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COAL LIQUEFACTION PROCESS

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ABSTRACT OF THE DISCLOSURE

Process for liquefying coal which comprises contacting colloidal size coal and solvent in the presence of hydrogen gas and recovering valuable liquid hydrocarbon products from the resulting liquid coal extract.

BACKGROUND OF THE INVENTION

This invention relates to a solvent extraction method. It also relates to a method for liquefying coal using a selective solvent. It particularly relates to a process for obtaining valuable liquid hydrocarbons from particulate coal utilizing the steps of solvation and, preferably, hydrogenation.

It has long been known that hydrocarbon gases, liquids, pitch and chemicals may be obtained in useful 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 a high pressure hydrogenation of coal technique to effectuate such conversion. Still more recently, methods involving solvent extraction techniques have been developed for obtaining useful fuels and chemicals from coal whereby the coal is contacted with a selective solvent which acts as a hydrogen-donor for supplying sufficient hydrogen to the coal to aid in converting it into a liquid state. Following the solvent extraction step, the prior art schemes have utilized various recovery procedures such as hydrogenation of the liquid coal extract for increasing its value and utility together with, for example, retorting or coking of the residual materials obtained from the solvent extraction step to still further convert these coal derived products into more commercially valuable products.

Therefore, for these and other reasons, none of the aforementioned prior art schemes have been sufficiently commercially attractive or feasible to warrant widespread commercial exploitation of converting coal into valuable liquid products. Generally, the deficiencies in the prior art schemes have not only involved capital investment problems and disposal problems of the residue or waste frequently having high metals content, but have also involved liquid product quantity and quality problems which have yet to be solved in an economical and facile manner.

Since it is clear to those skilled in the art that the vast mineral resources of bituminous coal represent an extremely important supply of energy and an extremely important source of raw materials for valuable chemicals, it would be desirable to improve upon the prior art techniques, particularly, the solvent extraction technique in order to reduce the cost of obtaining high quality petroleum type products from coal.

SUMMARY OF THE INVENTION

Therefore, it is an object of this invention to provide a process for the liquefaction of coal whereby valuable liquid hydrocarbons are obtained therefrom.

It is a specific object of this invention to provide an improved process for subjecting pulverized coal to solvent extraction for the conversion thereof into valuable liquid hydrocarbons.

It is a particular object of this invention to provide an improved method for producing hydrogen-enriched hydrocarbonaceous products from coal in a more facile and economical manner.

Therefore, in accordance with the practice of one embodiment of this invention, there is provided a method for the liquefaction of coal which comprises crushing particulate coal to colloidal size particles and subjecting said colloidal coal particles to solvent extraction under conditions sufficient to convert at least the portion of said particles to liquid coal extract.

Another embodiment of this invention includes the presence of hydrogen gas in the solvent extraction zone.

DETAILED DESCRIPTION OF THE INVENTION

Thus, it is to be noted from the summary of the present invention presented hereinabove that the benefits to be derived from the practice thereof are predicated on the feature of crushing particulate coal to colloidal size particles. Furthermore, additional benefits may also accrue in the practice of this invention by utilizing a hydrogenation catalyst in the solvent extraction zone as well as hydrogen gas.

The coal preferred for use in the practice of the present inventive process is of the bituminous type such as Pittsburg 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 m.a.f. coal (moisture and ash-free coal). Although the invention will be described with reference to the conversion of bituminous coal to valuable liquid hydrocarbons, it is within the concept of the present invention to apply the inventive process to subbituminous coal, lignite, and other solid carbonaceous materials of natural origin. For convenience, therefore, the term "coal" is intended to include all materials within the class consisting of bituminous coal, sub-bituminous coal, lignite, and other solid carbonaceous materials of natural origin.

Suitable solvents for use in the practice of this invention are those which are of hydrogen-donor type. Such hydrocarbons are at least partially hydrogenated and include naphthalenic hydrocarbons. Preferably, the solvent is one which is liquid phase at the recommended temperature and pressure for extraction. Mixtures of hydrocarbons are generally employed as the solvent and, preferably, are derived from intermediate or final products obtained from subsequent processing following the practice of this invention. Typically, the solvent hydrocarbons or mixtures of hydrocarbons boil between about 260° C. and 425° C. Examples of suitable solvents are tetrahydronaphthalene (tetralin), decalin, biphenyl, methylnaphthalene, dimethylnaphthalene, etc. Other types of solvents which may be added to the preferred 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 prior to the removal of the solvent from the liquid coal extract to add

an anti-solvent such as saturated paraffinic hydrocarbons like hexane to aid in the precipitation of tarry and solid residue, e.g., ash, from the coal extract of the invention.

However, in the selection of the suitable solvents it must be recognized that the solvent must have the ability to transfer hydrogen to the pulverized coal during the extraction step. In other words, it is a requirement that in the absence of added hydrogen the rich solvent leaving the extraction step having coal dissolved therein must have a reduced hydrogen content compared to the hydrogen content of the lean solvent which is added to the extraction zone. In a preferred embodiment of this invention there is embodied the selective hydrogenation of the solvent during extraction in order to increase its hydrogen content so that the hydrogen may be more easily transferred from the solvent to the coal during the solvent extraction operation.

One of the convenient ways for optimizing the preferred embodiment of this invention is to use the J-factor analysis for determining the degree to which hydrogen has been added to the solvent extraction zone. 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 employing a low ionizing voltage. The ionizing voltage is chosen such that only those hydrocarbons to be characterized are ionized while other hydrocarbon types are not ionized under the potential chosen. For example, since compounds more saturated that 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-

J-factor number:	Type of aromatic hydrocarbon
6	Alkyl benzenes and benzene.
8	Indanes, Tetralins.
10	Indenes.
12	Alkyl naphthalenes and naphthlene.
14	Acenaphthenes, dihydroanthracenes.
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.

Apparatus for use in pulverizing the lump or coarse coal feed to 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 colloidal dimensions; that is, coal particles wherein at least 90% by weight have a particle diameter of less than 2 microns and no more than 10% by weight have a particle diameter greater than 100 microns.

Conventional colloid mills known to those skilled in the art may be used to pulverize the coal to the proper average particle diameter. Of course, the coal may be pulverized either dry, or, preferably, may be pulverized wet utilizing a portion of the solvent as the wetting agent. In other words, it is within the concept of this invention that a slurry of relatively coarse coal in solvent be introduced into the proper crushing and grinding apparatus for the reduction to proper size. Those skilled in the art from the teachings presented herein are familiar with the proper crushing and grinding equipment which is commercially available to accomplish the result required in the practice of this invention.

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 atmospheric temperature to a relatively high temperature. It is distinctly preferred in the practice of this invention that the coal in the solvent be maintained at a relatively high temperature, say 300° C. to 500° C. during the pulverization step. 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 is separated in return 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.

Following the size reduction step wherein the oversized solid materials have been separated from the effluent of the pulverization zone, the coal product (both liquid and solid) is passed into a solvent extraction zone which, in effect, is a reaction zone for the substantial conversion of coal into liquid coal extract. It is within the concept of this invention that the pulverization zone and the extraction zone be the same vessel or may be separate vessels, the desirability of which will become evident from the discussion more fully developed hereinbelow.

The operating conditions for the solvent extraction zone include a temperature from 250° C. to 500° C., a pressure from 500 to 5000 p.s.i.g., a solvent to coal ratio from 0.2 to 10, a residence time from 30 seconds to 5 hours, and, preferably the presence of hydrogen gas sufficient to dissolve coal such that a total in excess of 50% by weight of m.a.f. coal feed into the solvent extraction zone has been liquefied.

Since the purpose of the extraction zone is to substantially convert coal into liquid coal extract, it may be desirable to add a catalyst to the extraction zone. The catalyst may be conventional, may be homogenous, or heterogenous, and may be introduced into the pulverization zone and/or extraction zone in a mixture either with the liquid solvent or with the solvent coal. Those skilled in the art, from a knowledge of the characteristics of the coal solvent and of the properties desired for the end product will know whether or not it may be desirable to use any or all of these features in the solvent extraction zone. If a catalyst is desired, conventional solid hydrogenation catalysts can be satisfactorily utilized, such as nickel-molybdate on an aluminasilica support, or a cobalt-molybdate catalyst, or any other hydrogenation catalyst known to those skilled in the art and applicable to the solvent-coal system environment maintained in the extraction zone, including the use of a slurry-catalyst system.

It is believed that hydrogenation in the extraction zone generally accomplishes the following functions: transfer

of hydrogen directly to coal molecules; transfer of hydrogen to hydrogen-donor molecules; transfer of hydrogen from hydrogen-donor molecules to coal molecules; and various combinations of the above. By way of emphasis, as used herein, the term "extraction zone" is intended to include the pulverization step, the digestion step, or combined pulverization-digestion as is known to those skilled in the art.

After separation of the gaseous materials, including hydrogen, undissolved coal residue (e.g., ash) and catalyst, if any, from the total effluent of the extraction zone, the liquid coal extract is passed into conventional recovery facilities wherein valuable liquid hydrocarbons are recovered. Typically, these recovery facilities comprise fractionation columns for the separation therein of the liquid coal extract into products such as normally gaseous hydrocarbons, relatively light hydrocarbons, comprising essentially middle oil, relatively heavy hydrocarbons comprising materials suitable for use as a coal solvent. Any bottoms fraction comprising residue material which is suitable for fuel. In essence, therefore, the valuable liquid hydrocarbons recovered from the liquid coal extract include, by way of example, gasoline boiling range products, and/or chemicals, aromatic hydrocarbon-containing fractions, heavy fuel oil fractions, and the like, the utility of which is well known to those skilled in the art.

The extraction of coal by means of a selective solvent is by definition at least a partial conversion of the coal since not only is the coal reacted to hydrogen which is transferred from the solvent, but is also reacted with the hydrogen which is added during the extraction step. In addition, there is also a solution phenomenom which actually dissolves the coal which has accepted the hydrogen into the solvent. Therefore, as used therein, the terms "liquid coal extract," and "liquid coal fraction" or words of similar import are intended to include the liquid product which is obtained from the solvent extraction of the coal with the selective solvent in the presence, preferably, of hydrogen gas, and generally, has been described on the basis of being "solvent-free" even though a portion of the extract comprises hydrocarbons suitable for use as the solvent.

In the event hydrogen gas is used in the extraction zone it may be present in an amount from 1,000 to 10,000 standard cubic feet of hydrogen per barrel of solvent. In other words, hydrogen may be utilized in the extraction zone in terms of hydrogen pressures ranging from 200 to 10,000 p.s.i.g.

The practice of the present invention is preferably performed under conditions which increase the kinetics of the reaction by maintaining the components therein primarily in liquid phase; although, in some cases it may be desirable to practice this invention in the presence of vaporized solvent using techniques known to those skilled in the art.

EXAMPLE 1

This example illustrates an advantage to using colloidal size coal during the solvent extraction step. An Eastern Kentucky Stoker Coal having the following properties was crushed to the following sizes:
95% less than 2 microns.
5% greater than 100 microns.

	Weight percent
Ash	3.67
Nitrogen	1.60
Sulfur	1.36
Oxygen	6.99
Free H_2O	1.61
Volatile matter	40.30
Carbon	79.66
Hydrogen	5.55

One (1) part of the colloidal coal was mixed with solvent and charged to a stirred autoclave, and pressured with hydrogen gas. The liquid coal extract was recovered from the contents of the autoclave by filtration and distillation (including solvent removal). The following results were obtained on two runs:

	Solvent	
	Methylnaphthalene	Tetralin
Pressure p.s.i.g., H_2	2,000	2,000
Temp., ° C	430	430
Solvent/coal ratio	3:1	3:1
Residence time, hours	1	2
Percent conversion, m.a.f. coal	71.3	90.0
Percent H_2 in extract		7.01

EXAMPLE 2

The runs in Example 1 were repeated except that the coal was crushed only to an average particle diameter for −14 Tyler Screen size. The results were as follows:

	Solvent	
	Methylnaphthalene	Tetralin
Pressure, p.s.i.g., H_2	2,000	2,000
Temp., ° C	430	430
Solvent/coal ratio	3:1	3:1
Residence time, hours	1	2
Percent conversion, m.a.f. coal	56.9	87.0
Percent H_2 in extract		6.81

The above data, comparing Example 1 with Example 2, demonstrates the unexpected improvement (from 56.9 to 71.3% or 87 to 90%) in conversion level by having the coal crushed to colloidal size. Note also the significant increase in H_2 content of the liquid coal extract. Similar benefits now would be expected at other applicable operating conditions and using various other applicable solvents.

Even though it is recognized that the strict definition of a colloid limits the particle size to between 10^{-5} centimeters and 10^{-7} centimeter, as used herein, the term "colloid" or "colloidal" is intended to include the mass of coal particles wherein at least 90% by weight have a particle size of less than 2 microns and no more than 10% by weight have a particle size greater than 100 microns. Preferably, the colloidal size of the coal particles includes the mass wherein at least 95% have a particle size of less than 2 microns and no more than 5% have a particle size greater than 100 microns.

PREFERRED EMBODIMENT

From the discussion presented hereinabove and in view of the example presented, the preferred embodiment of the present invention includes the method for obtaining valuable liquid hydrocarbons from particulate coal which comprises the steps of crushing particulate coal to colloidal size wherein said colloidal size includes coal particles having at least 90% by weight a particle diameter of less than 2 microns and no more than 10% by weight a particle diameter greater than 100 microns; contacting the colloidal size coal with a solvent in an extraction zone including extraction conditions of 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, and a residence time from 30 seconds to 5 hours sufficient to convert said colloidal coal particles to liquid coal extract in an amount exceeding 50% by weight m.a.f. coal.

A still further preferred embodiment of this invention includes the method hereinabove wherein hydrogen gas is present in an amount from 1,000 to 10,000 standard cubic feet of hydrogen per barrel of solvent.

The invention claimed:

1. Method for the liquefaction of coal which comprises crushing particulate coal to colloidal size particles of which at least 90% by weight have a particle diameter of less than 2 microns and no more than 10% by weight have a particle diameter greater than 100 microns, and subjecting said colloidal coal particles to solvent

extration with a hydrogen-donor type solvent under conditions including a temperature from 250° C. to 500° C. and a pressure from 500 to 5000 p.s.i.g.

2. Method according to claim 1 wherein said extraction conditions include a solvent to coal ratio from 0.2 to 10.0, and a residence time from 30 seconds to 5 hours sufficient to convert said coal particles to liquid coal extract in an amount exceeding 50% by weight m.a.f. coal.

3. Method according to claim 2 wherein said extraction conditions include the presence of hydrogen gas in an amount from 1,000 to 10,000 standard cubic feet of hydrogen per barrel of solvent.

4. Method according to claim 2 wherein at least 95% by weight of said colloidal size particles have a particle diameter of less than 2 microns and no more than 5% by weight have a particle diameter greater than 100 microns.

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