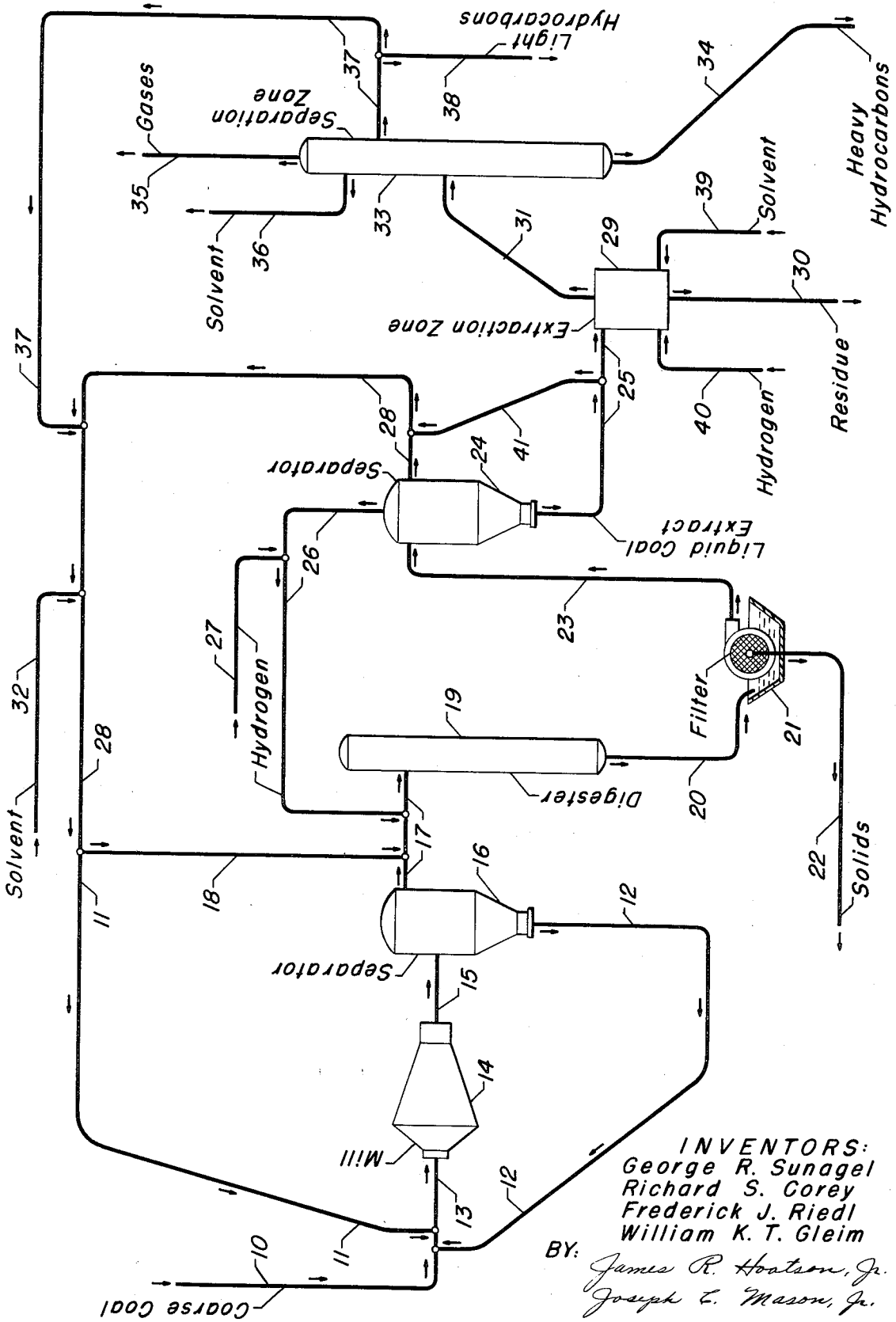
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METHOD FOR LIQUEFYING COAL

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METHOD FOR LIQUEFYING COAL

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ABSTRACT OF THE DISCLOSURE

A two-stage solvent extraction method for converting solid coal into liquid coal extract. The first stage uses the conventional solvents, such as polyaromatic hydrocarbons, alkylnaphthalenes, anthracene oil, or partially hydrogenated aromatics as for instance, Tetralin. The liquefied coal stripped of the solvent is then extracted with a ketone to produce a hydrogen-rich extract fraction and a hydrogen-lean extract phase. The hydrogen-rich fraction is recovered and used as a source for valuable chemicals and liquid fuels. The hydrogen-lean fraction may be used for plant fuel and/or as a source for additional hydrogen through conversion by the "water-gas" reaction.

BACKGROUND OF THE INVENTION

This invention relates to a solvent extraction method. It also relates to a method for liquefying coal using selective solvents. It particularly relates to a two-stage solvent extraction method for converting solid coal into liquid coal extract.

It has long been known that hydrocarbon gases, liquids, pitch, and the chemicals derived from or allied to these hydrocarbons, may be obtained in some form from coal which is mined from the earth. Usually, the prior art has employed destructive distillation or other gasification processes for the conversion of coal into these more valuable and useful products. Recently, the prior art has developed high pressure hydrogenation techniques to convert coal into valuable liquid products. Still more recently, methods involving solvent extraction techniques have been offered by the prior art for obtaining useful fuels and chemicals from coal wherein, broadly, the crushed coal is contacted with a selective solvent which acts at least in part as a hydrogen-donor for supplying sufficient hydrogen to the hydrogen deficient coal to aid in converting solid particulate coal to a liquid phase.

Following the solvent extraction step, the prior art schemes have generally utilized various product recovery procedures, such as hydrogenation of the liquid coal extract, for increasing its value and utility, together with retorting or coking of the residual materials obtained from the solvent extraction step to still further convert these coal derived products into more useful and valuable products.

One of the main difficulties in the liquefaction of coal using the solvent extraction process is in the separation step following extraction, i.e. the separation of the undissolved coal and inorganic material from the liquid. The prior art has attempted to make this separation by filtration methods using a pre-coated filter at a temperature which approaches atmospheric temperature. However, the prior art methods for separating the insoluble material from the liquid coal extract have been for the most part unsatisfactory in the commercial sense.

It is also known by the prior art that the solvent extraction method is basically non-selective. In other words, the solvent which is utilized to convert the coal into liquid coal extract generally accomplishes substantially total solution of the solid coal without regard to any selectivity

as to more valuable or less valuable components contained therein. Thus, when solid coal is dissolved with the conventional high boiling aromatic type solvent, it is technically very difficult to separate the resulting liquid coal extract from the insoluble materials contained therein both organic and inorganic. Basically, these aromatic type solvents dissolve the coal indiscriminately thereby producing a liquid coal extract containing components with a low hydrogen content as well as components with a high hydrogen content.

Therefore, since it is clear to those skilled in the art that the vast mineral reserves of bituminous coal represent an extremely important supply of energy, it would be desirable to improve upon the prior art processes, particularly the solvent extraction process, in order to render it more selective for the more desired valuable components and to reduce the cost of obtaining typical petroleum-type products from coal.

SUMMARY OF THE INVENTION

Accordingly, it is an object of this invention to provide a method for the liquefaction of coal whereby valuable hydrocarbon products may be obtained therefrom.

It is a specific object of this invention to provide an improved method for subjecting pulverized coal to solvent extraction utilizing a novel two-stage solvent extraction technique.

It is another specific object of this invention to provide an improved method for liquefying coal via solvent extraction whereby more valuable hydrogen-rich components are obtained as a separate product stream from the hydrogen-lean components contained in the basic liquid coal extract in a facile and economical manner.

This invention basically comprises a method aspect, although system aspects will be noticeable to those skilled in the art. In accordance with the practice of one embodiment of the method aspect, there is provided a method for liquefying solid particulate coal which comprises the steps of: (a) contacting said coal with a selective first solvent under conditions sufficient to convert said coal into liquid coal extract containing hydrogen-rich components and hydrogen-lean components; (b) separating the liquid coal extract from undissolved coal and from at least a portion of said first solvent; (c) contacting said separated liquid coal extract from step (b) under extraction conditions with a second solvent selective for said hydrogen-rich components; and, (d) recovering said hydrogen-rich components and said hydrogen-lean components as separate product streams.

Another embodiment of this invention includes the method hereinabove wherein said first solvent comprises aromatic hydrocarbons and said second solvent comprises a ketone.

A still further embodiment of this invention includes the method hereinabove wherein the extraction conditions of step (c) include the presence of a hydrogen-containing gas.

In other words, the method of the present invention utilizes a novel two-stage solvent extraction technique wherein in the first stage crushed coal is contacted with an aromatic hydrocarbon solvent to produce a liquid coal extract dissolved in the solvent. The extract is then separated, at least in part, from the solvent and subsequently contacted with a different type selective solvent in order to separate the hydrogen-rich components from the hydrogen-lean components. These separated components are then recovered as separate product streams.

DETAILED DESCRIPTION OF THE INVENTION

The coal preferred for use in the practice of the present inventive method is of the bituminous type, such as Pittsburgh seam coal. More preferably, however, the

bituminous coal is a high volatile content coal having a volatile content greater than about 20% by weight of the m.a.f. coal (moisture and ash-free coal).

Suitable solvents for use in the first stage extraction step of the present invention are those which, preferably, are of the hydrogen-donor type and which are at least partially hydrogenated, such as the naphthenic-aromatic hydrocarbons. Preferably, the first stage solvent is one which is in liquid phase at the recommended temperature and pressure for the extraction and/or pulverization step. Mixtures of hydrocarbons are generally employed and, preferably, are derived at least in part from the intermediate or final products obtained from subsequent processing following the practice of this invention.

Typically, these first stage solvent hydrocarbons or mixtures of hydrocarbons boil between about 260° C. and 425° C. Examples of suitable first stage solvents are tetrahydronaphthalene (Tetralin), Decalin, biphenyl, methylnaphthalene, dimethylnaphthalene, mixtures of phenanthrene and anthracene, etc. Other types of solvents which may be added to the preferred first stage solvents of this invention for special reasons include phenolic compounds, such as phenols, cresols, and xylenols. It is also to be recognized that in some cases, it may be desirable during a subsequent separation step, typically, prior to the second stage extraction operation, to add an anti-solvent, such as saturated paraffinic hydrocarbons, such as n-hexane, to aid in the precipitation of tarry and solid residue from the liquid coal extract of the invention.

However, in the search of a suitable solvent for the first stage liquefaction zone, it must be recognized that this solvent should have the ability to transfer hydrogen to the pulverized coal during this liquefying step. In other words, it is a requirement of this invention that in the absence of added hydrogen-containing gas that the rich solvent leaving the first stage extraction zone having liquid coal extract dissolved therein, have a reduced hydrogen content compared to the hydrogen content of the lean solvent which is added to the first stage extraction zone, usually in admixture with the feed coal.

A particularly preferred embodiment of this invention includes the use of a selective solvent of the type described above for use in the first stage extraction zone during the pulverization step whereby relatively coarse size coal is reduced to granular coal of optimum size for extraction. This preferred embodiment is predicated on the theory that having the presence of a hydrogen-rich solvent during the pulverization step 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 stage solvent for obtaining the same quality and quantity of liquid coal extract.

With respect to the benefit gained from having the solvent present during the pulverization step, it is believed that at the point of shear for the crushing and grinding of the coal, the shear site is extremely reactive and hydrogen, therefore, can be transferred into that site more easily than if the coal is pulverized prior to contact with the solvent. In addition, the small particles of coal which are sheared away from a large lump immediately expose not only the highly reactive shear site to the solvent, but also exposes a relatively large surface area to the solvent, thereby enabling the small particles of coal to almost immediately dissolve in the solvent and become a part of the liquid coal extract. While not desiring to be limited by this theory, the practice of this preferred embodiment of the invention is at least explained to those skilled in the art so that further work may be used along these lines to further improve upon the inventive concepts contained herein.

Apparatus for use in pulverizing the lump or coarse coal feed as practiced in 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 apparatus must be able to pulverize

lump or coarse coal in the presence of significant quantities of liquid solvent without difficulty. Those skilled in the art are familiar with the kinds of apparatus for processing wet solids and the crushing and grinding thereof, such that no detailed discussion of the apparatus need be presented herein. The primary requirement for crushing and grinding of the lump coal is that coarse coal usually having an average particle diameter in excess of 0.08 inch and, typically, about 0.25 to 2.0 inches must be processed thereto and reduced in size to an average particle diameter which would be reduced to an average particle size for −14 Tyler screen size. As used herein the term "Tyler screen" refers in all instances to the commercial Tyler standard screens. The correlation between Tyler screen mesh and average particle diameter is as follows:

Tyler screen mesh:	Average diameter of particles D_{avg} in.
−8 +10	0.0791
−10 +14	0.0555
−14+20	0.0394
−20 +28	0.0280
−28 +35	0.0198
−35 +48	0.0140
−48 +65	0.0099
−65 +100	0.0077
−100 +150	0.00496
−150 +200	0.0035

The conditions during the pulverization step may be varied widely according to the desires of those skilled in the art and practicing this invention. The temperature, of course, may be varied over a relatively broad range, from essentially ambient temperature to a relatively high temperature. It is distinctly preferred in the practice of this invention that the temperature of the coal and the solvent be mainained at a relatively high temperature, say, from 300° C. to 500° C. The pressure, in similar manner, may be varied over an extremely wide range from atmospheric pressure to, say, 10,000 p.s.i.g. with a preferred pressure being about 100 p.s.i.g. or typically, about 70 p.s.i.g.

The operation of the pulverization equipment is preferably performed so that the oversized material; that is, greater in size than the —8 Tyler screen size, be separated and returned to the apparatus for further pulverization. The utilization of the closed circuit technique is well known to those skilled in the art and is preferred in the practice of this invention. Unless otherwise stated, closed circuit operation of the pulverization equipment will be deemed inherent in the practice of this invention.

The amount of solvent which is used in the first stage extraction of the present invention generally will range from 0.2 to 10 pounds of solvent per pound of coal. Satisfactory results may be obtained in utilizing approximately equal amounts of solvent to coal on a weight basis. In the practice of the preferred embodiment of this invention, the conditions during the pulverization step should be chosen such that the coarse coal is reduced in size to at least a —8 Tyler screen size and the solvent has a chance to react and dissolve the coal to an extent such that the coal particles are at least partially dissolved in the solvent. As more fully developed hereinbelow, the conditions are chosen in the pulverization step such that from 10% to 40% of the m.a.f. coal is dissolved in the solvent with at least an additional 50% by weight being dissolved during the subsequent digestion zone.

The extraction of coal by means of a solvent is basically a partial conversion of the coal since not only is the coal reacted with the hydrogen, which is preferably transferred from the solvent, but there is also a solution phenomenon which actually dissolves the coal which has accepted the hydrogen into the solvent phase. Therefore, as used herein, the term "liquid coal extract," "liquefied coal fraction," "liquefied coal," or other words of similar import, is intended to include the liquid product which is obtained

from the various steps in the practice of this invention and, generally, will be described on the basis of being "solvent-free," even though a portion of the final liquid coal extract following the second extraction step comprises hydrocarbons suitable for use as the selective solvent in the first extraction zone. The practice of the present invention in both extraction zones is performed under conditions which increase the kinetics of the solvation reaction while maintaining the components therein in primarily liquid phase; although, in some cases it may be desirable to practice the first step of the extraction operation in the presence of a vaporized solvent using a gaseous extraction technique.

Suitable preferred solvents for use in the second stage extraction zone belong broadly to the class of compounds known as ketones, i.e. oxidative derivatives of secondary alcohols. Examples of ketones which may be used satisfactorily in the second extraction zone include acetone, methylethyl ketone, methylbutyl ketone, dibutyl ketone, etc. Other suitable solvents for use in the second stage extraction include monocyclic aromatic hydrocarbons (e.g. benzene, toluene, xylene, etc.) and naphthenic hydrocarbons (e.g. methylcyclohexane, etc.). It is to be noted by those skilled in the art that these classes of secondary extraction agents was found to have no effect on converting solid coal to a liquid coal extract. Therefore, it is a requirement of this invention that the first stage extraction zone utilize those solvents which are applicable to the conversion of solid coal particles to liquid form and that the second stage extraction zone be strictly limited to a solvent which serves to separate the hydrogen-rich components from the hydrogen-lean components contained in thte liquid coal extract produced in the first extraction step. In other words, it was found that the ketones, as well as the other above-mentioned secondary solvents are selective for the hydrogen-rich components to the substantial rejection of the hydrogen-lean components. The choice of selective solvent depends upon the extraction conditions desired in the second extration zone. The initial boil point of the solvent should be above the temperature selected for the second extraction zone. For practical purposes, the temperature selected for the second extraction zone should be at least 30° C. below the critical boiling point of, for example, the ketone in order to maintain the components in primarily liquid phase. As a rule, the temperature for the second extraction zone should not exceed 450° C.

The operating conditions for the second extraction zone utilizing the ketone solvent include a temperature from 50° C. to 450° C., preferably, from 100° C. to 300° C., a pressure from 100 p.s.i.g. to 1000 p.s.i.g., preferably from 350 p.s.i.g. to 700 p.s.i.g., a solvent to feed ratio from 0.5 to 5 by weight, a residence time from 0.5 LHSV to 5.0 LHSV and, preferably, the presence of a hydrogen-containing gas in an amount from 500 s.c.f. to 5000 s.c.f. per barrel of liquid feed to the second extraction zone. These conditions should be sufficient to substantially separate, on a selective basis, the hydrogen-rich components from the hydrogen-lean components which are contained in the liquid feed to the second extraction zone.

The liquid coal extract obtained from the first extraction zone will contain compounds of widely varying physical characteristics since the first extraction step is relatively non-selective. However, the liquefied coal may be characterized as being composed of basically two fractions, to wit: a hydrogen-rich fraction and a hydrogen-lean fraction. As used herein, the term "hydrogen-lean components" or words of similar import are intended to include those components which are basically insoluble in benzene. The hydrogen-lean components will typically have an average molecular weight of about 1500 and contain hydrogen on a weight percent basis from about 3% to about 5%. On the other hand, as used herein, the term "hydrogen-rich components" or words of similar import are intended to include those components which are basically soluble in benzene. The hydrogen-rich components, therefore, will typically have a molecular weight of less than 1500, e.g. from 300 to 1000 and, therefore, a hydrogen content on a weight basis in excess of 5%, e.g. from 6% to 9% by weight. The above characteristics of the two major fractions contained in liquefied coal, of course, are influenced to some extent by the solvent extraction conditions used in the first stage extraction zone including the depth of extraction employed in this first step. It is recognized, however, that the hydrogen-lean component characteristic of the liquid coal extract will only be influenced slightly by the extraction conditions, but will be influenced considerably by the kind of coal which is utilized as feed to the inventive process.

In summary, therefore, following the size reduction step wherein at least a portion of the coarse particulate coal has been dissolved in the first selective solvent and the oversized solid materials have been separated. The effluent product comprising first selective solvent having dissolved therein liquid coal extract and containing undissolved solid coal is passed, preferably, into a digestion zone for the substantial conversion of the coal into liquefied coal.

The operating conditions for the digestion zone include a temperature from 300° C. to 500° C., a pressure from atmospheric to 10,000 p.s.i.g., a solvent-to-coal weight ratio from 0.2 to 10, and a residence time from 30 seconds to 5 hours, sufficient to dissolve coal such that a total in excess of 50% by weight of m.a.f. coal has been liquefied.

It is to be noted that the temperature and pressure conditions during the digestion step may be the same, may be higher, may be lower, or may be any different configuration desired by those skilled in the art, of those conditions maintained in the pulverization zone. It has been satisfactory in the practice of this invention that the temperature and pressure in the digestion zone be maintained essentially at the same level as the temperature and pressure maintained in the pulverization zone.

Since the purpose of the digestion zone, including the preferred embodiment using the first selective solvent in the pulverization and digestion zones, is to substantially complete the conversion of the solid coal into a liquid coal extract, it may be desirable to add to the digestion zone additional solvent, add a hydrogen-containing gas to the digestion zone, and/or utilize a catalyst in the digestion zone. If a catalyst is required or desired, it may be of the conventional hydrogenation type either homogenous or heterogenous and may be introduced into the pulverization zone and/or digestion zone in admixture with the liquid first selective solvent or with the solid coal. Those skilled in the art from a knowledge of the characteristics of the coal, of the solvent, and of the properties desired for the end product will know from the teachings presented herein whether or not it would be desirable to use any or all of these features in the pulverization and/or digestion zone.

Examples of conventional hydrogenation catalyst which may be used in the first extraction zone include a cobalt-molybdate, a nickel molybdate, a nickel tungstate or any other hydrogenation catalyst which can operate in the presence of sulfur-containing charge stocks and is applicable to the solvent-coal system environment maintained in the first extraction zone, including the use of a slurry-catalyst system.

Hydrogenation in the digestion zone, generally, accomplishes the following functions: transfer of hydrogen directy to coal molecules; transfer of hydrogen to hydrogen-donor molecules to coal molecules; and combinations of the above. Homogenous catalyst may be introduced with the coal or with hydrogen-donor compounds in the pulverization step or in the digestion zone. By way of emphasis, as used herein, the term "first extraction zone" is intended to include the pulverization step, the digestion step or the combined pulverization-digestion step.

After separation of the undissolved coal residue of at

least a portion of the first selective solvent and catalyst, if any, from the total effluent of the digestion zone, the liquid coal extract is now contacted in a second extraction zone under extraction conditions with the previously mentioned second selective solvent of the ketone class. A residue comprising hydrogen-lean components is removed from the second extraction zone for use as fuel or for the conversion thereof into relatively pure hydrogen gas by use of the "water-gas" reaction. The produced hydrogen then may, of course, be utilized within the inventive method circuit as described herein. The rich solvent from the second extraction zone comprising the ketone having dissolved therein the hydrogen-rich components is further processed by means known to those skilled in the art, such as fractionation, in order to separate the liquid coal extract into more valuable products, such as relatively light hydrocarbons, relatively heavy hydrocarbons, chemicals, fuel, etc., the utility of which is well known to those skilled in the art. As previously mentioned, a portion of the separated products from the liquid coal extract may be satisfactory for use as at least a portion of the first selective solvent utilized in the first extraction zone as described herein.

The invention may be more fully understood with reference to the appended drawing which is a schematic representation of apparatus for practicing the detailed and preferred embodiment of the invention.

DESCRIPTION OF THE DRAWING

Referring now to the drawing, coarse coal having an average particle diameter generally in excess of 0.08 inch is introduced into the system via line **10**. A suitable selective first solvent enriched in hydrogen content, such as Tetralin, is introduced into admixture with the coarse coal from line **11**, the major source of which is more fully discussed hereinafter. As previously mentioned, the over-sized solid material from the pulverization zone is also preferably returned to the pulverization zone via line **12**. The entire admixture of coarse coal and first selective solvent is passed via line **13** into mill **14** which conventionally may be of the ball mill type adaptable for the use in the presence of a liquid according to means well known to those skilled in the art.

Suitable pulverization conditions include a temperature of about 380° C., a pressure of about 70 p.s.i.g., and a solvent to coal ratio of about 1.0 is maintained in mill **14**, such that the coarse coal is reduced to an average particle diameter between 0.08 and 0.04 inch, and at least a portion of the coal, say, about 17% by weight is dissolved into the Tetralin.

The effluent from mill **14** containing Tetralin having dissolved therein the liquid coal extract and containing undissolved coal of proper small particle size and undissolved coal of oversize is passed via line **15** into separator **16** which may be of the cyclone type. Conditions are maintained in separator **16** whereby the oversized coal particles, preferably, in admixture with at least a portion of the liquid material is removed via line **12** and returned to mill **14** in a manner previously discussed.

First selective solvent, e.g. Tetralin, having dissolved therein at least a portion of the coal plus undissolved pulverized coal is admixed, preferably, with a hydrogen-containing gas from line **26** and passed via line **17** into digestion zone **19** which may be a jacketed stirred type vessel. Added Tetralin solvent, if any, may be introduced into the system via line **18** in an amount sufficient to maintain the solvent to coal ratio at the desired level and/or to maintain the hydrogen content present in digester **19** at a sufficiently high level. Furthermore, hydrogenation catalyst (from means not shown) advantageously may be used in the digestion step. Make-up hydrogen, if any, may be added to the system via line **27**. Preferably, the amount of hydrogen present in the digestion zone is from 1,000 to 100,000 standard cubic feet per barrel of coal-solvent mixture entering digester **19** via line **17**.

The entire effluent from digestion zone **19** is passed via line **20** into filtration zone **21** wherein solid residue, including solid hydrogenation catalyst, if any, is separated from the liquid material and removed from the system via line **22**. Filtration zone **21**, preferably, is a rotary filter device, pre-coated with conventional filter aids and is, typically, operated at a pressure from 50 to 100 p.s.i.g. sufficient to effect removal of substantially all of the suspended solid matter including undissolved carbonaceous matter. The filter cake is washed and dried by conventional means to recover absorbed liquid material. The mother liquor, including any gaseous materials, is removed from filtration zone **21** via line **23**. The material in line **23** comprises solvent having dissolved therein liquid coal extract comprising both hydrogen-rich components and hydrogen-lean components.

As previously mentioned, if desired, by means not shown, an anti-solvent, such as a light hydrocarbon of the hexane type, may be added to filtration zone **21** in an effort to further aid in removing tars and solid materials from the desired solvent and liquid hydrocarbons making up the liquid coal extract. If an anti-solvent is used, the material in line **23** will also contain such added light hydrocarbons.

The material from filtration zone **21** is passed through line **23** into separator **24** which may comprise one or more separation vessels, including fractionation columns for the separation of the hydrogen gas, added light hydrocarbons, if any, from the other hydrocarbonaceous material. Although separation zone **24** has been shown in a position following filtration zone **21**, it is within the concepts of the present invention to arrange for the separation of gaseous materials, such as hydrogen gas, prior to filtration zone **21**. In other words, another embodiment of this invention would include a gaseous (e.g. hydrogen) separation zone, not shown, in line **20** between digester **19** and filter **21**. However, for purposes of this illustrative embodiment only, separation zone **24** has been placed between filtration zone **21** and secondary extraction zone **29**, more fully discussed hereinbelow.

In keeping with the present illustrative embodiment, hydrogen gas is removed from separation zone **24** via line **26** and returned to digester **19**. Preferably, that portion of the normally liquid material entering separation zone **24** from line **23** which comprises first selective solvent component (Tetralin) is withdrawn via line **28** and returned to the digestion zone and/or pulverization zone, as previously discussed. Therefore, the liquid coal extract, substantially free of solid matter, free of hydrogen gas, and free of normally gaseous hydrocarbons and, preferably, free of first selective solvent components, is removed from separator **24** via line **25**.

The material in line **25**, comprising liquid coal extract substantially free of solvent (although, it is recognized that a portion of the liquid coal extract may be suitable for use as the first selective solvent more fully developed hereinbelow) is passed into secondary extraction zone **29**. If desired, a portion of the material in line **25** may be returned via line **41** into line **28** for recycle to the digestion zone **19** and/or pulverization zone **14**.

Extraction zone **29** is maintained under extraction conditions, including the presence of a ketone class solvent which enters the system via line **39** and a temperature of about 150° C., a solvent to extract ratio of about 3, a pressure of about 500 p.s.i.g., and, preferably, having introduced into the zone added hydrogen gas via line **40** in an amount of about 100 s.c.p./barrel of extract entering zone **29**. A residue comprising hydrogen-lean components is withdrawn from second extraction zone **29** via line **30** and disposed of as fuel or as a source of additional hydrogen through a water-gas reaction (by means not shown).

The rich solvent comprising ketone having dissolved

therein hydrogen-rich components, such as naphthenic and naphthenic aromatic hydrocarbons and gasoline boiling range hydrocarbons is passed via line **31** into separation zone **32** which comprises a plurality of separatory means including fractionation columns. Conditions are maintained in separation zone **33**, which are known to those skilled in the art from the teachings herein, sufficient to recover the ketone solvent which is withdrawn via line **36**, to recover the normally gaseous materials, if any, which are withdrawn from line **35**, to recover and separate naphthenic and naphthenic aromatic type hydrogen-rich components suitable for use as the first selective solvent which is withdrawn via line **37** and returned to digestor **19** and mill **14** in the manner previously discussed, with the net production of light hydrocarbon components being withdrawn from the system via line **38**, and to separate and recover the relatively heavy hydrocarbons, also hydrogen-rich, which are withdrawn from the system via line **34**.

The residual fraction in line **34** comprises basically a heavy fuel oil and is used desirably in a fuel system. Added first selective solvent, such as Tetralin, external of the process may be added to the inventive system via line **32**, if desired.

The invention may be now fully understood by reference to the following examples which illustrate the dual solvent technique:

EXAMPLE 1

Pulverized bituminous coal was liquefied via solvent extraction using anthracene oil at 430° C. and the presence of hydrogen gas. The solid residue was removed and a liquid coal extract obtained.

100 grams of the liquid coal extract was contacted with boiling methylethylketone. The resulting ketone-extract product was filtered to remove solid residue and ash. The solvent was distilled off and a final extract obtained (40 grams). The final extract and the liquid coal extract were analyzed for hydrogen with the following results:

	Wt. percent hydrogen
1st stage, liquid coal extract	5.2
2nd stage, final extract	5.7

It is evident from this data that the second solvent extraction step significantly upgraded the liquefied coal, e.g., the 0.5% increase in hydrogen content.

Similar results would be expected from using any of the other above defined brand class of ketone secondary solvents.

EXAMPLE 2

Bituminous particulate coal was pulverized and divided into two batches. The first batch was liquefied by contacting the coal with Tetralin in the presence of hydrogen gas and a hydrogenation catalyst. Operating conditions and catalyst were as defined hereinabove. A first liquid coal extract was obtained. The second batch was liquefied under similar conditions except that no hydrogenation catalyst was present. A second liquid coal extract was also obtained. Analytical data was as follows:

	Batch No. 1	Batch No. 2
	Liquefied with catalyst	Liquefied without catalyst
Percent extract (m.a.f. basis)	89.0	85.5
Percent C, wt	87.70	86.00
Percent H, wt	7.42	7.18
Molecular weight	481	503

Each extract was filtered to remove solid residue and ash and then subjected to a second extraction step using cyclohexene at 55° C. for two (2) hours. The secondary solvent was removed by distillation and each extract and each remaining insoluble material was analyzed with the following results:

SECOND EXTRACTION

Original Extract No	1	2
1. Percent cyclohexane soluble	40	40
Percent C, wt	86.36	85.46
Percent H, wt	8.33	8.29
Mol. wt	340	348
2. Percent benzene soluble	38	36
Percent C, wt	84.32	84.97
Percent H, wt	8.45	7.20
Mol. wt	605	553
3. Percent insoluble residue	32	34
Percent C, wt	85.55	84.41
Percent, H wt	5.52	5.87
Percent ash	Nil	Nil
Mol. wt	1,140	1,130
1 and 2 percent combined sol. prod	78	76
Percent H, wt	8.39	7.75
Mol. wt	472	450
Percent soluble based on original m.a.f. basis	70	65
Percent soluble based on original coal charge	66	61

The above data shows the benefits obtained by using the dual solvent technique. First, each secondary extract (a final extract) had a significantly higher hydrogen content; e.g. Batch 1, from 7.42% to 8.39%. Second, the insoluble residue in both instances was substantially ash-free, and since its properties were similar to the original coal, it could be recycled essentially to extinction. Third, the effect of the catalyst when Batch 1 is compared to Batch 2, is clearly evident. Batch 1 extract had a higher hydrogen content (e.g. 8.39 vs. 7.75) and a higher overall yield of liquefied product (e.g. 70% vs. 65%).

Similar results would be expected by using a single ring aromatic hydrocarbon such as benzene as the secondary solvent.

PREFERRED EMBODIMENT

From the discussion presented hereinabove, the preferred embodiment of the present invention includes a method for liquefying coal which comprises the steps of: (a) admixing coarse size bituminous coal with a first solvent selective for dissolving coal; (b) introducing the solvent-coarse coal admixture into a pulverization zone under conditions including a temperature from 300° C. to 500° C., a pressure from atmospheric to 10,000 p.s.i.g., solvent to coal ratio from 0.2 to 10.0 sufficient to reduce said coarse coal to at least a —8 Tyler screen size and to partially dissolve coal into said solvent; (c) passing the pulverized coal-solvent product including dissolved coal into a liquefaction zone maintained under conditions sufficient to dissolve coal such that a total in excess of 50% by weight of m.a.f. coal is liquefied as liquid coal extract; (d) separating said liquid coal extract from undissolved coal and from said solvent thereby producing a substantially solvent-free liquid coal extract; (e) introducing said solvent-free liquid coal extract into an extraction zone maintained under extraction conditions including a second solvent selective for hydrogen-rich components in said extract; (f) withdrawing from said extraction zone a rich solvent having hydrogen-rich liquid coal components dissolved therein; and, (g) recovering said hydrogen-rich components in high concentration.

A distinctly preferred embodiment includes the method hereinabove wherein said first solvent comprises naphthalenic hydrocarbons and said second solvent comprises a ketone.

It will be recalled that hydrogen gas was preferably used during the digestion step and during the secondary extraction step. It is important to note that these are separate and distinct hydrogenation operations. In order to carefully control the degree of hydrogenation, it is convenient to use the J-factor analysis for determining the degree to which hydrogen has been added to the materials to be hydrogenated in both digestion zone **19** and extraction zone **29**. This analytical technique permits the characterization of various types of aromatics in a hydrocarbon mixture by means of the J-factor analysis. The technique utilizes mass spectrometer analysis em-

ploying a low ionizing voltage. The ionizing voltage is chosen such that only those hydrocarbon types are not ionized under the potential chosen. For example, since compounds more saturated than aromatic hydrocarbons, such as the paraffin hydrocarbons, have an ionization level above 10 volts, the ionization chamber is thus maintained at a potential of about 7 volts so that only the aromatic hydrocarbons are ionized and the saturated compounds will not be observed on the mass spectrum. As those skilled in the analytical art know, the mass spectrum reveals molecular ion peaks which correspond to the molecular weight of the aromatic compound. Thus, the technique permits characterization of the aromatic hydrocarbons by means of the general formula C_nH_{2n-J} where "J" is the herein referred to "J-factor" for the practice of the present invention. The following table shows the relationship between the J-factor and the type of aromatic.

J-factor number:	Type of aromatic hydrocarbon
6	Alkyl benzenes and benzene.
8	Indanes, Tetralin.
10	Indenes.
12	Alkyl naphthalenes and naphthalene.
14	Acenaphthenes, tetrahydroanthracene.
16	Acenaphthalenes, dihydroanthracenes.
18	Anthracenes, phenanthrenes.

Using this J-factor analysis in characterizing the hydrotreating step of the present invention allows for the optimum treatment of said solvent to produce a high quality hydrogen enriched solvent for use in converting coal into liquid coal extract. However, as previously mentioned, the important control technique of the present invention is that in the absence of added hydrogen gas the hydrogen content of the initial solvent charged to the first extraction zone in admixture with the coal is greater than the solvent leaving the pulverization zone having dissolved therein the liquid coal extract. In similar manner, the other control technique is that the hydrogen content of the solvent which has been recovered from the effluent of the pulverization zone is less than the hydrogen content of the solvent leaving the digestion zone and being recycled to the pulverization zone. The J-factor analysis is simply a convenient means for optimizing the hydrotreating steps in the practice of the invention.

The invention claimed:

1. Method for liquefying solid particulate coal which comprises the steps of:

(a) contacting said coal with a first solvent selective for dissolving coal under conditions sufficient to convert said coal into liquid coal extract containing hydrogen-rich components and hydrogen-lean components;

(b) separating the liquid coal extract from undissolved coal, and from at least a portion of said first solvent;

(c) contacting said separated liquid coal extract from step (b) under extraction conditions with a second solvent different than said first solvent and selective for said hydrogen-rich components and being selected from the group consisting of ketones, monocyclic aromatic hydrocarbons and naphthenic hydrocarbons; and

(d) recovering said hydrogen-rich components and said hydrogen-lean components as separate product streams.

2. Method according to claim 1 wherein said first solvent comprises polycyclic aromatic hydrocarbons or polycyclic naphthenic-aromatic hydrocarbons.

3. Method for liquefying coal which comprises the steps of:

(a) admixing coarse size bituminous coal with a first solvent selective for dissolving coal;

(b) introducing the solvent-coarse coal admixture into a pulverization zone under conditions including a temperature from 300° C. to 500° C., pressure from atmospheric to 10,000 p.s.i.g., solvent to coal ratio from 0.2 to 10.0 sufficient to reduce said coarse coal to at least a —8 Tyler screen size, and to partially dissolve coal into said solvent;

(c) passing the pulverized coal-solvent product including dissolved coal into a liquefaction zone maintained under conditions sufficient to dissolve coal such that a total in excess of 50% by weight of m.a.f. coal is liquefied as liquid coal extract;

(d) separating said liquid coal extract from undissolved coal, and from said solvent thereby producing a substantially solvent-free liquid coal extract;

(e) introducing said solvent-free extract into an extraction zone maintained under extraction conditions including the presence of a second solvent different than said first solvent and selective for hydrogen-rich components in said extract and being selected from the group consisting of ketones, monocyclic aromatic hydrocarbons and naphthenic hydrocarbons;

(f) withdrawing from said extraction zone a rich solvent having hydrogen-rich liquefied coal components dissolved therein; and,

(g) recovering said hydrogen-rich components in high concentration.

4. Method according to claim 3, wherein said first solvent comprises naphthalenic hydrocarbons and said second solvent comprises a ketone.

5. Method according to claim 2 wherein said conditions of step (c) includes the presence of a hydrogen-containing gas.

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