by treating this residue with a selective monocyclic aromatic, cyclohexane or ketone solvent. This extract, relatively free of solid particulate material is then separately hydrorefined to produce an improved hydrogen content liquid fuel. The resultant extraction residue contains the majority of the undissolved coal and ash present in the original coal-solvent product as well as the lowest hydrogen to carbon atomic ratio asphaltene components. By carbonizing this material to yield a coal tar distillate and char material, the original coal extract materials are recovered in an efficient, new manner. This is important because the physical and chemical characteristics of each of the described coal extract segments require different processing techniques, to be described in detail hereinafter, to complete, in an efficient manner, the conversion of coal to a valuable liquid product.

In an embodiment, this invention relates to a process for the conversion of solid coal containing coal particles into liquid products which comprises the steps of: (a) contacting said coal with a first coal solvent capable of converting coal to liquid products in a coal liquefaction zone, under extraction conditions, and under hydrogen pressure to produce a liquefaction zone product comprising a liquid coal extract of hydrogen-rich components and hydrogen-lean asphaltene phase distillate of relatively high and low hydrogen to carbon atomic ratios in admixture with unconverted coal and ash particles; (b) contacting, said liquefaction zone product, with a second, light aliphatic solvent, selective for said hydrogen-rich coal extract components, in a first extraction zone, under extraction conditions, to provide a first extraction zone effluent comprising a hydrogen-rich, second solvent, liquid phase essentially free of asphaltenes, solid coal and ash particles and a hydrogen-lean, asphaltene coal extract phase containing unconverted coal and ash particles; (c) contacting separat, from said hydrogen-rich phase, at least a portion of said hydrogen-rich coal extract, under refining conditions in a first refining zone to provide a refined liquid coal product; (d) separating, from said high hydrogen to carbon atomic ratio asphaltene phase at least a portion of said third solvent to provide a relatively high hydrogen to carbon atomic ratio asphaltene containing coal extract; (e) hydrorefining said high hydrogen to carbon atomic ratio asphaltene coal extract at hydrorefining conditions in a second refining zone to provide a hydrogen enriched coal product; and, (f) carbonizing, at least a portion of said low hydrogen to carbon atomic ratio asphaltene phase to provide a coal tar distillate and a solid char material.

In another embodiment this invention relates to a process for the conversion of solid coal containing coal particles into liquid products which comprises the steps of: (a) contacting a coal solvent with a first coal solvent capable of converting coal to liquid products in a pulverization zone maintained at pulverization conditions, including a temperature of about 0°C. to about 200°C., a pressure of about atmospheric to about 100 p.s.i.g., a solvent-to-coal weight ratio of about 0.2 to about 10, said pulverization conditions sufficient to provide a pulverized coal-solvent product wherein at least a portion of said coal is reduced to about at least —8 Tyler Standard Screen Size; (b) passing at least a portion of the coal-solvent product to a coal liquefaction zone maintained under coal liquefaction conditions and under hydrogen pressure to provide a liquefaction zone product comprising a liquid coal extract comprised of hydrogen-rich components and hydrogen-lean asphaltene components of relatively high and low hydrogen to carbon atomic ratios in admixture with unconverted coal and ash particles, wherein in an excess of 50 weight percent of the MAF coal is converted to hydrogen-rich components and hydrogen-lean asphaltene components of relatively high and low hydrogen to carbon atomic ratios; (c) contacting, said liquefaction zone product with a second, light aliphatic solvent selective for said hydrogen-rich coal extract components, in a first extraction zone, under extraction conditions to provide a first extraction zone effluent comprising a hydrogen-rich second solvent, liquid phase essentially free of asphaltenes, solid coal and ash particles and a hydrogen-lean, asphaltene coal extract phase containing unconverted coal and ash particles; (d) separating, from said hydrogen-rich phase, at least a portion of said second selective solvent to provide a hydrogen-rich coal extract; (e) refining, at least a portion of said hydrogen-rich coal extract, under refining conditions in a first refining zone to provide a refined liquid coal product; (f) contacting, said hydrogen-rich asphaltene containing phase with a third selective solvent, under extraction conditions in a second extraction zone to provide a second extraction zone effluent comprising a relatively high hydrogen to carbon atomic ratio asphaltene coal extract, third solvent phase and an unconverted coal, ash and relatively low hydrogen to carbon atomic ratio asphaltene phase; (g) separating, from said high hydrogen to carbon atomic ratio asphaltene phase at least a portion of said third solvent to provide a relatively high hydrogen to carbon atomic ratio asphaltene containing coal extract; (h) hydrorefining said high hydrogen to carbon atomic ratio asphaltene coal extract at hydrorefining conditions in a second refining zone to provide a hydrogen enriched coal product; and, (i) carbonizing, at least a portion of said low hydrogen to carbon atomic ratio asphaltene phase to provide a coal tar distillate and solid char material.

In further, more limited embodiments the foregoing first coal solvent is a polycyclic naphthenic-aromatic such as tetrahydroanthracene, the second light aliphatic solvent is a C8-C12 paraffin-aromatic such as heptane, and the third selective solvent is either a monocyclic aromatic such as cyclohexane, a naphthenic such as cyclohexane, or a ketone. Further limited embodiments and a definitive discussion of processing and refining conditions will be found in the following more detailed description of the present invention.
DESCRIPTION OF PREFERRED EMBODIMENTS

The coal preferably utilized in the process of the present invention is bituminous coal such as Pittsburgh seam coal. More preferably this bituminous coal has a high volatile content and typically greater than about 20% by weight of the moisture and ash free (MAF) coal.

Preferred solvents for use in the coal liquefaction zone of the process of the present invention as a first coal solvent capable of converting coal to liquid products are those which are of the hydrogen donor type and which are partially hydroprocessed such as the naphthenic-aromatic hydrocarbons. Preferably, the first coal solvent is one which is in the liquid phase at the hereinafter described temperatures and pressures utilized in the extraction and/or pulverization step of this process. Typically, these solvents are employed as mixtures of hydrocarbons and are derived at least in part from the intermediate or final products obtained from subsequent processing of the liquid coal extract following the practice of this invention.

Typically these first coal solvents utilized in the coal liquefaction zone boil between 200° and 350° C. Examples of the preferred naphthenic-aromatic liquefaction zone solvents are the di- or tetra-hydro derivatives of anthracene and phenanthrene. Also preferred are the aromatic hydro derivatives of naphthalene such as tetrahydro-naphthalene (Tetralin). As used herein, naphthenic-aromatic solvents refer to polycyclic compounds wherein at least one of the rings of the compound is aromatic and at least one of these rings is not aromatic. These compounds are also commonly referred to as polynuclear compounds.

Also suitable for utilization within the process of the present invention are the completely aromatic polycyclic compounds such as biphenyl, the methyl naphthalenes, the dimethyl naphthalenes, mixtures of phenanthrene and anthracene, etc., as well as their alkyl derivatives. Other types of solvents which may be utilized as a first coal solvent in the coal liquefaction zone include phenolic compounds such as phenols, cresols, xylenols, particularly when used in admixture with any of the foregoing solvents, particularly tetrahydro naphthalene. In general, the partially hydrogenated aromatic compounds referred to hereinafter as naphthenic-aromatic compounds are preferred over the completely aromatic polycyclic hydrocarbons. In any event the solvent suitable for use in the coal liquefaction zone must be a solvent having the capability of depolymerizing particulate coal under extraction conditions as hereinafter defined, and capable of converting the coal to liquid products.

A particularly preferred embodiment of the process of the present invention includes the use of a first coal solvent of the type hereinafter described for use in the coal liquefaction zone during the pulverization of the coal whereby a relatively coarse size coal is reduced to granular coal of optimum size for extraction in the coal liquefaction zone. This preferred embodiment is predicated on the theory that having the presence of a hydrogen rich solvent during the pulverization of the coal results in a substantial increase in the efficiency of the operation and in many cases results in a decreased use of the first coal solvent in obtaining the same quality and quantity of liquid coal extract.

The benefit gained from having a first coal solvent present during the pulverization of the coal appears to be the result of an extremely reactive shear point during the grinding and coating of the coal. In other words, the shear site is extremely reactive and hydrogen can be transferred to the coal at this site more easily when the solvent is present than when the coal is pulverized in the absence of the solvent.

In addition, the small particles of coal thus sheared away from a large coal lump are not only exposed to a highly reactive shear site but also immediately expose a relatively large coal surface area to the solvent enabling and facilitating the penetration of the solvent into the small particle which is necessary for optimum conversion of the coal to liquid coal products.

Apparatus suitable for use in pulverizing lump or coarse size coal as practiced in the process of the present invention may be of any type known to those skilled in the art. Conventional ball mills or rod mills may be used with satisfactory results. Preferably, the particular pulverization apparatus utilized is capable of pulverizing size coal in the presence of significant quantities of liquid solvent without difficulty. Those skilled in the art are familiar with the kind of apparatus required for processing wet solids and the crushing and grinding thereof so that no detailed discussion of these apparatus need be presented herein. The prime requirement for crushing and grinding of coarse lump coal is that the coarse coal, usually having an average particle diameter in excess of 0.08 inch and typically about 0.25 to about 2 inches must be processed and reduced in size to an average particle diameter equivalent to at least a —14 Tyler Screen Size. As used herein the term “Tyler Screen Size” refers to all sizes to the commercial Tyler Standard Screens. The correlation between Tyler Screen Size and particle size can be found in most standard reference books such as Perry’s Chemical Engineers Handbook, Fourth Edition, pages 21—51.

The conditions utilized during the pulverization of the coarse size coal may be varied widely in practicing the present invention according to the desires of those skilled in the art. The temperature may be varied over a relatively broad range from essentially ambient temperatures to a relatively high processing temperature. It is distinctly preferred however, for the practice of this invention that the temperature of the coal and first coal solvent be maintained at a temperature such as from about 0° C. to about 200° C. to prevent agglomeration of the coal on the pulverization equipment. The pressure in a similar manner may be varied over an extremely wide range of from atmospheric pressure to about 1000 p.s.i.g. with a preferred pressure being from about 50 p.s.i.g. to about 200 p.s.i.g. This pressure during the pulverization of the coal is preferably maintained, at least in part, by a hydrogen-containing gas. It is preferred that the pressure be of such degree to maintain the first coal solvent in the liquid phase during the pulverization and subsequent liquefaction steps.

The operation of the pulverization equipment is preferably performed in a manner such that the oversized material; that is, that material greater in size than about a —8 to a —10 Tyler Screen Size is separated and returned to the pulverization apparatus for further reduction in particle size. The utilization of such a close circuit technique is well known to those skilled in the art and it is preferred for the practice of the present invention to insure a most optimum and complete utilization of the solid particulate coal. Unless otherwise stated a close circuit recycle operation of the pulverization equipment will be deemed inherent in the practice of the present invention. It is to be noted that the separation of the coarse size coal from the smaller coal particles, even in the presence of the first coal solvent is readily accomplished without difficulty since only the coarse, larger size coal particles are removed and recycled. The finer particulate coal is not to be removed since it is to be subjected to further extraction in the coal liquefaction zone. This size coal removal can be readily accomplished by gravity-type separations including hydrocyclones, centrifuges, etc.

The amount of first coal solvent to be utilized in converting coal to liquid products according to the process of the present invention and including the amount of solvent utilized, if at all, during the pulverization of the coal as well as the amounts used in the coal liquefaction zone generally will range from about 0.2 to about 10 lbs. of
solvent per pound of coal. Satisfactory results are obtained in utilizing approximately a 1:1 to 3:1 solvent to coal weight ratio. In the practice of the preferred embodiment of this invention, conditions utilized during the pulverization of the particulate coarse coal should be chosen so that the coarse coal is reduced in size to at least a 8 Tyler Screen Size.

The extraction of coal by means of solvent extraction is basically a partial conversion of the coal ash as well as an extraction is effected with hydrogen, which is preferably transferred from the solvent and there is, in addition, a solution phenomena which actually dissolves the coal which has accepted the hydrogen from the coal solvent. Therefore, as used herein the terms "liquid coal extract," "extracted coal fraction," "extracted coal" or other words of similar import are intended to include the liquid product which is obtained from the various steps utilized in the practice of the process of the present invention and generally will be described on the basis of being solvent free, even though a portion of the liquid coal extract obtained following a first solvent extraction and a second solvent extraction of the coal liquid zone product comprises hydrocarbons suitable for use as a selective solvent in the coal liquefaction zone. Preferably, the practice of the present invention in both the coal liquefaction zone and subsequent extraction zones is performed under conditions which increase the kinetics of the solvation and extraction reactions while maintaining the various coal and solvent components therein in primarily the liquid phases, although in some cases it may be desirable to practice either of these steps in the presence of a vaporized solvent using a gaseous extraction technique.

The coal liquefaction zone of the process of the present invention includes a liquefaction step wherein the coal is either initially contacted with a first coal solvent, if none were present, during the pulverization of the coal, or more preferably the coal in the pulverization step effluent where solvent was utilized during the pulverization of the coal, is fedly extracted with coal solvent to form a liquid coal extract. This zone also includes separation means, if present, for removal of excess coal solvent. The operating conditions for the coal liquefaction zone include a temperature of about 300 °C. to about about 500 °C., a hydrogen pressure from about atmospheric to about 10,000 p.s.i.g., a solvent to coal weight ratio from about 10 to about 100, and a residence time from about 30 seconds to about 5 hours, and preferably so correlated as to dissolve in excess of 50% by weight of the MAF coal and to convert this coal to extracted liquid products.

It is to be noted that the temperature and/or pressure utilized during the coal liquefaction step may be the same, higher, lower, or any different configuration desired by those skilled in the art over those conditions maintained during the pulverization of the coal. It is preferred however in the practice of the process of the present invention to maintain the temperatures during the coal liquefaction step at substantially higher than those temperatures and pressures utilized during the pulverization of the coal.

Since the purpose of the coal liquefaction zone, including the process of the preferred embodiment wherein a first coal solvent is utilized during the pulverization of the coal, to complete the conversion of the solid coal particles into a liquid coal extract, it is desirable to add to this liquefaction step additional solvent over that added in the pulverization step, a hydrogen containing gas, and/or a hydrogenation catalyst to the coal liquefaction step. If such a catalyst is required or desired, it may be of a conventional hydrogenation type and may be used either homogeneously or heterogeneously. Thus, this catalyst may be introduced into either the coal liquefaction step or coal pulverization step in admixture with the liquid first coal solvent or with the solid particulate coal.

Those skilled in the art having knowledge of the characteristics of the coal, solvent, utilized, properties required for the final coal product can derive from the teachings presented herein the desirability to use any or all of these enumerated features during the pulverization and/or coal liquefaction.

Examples of conventional hydrogenation catalysts which may be used in the coal liquefaction zone include those utilizing cobalt, molybdenum, nickel, tungsten, zirconium chloride, vanadium sulfide, and other hydrogenation catalysts capable of operation in the presence of sulfur containing coal charge stocks. These catalysts are applicable to the solvent coal system environment maintained in the coal liquefaction zone, including a slurry catalyst system and a homogeneous catalyst system. The hydrogenation in the coal liquefaction zone generally accomplishes the transfer of hydrogen directly to the coal molecules, the transfer of hydrogen to hydrogen donor molecules and the transfer of hydrogen from donor molecules to coal molecules and in any combination of the foregoing. In any event the resultant coal liquefaction zone product may have a hydrogen to carbon ratio of about 0.5 to about 1.5 and a product density of about 0.8 to about 1.0. The hydrogenation in the coal liquefaction zone includes the combination of hydrogenation and also includes hydrocracking reactions considering the hydrogen status of the coal.

The liquid coal extract obtained from the coal liquefaction zone contains compounds of widely varying physical characteristics since the coal liquefaction is relatively non-segmental. However, the coal extract may be characterized as being composed of essentially three fractions of segments, namely a separate hydrogen-rich fraction and a hydrogen-rich asphaltenate fraction which is subdivided into a separate fraction having a relatively high hydrogen to carbon atomic ratio and a separate fraction having a relatively low hydrogen to carbon atomic ratio as determined in relation to each other and to the components in the so called hydrogen-rich fraction. As used herein, the term "hydrogen-rich asphaltenate components" or words of similar import are intended to include those components which are basically insoluble in light aliphatic solvents, such as pentane, hexane or heptane. These hydrogen lean asphaltenate components, as a whole group have an average molecular weight of about 600 to 2000 and contain about 5% to about 8% by weight of sulfur. Within this hydrogen lean fraction, however, are two distinct classes of hydrocarbons, one having a relatively higher hydrogen to carbon atomic ratio than the other, with the higher distinct fraction having a hydrogen to carbon atomic ratio of about 0.8:1 to 1.0:1 and the lower hydrogen to carbon atomic ratio distinct fraction having an atomic ratio of about 0.5:1 to about 0.7:1. These
lower hydrogen to carbon atomic constituents are further characterized as being substantially insoluble in benzene. Because of these differences in chemical properties, these separate fractions require different processing techniques, as will be developed later, to further convert the liquid coal to valuable coal products such as gasoline, etc.

On the other hand as used herein, the term, "hydrogen-rich components" or other words of similar import include those components which are basically soluble in light aliphatic solvents such as pentane, hexane or heptane. These hydrogen-rich components typically have a molecular weight of less than one from about 300 to about 1000 and have a hydrogen content on a weight basis in excess of 5% and typically have a hydrogen content from about 6 to 9 weight percent. In addition to the foregoing distinctions, the hydrogen-rich components are essentially free of organometallic compounds which exist in a concentration of about 0.01 to about 0.05 wt. percent in the hydrogen-lean asphaltene fraction. The above characteristics of the three major fractions contained in the liquid coal extract are, of course, related to some extent by the solvent extraction conditions utilized in the coal liquefaction zone including the depth of extraction (or conversion) employed in that zone. It is to be recognized that the characteristics and yields of the hydrogen lean asphaltene components contained in the coal extract will be influenced not only by the extraction conditions but also by the type of coal utilized as a feed to this process.

Suitable solvents for use in the first extraction zone of the process of the present invention wherein the liquid coal extract produced in the coal liquefaction zone is first extracted with a second selective solvent, belonging to the broad class of compounds known as light aliphatic hydrocarbons and include the C_6-C_9 aliphatic paraffins either as a mixture of such compounds or as an individual species. Preferred solvents include pentane, hexane and heptane, particularly normal heptane. It is to be noted by those skilled in the art that these classes of secondary aliphatic extraction solvents have no substantial effect on the conversion of solid coal to a liquid coal extract. Therefore, it is a requirement of the present process that the coal liquefaction zone utilize those solvents which are applicable to the conversion of solid coal particles to the liquid form and the first extract zone extraction solvent be limited to those solvents which serve to separate the hydrogen rich components from the hydrogen lean asphaltene fraction in admixture with undissolved coal, ash, etc., contained in the liquid coal extract produced in the coal liquefaction zone. In other words, it has been found that light aliphatic solvents such as a C_6-C_9 alkanes including their various isomeric forms, are selective for the hydrogen-rich components to the substantial rejection of the hydrogen-lean asphaltene components and, as importantly, the undissolved coal and ash residue. The exact choice of a selective second solvent depends on the extraction conditions desired in the first extraction zone. For practical purposes the temperature selected for the first extraction zone should be at least 30°C below the critical temperature of the first stage extraction zone solvent in order to maintain the components with the proper pressure in primarily the liquid phase. In general the temperatures utilized for the first stage extraction zone should not exceed 300°C.

A second solvent suitable for utilization in the first extraction zone of the process of the present invention includes an unreformed naptha hydrocarbon stream, namely a hydrocarbon stream having a boiling range of from about 200 to about 300°F and containing less than about 20% by volume aromatic hydrocarbons.

The operating conditions to be utilized in the first stage extraction zone utilizing second solvents such as heptane include a temperature of about 50°C to about 300°C and more preferably from about 50 to about 150°C, a hydrogen pressure from about 100 p.s.i.g. to about 1000 p.s.i.g. and more preferably from about 350 p.s.i.g. to about 700 p.s.i.g., a solvent to feed ratio from about 0.5 to about 5 by weight, a total liquid hourly space velocity from about 0.5 to about 5 ore more, and in the presence of a hydrogen containing gas in an amount from about 500 standard cubic feet to about 5,000 standard cubic feet per barrel of liquid feed present in the first extraction zone. These conditions are sufficient to substantially separate on a selective basis the hydrogen-rich components from the hydrogen-lean asphaltene components, coal, and ash contained in the liquid coal feed passed to the first extraction zone from the coal liquefaction zone.

In any event, after the liquid coal extract-solid coal mixture is contacted with the foregoing second light aliphatic solvent a two-phase liquid system results. An upper phase containing the hydrogen-rich liquid coal components (typically 40-60% of the liquid coal formed) dissolved in the second light aliphatic solvent and essentially free of undissolved coal, ash etc. (i.e. less than 0.005 wt. percent solids) is separated from a lower phase containing the hydrogen-lean liquid coal asphaltene components in admixture with any undissolved coal ash, catalyst (if any) etc. This hydrogen-lean asphaltene phase containing undissolved coal etc. is removed as a slurry from the first extraction zone for further processing and extraction with a third selective solvent in a second extraction zone as will be described hereinafter.

The upper rich solvent phase from the first extraction zone comprising the second light aliphatic solvent having dissolved therein the hydrogen rich components is further processed by means well known to those skilled in the art, such as fractionation, hydrogenation, hydrocracking, etc. in order to separate and convert the hydrogen rich liquid coal extract into more valuable products such as relatively light aliphatic hydrocarbons, relatively heavy hydrocarbons, chemicals, fuels, etc., the utility of which are well known to those skilled in the art. As previously mentioned, a portion of these separated products in the liquid coal extract may be satisfactorily utilized as at least a portion of the first coal solvent utilized in the coal liquefaction zone.

Preferably, at least a portion of the second light aliphatic solvent and particularly the majority is removed from the hydrogen rich components before these components are further refined in a refining zone at refining conditions. While it is within the scope of this invention to catalytically hydrogenate the components in the second extract, it is preferred, in order to produce a more valuable liquid fuel such as gasoline, to hydrocrack these components. This hydrocracking is preferably effected by a three stage process, the first being a sulfur, nitrogen and oxygen removal stage, the second being a hydrocracking stage followed, if desired, by a reforming of the low-octane constituents thus produced. These conversions may be performed by means well known to the art in conventional fixed-bed desulfurization, denitrogenation, deoxygenation, hydrocracking, reforming, etc. units since the hydrogen rich coal extract produced in the first extraction zone by the second light aliphatic solvent extraction zone and or as an individual solid materials and coke forming hydrogen-lean asphaltene materials.

The hydrogen-lean asphaltene containing phase removed from the first extraction zone and containing asphaltene components of relatively high hydrogen to carbon atomic ratios in admixture with undissolved coal, ash, etc., is then contacted with a third selective solvent at extraction conditions in a second extraction zone to provide a second extraction zone effluent comprising a relatively high hydrogen to carbon atomic ratio asphaltene coal extract-third solvent phase and an unconverted coal, ash and relatively low hydrogen to carbon atomic ratio asphaltene phase. Suitable solvents for use in this second extraction zone belong to the broad class of compounds known as ketones, monocyclic aromatics, and their naphthenic derivatives.
Examples of ketones which may be used satisfactorily in the second extraction zone of the present invention include acetone, methylketone, methylnitrite ketone, methylisobutyl ketone, dibutyl ketone etc. Other solvents applicable, as stated, include the mononuclear aromatic hydrocarbons such as benzene, toluene, xylenes etc. and their corresponding naphthenic derivatives such as cyclohexanes. As in the case of the secondary extraction solvents used in the first extraction zone the tertiary solvents utilized in the present second extraction zone have no substantial effect on the conversion of the solid coal to a liquid coal extract. Therefore, it is a requirement of the present invention, as hereinafter stated, that the coal liquefaction zone utilize those solvents which are applicable to the conversion of solid coal particles to the liquid form and that the first stage and second stage extraction zone solvents be limited to those solvents which separate the various components produced during the coal liquefaction step. In other words, it has been found that the ketones, mononuclear aromatic, cyclohexane and alkyl cyclohexanes are selective for those hydrogen-lean asphaltene components having a relatively high hydrogen to carbon atomic ratio when compared to the other hydrogen-lean asphaltene components to the substantial rejection of the relatively low hydrogen to carbon atomic ratio asphaltene components and undissolved coal and ash. The exact choice of a second selective solvent depends on the extraction conditions desired in the second extraction zone. For practical purposes, the temperature selected for the second extraction zone should be at least 30°C below the critical temperature of the third selective solvent in order to maintain the components with the proper pressure in primarily the liquid phase. In general the temperatures utilized for the second stage extraction zone should not be in the case of the first stage extraction zone, exceed 300°C.

The operating conditions to be utilized in the second stage extraction zone utilizing a third selective solvent, namely a ketone, mononuclear aromatic or cyclohexane solvent include conditions similar to those conditions utilized in the first extraction zone utilizing a second selective solvent namely a temperature from about 35°C to about 300°C and more preferably from about 50 to about 150°C, a hydrogen pressure from about 100 p.s.i.g. to about 1000 p.s.i.g. and more preferably from about 350 p.s.i.g. to about 700 p.s.i.g., a solvent feed ratio from about 0.5 to about 5 by weight, liquid hourly space velocity from 0.5 to about 5 and in the presence of a hydrogen containing-gas, in an amount, added from about 500 standard cubic feet to about 5,000 standard cubic feet per barrel of liquid feed present in the second extraction zone. These conditions are sufficient to substantially separate on a selective basis those hydrogen-lean asphaltene components having a relatively high hydrogen to carbon atomic ratio from those hydrogen-lean asphaltene components having a relatively low hydrogen to carbon atomic ratio as contained in the liquid feed passed to the second extraction zone from the first extraction zone.

In any event, after the liquid coal extract-solid coal mixture is contacted with the foregoing third selective solvent a two-phase liquid system results. An upper phase containing the asphaltene components with a relatively high hydrogen to carbon atomic ratio (typically 30 to 50%) of the liquid coal formed in the coal liquefaction zone and about 80 to 95% of the hydrogen-lean asphaltene components present in the effluent from the first extraction zone containing very minor amounts of undissolved coal, ash etc. having an extremely small particle size such as less than 0.01 micron is separated from a lower phase containing the hydrogen lean asphaltene components having a relatively lower hydrogen to carbon atomic ratio, in comparison to those components contained in the upper phase, and in admixture with essentially all of the undissolved coal, ash etc. present both in the liquefaction zone effluent and extraction zone one effluent. This low hydrogen to carbon atomic ratio asphaltene solid coal slurry is removed from the second extraction zone for further processing as will be hereinafter described.

From the upper phase recovered from the second extraction zone, a portion, and preferably all of the third selective solvent is removed to yield a liquid coal product containing the richest in terms of hydrogen content, of the hydrogen-lean asphaltene components. In addition, there is a very minor amount (i.e., less than 0.05 wt. percent) of finely divided coal, ash and other solid particulate matter. Further the recovered asphaltene contain themselves a number of organometallic compounds.

To convert the hydrogen-lean asphaltene components to more valuable hydrocarbon products such as gasoline, these components must be first hydrogenated since hydrocracking or fluid catalytic cracking of these asphaltene without hydrogenation would result in great amounts of coke and, in general, insufficient conversions. Unfortunately, these hydrogen-lean asphaltene compounds cannot be processed in conventional fixed-bed catalytic processes because of the rapid catalyst deactivation caused by the organometallic compounds and the fine particulate matter such as ash contained therein. Further, the ash like material, gradually creates deposits in the catalyst bed which eventually cause the catalyst bed to plug and/or have excessively high pressure drops rendering practical hydrocarbon processing uneconomical and subsequent removal of the catalyst difficult. Further, even if such fixed bed operations as utilized in the first refining zone could be utilized in hydrogenate asphaltene, the hydrogenation of these asphaltene is best effected separately from the processing of the hydrogen rich components recovered from the first extraction zone because of the different processing conditions and catalysts required to efficiently hydrogenate and otherwise upgrade each fraction.

Accordingly, the higher hydrogen to carbon atomic ratio asphaltene constituents are to be processed in a non-fixed bed catalytic hydroreforming zone designated herein as a second refining zone such as a slurry process or an ebullating bed process at hydroreforming conditions. As used herein "hydroreforming" includes the myriad of hydrogen consuming reactions such as desulfurization, denitrogenation and hydrocracking as well as hydrogenation, with such reactions often proceeding simultaneously. Suitable catalysts for use in this hydroreforming zone are to contain a catalytically active metal matrix by controlling and hydrogenation activity such as the metals of Group V-B, VI-B, and VIII of the Periodic Table. Of these, preferred are vanadium, chromium, iron, cobalt, nickel, niobium, molybdenum, tantalum and/or tungsten.

Group VIII noble metals are undesirable only because of economic considerations, while these catalytic metals may be deposited on known porous support materials such as alumina, silica-alumina, zeolitic aluminosilicates, etc., it is preferred to use unsupported versions of these metals since the supported catalysts will readily deactivate and are not readily regenerable.

Therefore, it is preferred for the process of the present invention to utilize active catalyst composites of finely divided unsupported sulfides of the foregoing metals, particularly the Group V-B metals, namely tantalum, niobium, and vanadium sulfides. Particularly effective and preferred are the non-stoichiometric vanadium sulfides having a molar ratio of sulfur to vanadium not less than about 1.8:1 such as V₂S₃ or V₃S₅. This vanadium sulfide catalyst actually does not have a single specific sulfur to vanadium ratio but rather is a mixture of vanadium sulfides having a sulfur to vanadium mole ratio in the aforesaid range.

Vanadium sulfides may be prepared in any manner known to the art, the preferred method not being essential to the present invention. For example, vanadium pentoxide may be reduced with sulfur dioxide and water to yield a solid vanadyl sulfate hydrate. Treatment of this sulfate with hydrogen sulfide at a temperature of about 300°C.
forms vanadium tetrasulfide which, when reduced with hydrogen at the same temperature, produces vanadium sulfide to be slurried with the coal oil extract in the hydrorefining zone of the present invention.

The precipitation of vanadium sulfides to be slurried with the aforesaid carbonaceous coal oil feed stock is within the range of about 0.4% to about 10% by weight, calculated as an elemental metal. Excessive concentrations have no beneficial effect and preferred are concentrations within the range of about 3 to about 7% by weight. The vanadium exists as a multiplicity of sulfides such as V₂S₃, V₂S₅, V₃S₈, V₅S₁³, V₇S₁₄ and V₈S₁₅ and, which during the hydrorefining reaction are converted to one or more of these and other forms. While the hydrorefining reaction may be effected in a down-flow fashion, it is preferred to effect this reaction in a second refining zone by contacting the described coal extract with a finely-divided, unsupported vanadium sulfide catalyst in an upflow manner at hydrorefining conditions which include a hydrogen pressure of about 1000 p.s.i.g. to 4000 p.s.i.g. and preferably, about 1500 to 3500 p.s.i.g. and a temperature of about 300 °C. to about 500 °C. The hydrogen is preferably admixed with the coal extract prior to the hydrorefining zone in an amount of about 10,000 to about 100,000 s.c.f./bbl. of said charge stock.

The effluent from this hydrorefining zone is continuously withdrawn, separating therefrom upgraded hydrocarbons by known means and which hydrocarbons are suitable for further processing. If desired, in the hereinbefore described first refining zone. This converted material withdrawn has an upgraded hydrogen to carbon atomic ratio of about 1.1:1 to about 1.4:1 and is free from asphaltene and finely divided coal and ash. The unconverted material along with carbonaceous catalysts, etc., is withdrawn and recycled to form a portion of the feed to the hydrorefining zone with a drop in the withdrawn from this converted material to control the solids level in the zone and to recover and continuously regenerate a portion of the catalyst.

To maximize the amount of liquid coal products produced from the extracted coal, the relatively low hydrogen to carbon atomic ratio asphaltene withdrawn from the second extraction zone in admixture with unconverted coal and ash are carbonized by a low temperature carbonization step, i.e. distillation of the coal material in the temperature range of 400 °C. to about 800 °C. This method of conversion is conducted by methods well known in the art not in the present invention herein, nor is the exact method of operation critical to the process of the present invention. Recovered is a liquid coal tar product free of solid particulate matter and having an enriched hydrogen content in comparison to the char produced and the hydrocarbons carbonized, namely this liquid distillate product has a hydrogen to carbon atomic ratio of about 0.6:1 to about 1.1:1. This material may then be passed to either the hereinbefore described first or second refining zone for further hydrogenation and conversion to liquid products such as gasoline. Since this material is free of solid particulate matter and organometallic compounds, it is suitable for processing, by means known to the art, in fixed bed conversion units such as described for the first refining zone. The highly carbonaceous char or coke material produced is withdrawn and utilized in the process of the present invention either as a fuel source for heat or for conversion with hydrogen to carbon monoxide. It is the subject of this process by the water-gas reaction. It is preferred that this char or coke material have a volatile content of about 3% to 30% by weight.

In summary, therefore, the process of the present invention thus entails reducing coal to a fine, particulate size either in the presence or absence of a first coal solvent converting the coal in the presence of a first coal solvent to a liquid coal product of hydrogen rich components and hydrogen-lean asphaltene components; extracting the hydrogen-rich components with a second light aliphatic solvent and refining these components in a first refining zone; extracting from the hydrogen-lean asphaltene components, the components with a relatively high hydrogen to carbon atomic ratio with a third selective aromatic, ketone or naphtha solvent and hydrorefining the resultant extract in a second refining zone; and, carbonizing the lower hydrogen to carbon atomic ratio asphaltene components to produce a coal tar distillate which may be refined in either the first or second refining zone. Of importance is that this process eliminates the need for any intermedia extractions heretofore utilized for the separation of unconverted coal from the liquid coal products.

The process of the present invention may be more fully understood by reference to the appended schematic flow diagram illustrating the practice of this invention. For sake of brevity and a more clear understanding, this diagram is presented, showing only the functional sequences and not the specific apparatus utilized, since such are within the general knowledge of those skilled in the art.

**BRIEF DESCRIPTION OF THE DRAWING**

Referring to the appended drawing, coarse size coal having an average particle diameter generally in excess of 0.08 inch and less than 2.5 inches is introduced to liquefaction zone 4 via line 1. A suitable first coal solvent having an enriched hydrogen content such as tetrahydro-naphthenilene and hydrogen gas enter the liquefaction zone via lines 2 and 3 respectively. As depicted, this liquefaction zone includes a pulverization step and an actual coal liquefaction step. In this pulverization step, the coal in admixture with coal solvent and maintained under hydrogen pressure is pulverized by conventional means under pulverization conditions including a temperature of about 100 °C., a hydrogen pressure of 70 p.s.i.g. and a solvent to coal weight ratio of about 2, to reduce the coarse size coal to an average particle diameter between about 0.08 to 0.04 inch. After removal of unpulverized, oversized coal, the resultant coal solvent-coal mixture is passed to a liquefaction step wherein the coal is actually dissolved and/or extracted by the coal solvent at a temperature of about 500 °C. and in the presence of about 1000 to about 100,000 standard cubic feet of hydrogen per barrel of coal solvent-coal mixture present therein. At the completion of this liquefaction step, excess coal solvent and hydrogen are removed, although not necessary, by conventional means; the means will be apparent to those skilled in the art. The residue stream comprising unconverted coal, ash and other solid particulate matter in admixture with the hydrogen-rich components with a second light aliphatic solvent and refining these components in a first refining zone; extracting from the hydrogen-lean asphaltene components, the components with a relatively high hydrogen to carbon atomic ratio with a third selective aromatic, ketone or naphtha solvent and hydrorefining the resultant extract in a second refining zone; and, carbonizing the lower hydrogen to carbon atomic ratio asphaltene components to produce a coal tar distillate which may be refined in either the first or second refining zone. Of importance is that this process eliminates the need for any intermedia extractions heretofore utilized for the separation of unconverted coal from the liquid coal products.

Within extraction zone 1, the coal liquefaction zone effluent 5 is contacted with a second light aliphatic solvent such as heptane, entering via line 11, under extraction conditions including a temperature of about 150 °C., a solvent to extraction zone feed weight ratio of about 3, a pressure of about 500 p.s.i.g. and preferably in the presence of added H₂ gas, added by means not shown at a rate of about 100 s.c.f./bbl. of extraction zone 1 feed. Within this zone 6, the second solvent selectively removes the hydrogen-rich liquid coal components and excess coal solvent, if present, from the hydrogen lean asphaltene liquid coal products and undissolved coal, ash, etc. to form a solid and asphaltene free, solvent-hydrogen rich liquid-coal phase which after removal of the excess solvent is, withdrawn via line 7. This stream is then passed via line 7 to refining zone 8, the presence of H₂ entering line 8, the liquid coal is hydrorefined to more valuable products which are removed via line 10. Preferably this hydrorefining in refining zone 9 comprises a first stage desulfurization and dehydrogenation followed by a second stage hydrocracking, both stages comprising fixed-bed catalytic processes.

A residue stream comprising unconverted coal, ash and other solid particulate matter in admixture with...
hydrogen-lean asphaltene components having a segment with a relatively high hydrogen to carbon atomic ratio and a segment with relatively low hydrogen to carbon atomic ratio in asphaltenes, as described, if also is withdrawn from extraction zone I 6 via line 12 and passed via line 12 to extraction zone II 14 wherein this residue is extracted with a third selective solvent entering via line 13. This solvent comprising either ketone, monomeric aromatic or cyclohexane solvent, preferably a monomeric aromatic solvent such as benzene, is contacted with extraction zone I residue at extraction conditions including a temperature of about 150° C., a solvent to extraction zone feed ratio of about 3, a pressure of about 500 p.s.i.g. and preferably in the presence of hydrogen gas added by means not shown at a rate of about 100 s.c.f./bbl. of extraction zone II 14 feed. Within extraction zone II 14, the third selective solvent selectively removes the asphaltene constituents with a relatively higher hydrogen to carbon atomic ratio from the relatively lower hydrogen to carbon atomic ratio constituents to form a solvent-higher hydrogen to carbon atomic ratio asphaltene liquid coal phase relatively free of solid material and containing a very minor amount (0.01 wt. percent) of material less than .01 micron in size after removal of excess solvent. This material is removed and passed via line 15 to refining zone II 17 where, in presence of hydrogen added via line 16, the high hydrogen to carbon atomic ratio constituents are hydrogen-refined, preferably by contacting in an upflow manner with an unsupported vanadium sulfide catalyst at hydrogen refining conditions including a temperature of about 425° C., a hydrogen pressure of about 3,000 p.s.i.g., and a hydrogen to feed ratio of about 15,000 s.c.f./bbl. of feed. Upgraded hydrogenated product is withdrawn via line 18 and may, if desired, be further refined in refining zone I 9.

Extraction zone II 14 residue comprising the low hydrogen to carbon atomic ratio asphaltene constituents in admixture with unconverted coal ash, etc. is removed and passed via line 19 to carbonization zone 20 where, at carbonization conditions including a temperature of 590° C., this material is carbonized to form a liquid coal tar distillate product withdrawn and passed via line 21, and further processed in refining zone II 17. Alternatively, this coal tar distillate may be passed directly to refining zone I 9. A highly carbonaceous char solid residue is withdrawn and passed via line 22 to hydrogen generation zone 23 wherein by means well known to the art, the water-gas shift reaction is effected and hydrogen gas suitable for utilization in the hydrogen consuming steps of the present invention is withdrawn via line 24. Other gaseous materials are removed via line 25 and unreacted char is removed via line 26.

The process of the present invention for the conversion of coal into liquid products is further illustrated by the following illustrative example. This example is, however, not presented to limit the process of this invention, which is to be limited only by the appended claims, but to further illustrate the hereinafter described embodiments.

ILLUSTRATIVE EMBODIMENTS

A 1,000 gram sample of Pittsburgh Seam, bituminous coal containing 5.83 weight percent hydrogen and 84.7 weight percent carbon was crushed to 100 mesh and smaller size, mixed with 3.60 grams of tetrahydroammonium thiolate solution and placed in an Eppeombok Colloid mill for further size reduction of the particulate coal. After 5 hours operation at room conditions a coal-solvent mixture wherein all of the coal was less than 100 microns in diameter and about 75% less than two microns in diameter was produced. The resulting colloid-solvent mixture was then subjected to the following extraction conditions to convert the coal into liquid coal products:

Temperature—430° C.
Pressure—2000 p.s.i.g.

Solvent/coal wt. ratio—3/1
Hydrogen/coal-solvent mixture (s.c.f./bbl.) ratio—4000
Coal residence time—0.5 hour

The resultant liquid extraction product, after removal of coarse coal particles in excess of 10 microns in diameter and removal by fractionation of excess solvent possessed the following properties:

Molecular weight — 503
Percent hydrogen, wt. — 7.18
Percent carbon, wt. — 87.70
Percent solids (coal, ash, etc.), wt. — 0.50

The liquid coal extraction product was then mixed with heptane at a 5:1 heptane to liquid coal weight ratio and subjected to an extraction at 150° C. for a period of 0.5 hour. At the completion of this period, the mixture was allowed to cool to room temperature and settle with two phases forming a hydrogen-rich lower (heptane) phase and a hydrogen lean asphaltene lower phase. These phases are separated, with 51% of the original coal extract contained in the upper heptane phase. This liquid coal product, after removal of the heptane solvent is free of solid particulate matter and contains 8.65 wt. percent hydrogen, and has an average molecular weight of about 370. The lower residue containing phase contains 6.53 wt. percent hydrogen, 83.30 wt. percent carbon, has an average molecular weight of about 780 and contains all of the solids present in the original, filtered coal-liquid extract product.

This lower residue phase was then admixed with benzene at a 5:1 benzene to residue weight ratio and subjected to extraction at 150° C. for a period of 0.5 hour. At the completion of this period, the mixture is allowed to cool and settle with two phases forming, an upper benzene phase containing the asphaltene components of the higher hydrogen to carbon atomic ratio, relatively free of solid particulate matter (i.e. 0.01 wt. percent of particles less than .01 micron in diameter) and a lower phase containing the lower hydrogen to carbon atomic ratio asphaltene components. The liquid coal contained in the upper phase was 43% of the original liquid coal extract or 88% of the heptane insoluble residue. This material after benzene removal has an average molecular weight of 680, contains 6.75 wt. percent hydrogen and 83.01 wt. percent carbon. The insoluble residue, comprising 6% of the original coal extract or 12% of the heptane insolubles has an average molecular weight of 1500 contains 5.64 wt. percent hydrogen and 86.07 wt. percent carbon.

The asphaltenes contained in the benzene phase after removal of the benzene, is processed in a conventional pilot plant for up-flow slurry processing in the presence of 6 wt. percent vanadium sulfide catalyst, expressed in elemental form, at a pressure of 3,000 p.s.i.g., a liquid hourly space velocity of 0.5, and a temperature profile from reactor bottom to reactor top of about 380° to about 435° C. A hydrogen circulation rate of about 15,000 s.c.f./bbl. is also maintained. Recovered is a product having a weight percent hydrogen of about 9.66 and a weight percent carbon of about 89.80. This product is comparable to the coal product obtained in the heptane extraction and is suitable for further processing if desired in the same manner as this heptane soluble fraction.

The low hydrogen to carbon atomic ratio asphaltene fraction containing the unconverted coal was subjected to a low temperature carbonization at 590° C., recovering therefrom a coal tar distillate having a molecular weight of about 590 containing 84.8 wt. percent carbon and 7.9 wt. percent hydrogen and suitable for further hydroprocessing in the same manner as either the high hydrogen to carbon atomic ratio asphaltene fraction or the hydrogen rich heptane soluble fraction.

From the foregoing example, the beneficial import of the process of the present invention is readily ascertainable by those trained in the art. Not only are the more
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17 readily processed hydrogen-rich components separated from the hydrogen-lean asphaltene components with each fraction separately processed to insure maximum utilization of each fraction, but each of these fractions are obtainable essentially free of solid coal and ash particles, thus avoiding the cumbersome filtration type processes required commonly with the solid removal heretofore utilized by the art. Similar results are obtained utilizing alternative solvents as hereinafter described in this specification.

I claim as my invention:

1. A process for the conversion of solid, ash-containing coal particles into liquid products which comprises the steps of:

(a) contacting said coal with a first coal solvent capable of converting coal to liquid products in a coal liquefaction zone, under extraction conditions, and under hydrogen pressure to produce a liquefaction zone product comprising a liquid coal extract of hydrogen-rich components and hydrogen-lean asphaltene components of relatively high and low hydrogen to carbon atomic ratios in admixture with unconverted coal and ash particles;

(b) contacting said liquefaction zone product with a second, light aliphatic solvent, selective for said hydrogen-lean asphaltene extract components, in a first extraction zone, at extraction conditions, to provide a first extraction zone effluent comprising a hydrogen-rich, second solvent, liquid phase essentially free of asphaltenes, solid coal and ash particles and a hydrogen-lean asphaltene coal extract phase containing unconverted coal and ash particles;

(c) separating, from said hydrogen-rich phase, at least a portion of said second selective solvent to provide a hydrogen-rich coal extract;

(d) refining, at least a portion of said hydrogen-rich coal extract, under refining conditions in a first refining zone to provide a refined liquid coal product;

(e) contacting said hydrogen-lean asphaltene containing phase with a third selective solvent at extraction conditions in a second extraction zone to provide a second extraction zone effluent comprising a relatively high hydrogen to carbon atomic ratio, asphaltene coal extract, third solvent phase and an unconverted coal, ash and relatively low hydrogen to carbon atomic ratio asphaltene phase;

(f) separating from said high hydrogen to carbon atomic ratio asphaltene phase at least a portion of said third solvent to provide a relatively high hydrogen to carbon ratio asphaltene containing coal extract;

(g) hydrotreating said high hydrogen to carbon atomic ratio asphaltene coal extract at hydrotreating conditions in a second refining zone to provide a hydrogen enriched coal product; and,

(h) carbonizing, at least a portion of said low hydrogen to carbon atomic ratio asphaltene phase to provide a coal tar distillate and a solid char material.

2. The process of claim 1 further characterized in that said first coal solvent is a poly cyclic naphthenic-aromatic compound.

3. The process of claim 2 further characterized in that said compound is tetrahydrobenzene.

4. The process of claim 1 further characterized in that said second light aliphatic solvent is a C₅-C₉ paraffin.

5. The process of claim 4 further characterized in that said paraffin is a heptane.

6. The process of claim 1 further characterized in that said third selective solvent is a monocyclic aromatic or a cyclohexane.

7. The process of claim 6 further characterized in that said solvent is a C₅-C₉ aromatic hydrocarbon.

8. The process of claim 1 further characterized in that said third selective solvent is a ketone.

9. The process of claim 1 further characterized in that said hydrotreating in said second refining zone comprises contacting said coal extract with a finely divided, unsupported vanadium sulfide catalyst in an upflow manner and said hydrotreating conditions include a hydrogen pressure of from about 1,000 to about 4,000 p.s.i.g., a temperature of about 300°C, to about 500°C, and a hydrogen to coal extract ratio of about 10,000 s.c.f./lb. of coal at 150°F/C/lb.

10. A process for the conversion of solid ash containing coal particles into liquid products which comprises the steps of:

(a) contacting coarse size coal with a first coal solvent capable of converting coal to liquid products in a pulverization zone maintained at pulverization conditions, including a temperature of about 0°C, to about 200°C, a pressure of about atmospheric to about 100 p.s.i.g., a solvent to coal weight ratio of about 0.2 to about 10, said pulverization conditions sufficient to provide a pulverized coal-solvent product wherein at least a portion of said coarse coal is reduced to about at least —8 Tyler Standard Screen Size;

(b) passing at least a portion of said coal-solvent product to a coal liquefaction zone maintained under coal liquefaction conditions and under hydrogen pressure to provide a liquefaction zone product comprising a liquid coal extract of hydrogen-rich components and hydrogen-lean asphaltene components of relatively high and low hydrogen to carbon atomic ratios in admixture with unconverted coal and ash particles wherein an excess of 50 weight percent of the MAF coal is converted to hydrogen-rich components, and hydrogen-lean asphaltene components of relatively high and low hydrogen to carbon atomic ratios;

(c) contacting said liquefaction zone product with a second, light aliphatic solvent selective for said hydrogen rich coal extract components, in a first extraction zone at extraction conditions comprising a liquid coal extract comprising of hydrogen-rich components and hydrogen-lean asphaltene components of relatively high and low hydrogen to carbon atomic ratios, liquid phase essentially free of asphaltenes, solid coal and ash particles and a hydrogen-lean asphaltene coal extract phase containing unconverted coal and ash particles;

(d) separating, from said hydrogen-rich phase, at least a portion of said second selective solvent to provide a hydrogen-rich coal extract;

(e) refining at least a portion of said hydrogen-rich coal extract, under refining conditions in a first refining zone to provide a refined liquid coal product;

(f) contacting said hydrogen-lean asphaltene containing phase with a third selective solvent, at extraction conditions in a second extraction zone to provide a second extraction zone effluent comprising a relatively high hydrogen to carbon atomic ratio asphaltene coal extract, third solvent phase and an unconverted coal, ash and relatively low hydrogen to carbon atomic ratio asphaltene phase;

(g) separating from said high hydrogen to carbon atomic ratio asphaltene phase at least a portion of said third solvent to provide a high hydrogen to carbon atomic ratio asphaltene containing coal extract;

(h) hydrotreating said high hydrogen to carbon atomic ratio asphaltene coal extract at hydrotreating conditions in a second refining zone to provide a hydrogen enriched liquid-coal product; and,

(i) carbonizing at least a portion of said low hydrogen to carbon atomic ratio asphaltene phase to provide a coal tar distillate and a solid char material.

11. The process of claim 10 further characterized in that said first coal solvent is a polycyclic naphthenic-aromatic compound.
12. The process of claim 11 further characterized in that said compound is tetrahydronaphthalene.

13. The process of claim 10 further characterized in that said second light aliphatic solvent is a C$_4$–C$_9$ paraffin.

14. The process of claim 13 further characterized in that said paraffin is a heptane.

15. The process of claim 10 further characterized in that said third selective solvent is a monocyclic aromatic or a cyclohexane.

16. The process of claim 15 further characterized in that said solvent is a C$_5$–C$_9$ aromatic hydrocarbon.

17. The process of claim 10 further characterized in that said third selective solvent is a ketone.

18. The process of claim 10 further characterized in that said hydrorefining in said second refining zone comprises contacting said asphaltene containing coal extract with a finely divided unsupported vanadium sulfide catalyst in an upflow manner and said hydrorefining conditions include a hydrogen pressure of from about 1,000 to about 4,000 p.s.i.g., a temperature of about 300 to about 500° C. and a hydrogen to coal extract ratio of about 10,000 s.c.f./bbl. to about 100,000 s.c.f./bbl.

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