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COAL LIQUEFACTION PROCESS

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7 Claims

ABSTRACT OF THE DISCLOSURE

Process for liquefying coal which comprises contacting coal and solvent in the presence of hydrogen sulfide 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 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 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.

In all of these prior art procedures, however, there has been a remaining persistent problem and that is the problem of removing the small quantities of metallic contaminants, e.g. inorganic materials, hereinafter referred to as "ash" from the extract. If these contaminants are not removed from the liquid coal extract, considerable processing difficulties are incurred in subsequent recovery procedures, particularly in the subsequent hydrogenation steps which utilize a catalyst. These contaminants have the effect of depositing on the catalyst, hereby causing at least in part rapid deactivation or poisoning of the catalyst.

In addition, these contaminants are extremely difficult to remove via filtration techniques, even through filtration is one of the most economical and facile methods for attempting to remove ash from liquid coal extract.

Therefore, for these and other reasons, none of the aforementioned prior art procedures 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

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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 process 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 an improvement in a process for producing hydrogen-enriched hydrocarbonaceous products from coal by subjecting said coal to solvent extraction at a temperature from 250° C. to 500° C. and a pressure from 500 p.s.i.g. to 5,000 p.s.i.g. and subsequently recovering hydrogen-enriched hydrocarbonaceous products which comprises introducing hydrogen sulfide into the solvent extraction zone in contact with said coal and solvent.

Another embodiment of the invention includes the presence of hydrogen gas in the solvent extraction zone in addition to the hydrogen sulfide gas.

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 presence of hydrogen sulfide during the solvent extraction step. It is believed that one of the reasons the practice of this invention produces such desirable results is that hydrogen sulfide gas acts in some way as a catalytic agent, thereby improving the total conversion of the coal into liquid coal extract, rendering the ash more readily filterable and producing a liquid coal extract having a higher hydrogen content than would otherwise be obtained. 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 and the critical amount of hydrogen sulfide.

The coal preferred for use in the practice of the present inventive process 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 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 sub-bituminous 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 the hydrogen-donor type and are at least partially hydrogenated and include naphthalenic hydrocarbons. Preferably, the solvent is one which is in 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 xlenols. 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 a suitable solvent 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 hydrogen may be more easily transferred from the solvent to the coal during the solvent extraction operation. The essence of the present invention is based on the discovery that the presence of from 1% to 2% by volume of hydrogen sulfide (based on the amount of hydrogen present) will considerably enhance the efficiency and effectiveness of the conversion of solid coal to liquid coal extract. Preferably, the amount of hydrogen sulfide added will be from 4% to 8% by volume based on hydrogen gas. In the event added hydrogen gas is not present in the extraction zone, the amount of hydrogen sulfide present should be from 10% to 40% based on the amount of coal feed into the solvent extraction zone.

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 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 hydrocarbon 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.

Type of aromatic hydrocarbon:	J-factor No.
Alkyl benzenes and benzene	6
Indanes, tetralins	8
Indenes	10
Alkyl naphthalenes and naphthalene	12
Acenaphthenes, tetrahydroanthracene	14
Acenaphthalenes, dihydroanthracenes	16
Anthracenes, phenanthrenes	18

Using this J-factor analysis in characterizing the hydro-treating step of the present invention allows for the optimum treating 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 inches 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 of at least —8 Tyler screen size and, preferably, 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 atmospheric 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 maintained 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.

Following the size reduction step wherein the oversized solid materials have been separated from the effluent of the pulverization zone, the product is passed into a solvent extraction zone which, in effect, is a reaction zone for the substantial conversion of the coal into liquid coal extract.

The operating conditions for the solvents extraction zone include a temperature from 250° C. to 500° C., a pressure from 500 to 5,000 p.s.i.g., a solvent to coal weight ratio from 0.2 to 10, a residence time from 30 seconds to 5 hours, the presence of hydrogen sulfide gas (previously discussed hereinabove), and, preferably, the presence of hydrogen 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 to the extraction zone a catalyst. The catalyst may be conventional, may be homogenous or heterogenous and may be introduced into the pulverization zone and/or extraction zone in admixture with either the liquid solvent or with the solid 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 catalyst can be satisfactorily utilized, such as nickel-molybdate on an alumina-silica 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.

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, hydrogen sulfide, 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 and a bottoms fraction comprising residue material which is suitable for fuel. In essence, therefore, the valuable liquid hydrocarbons recovered from the liquid coal extract include, for 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 with 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 phenomenon which actually dissolves the coal which has accepted the hydrogen into the solvent. Therefore, as used herein, the terms "liquid coal extract" and "liquid coal fraction" or other 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 of hydrogen sulfide 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.

The practice of the present invention is preferably performed under conditions which increase the kinetics of the reaction while maintaining the components therein in primarily liquid phase; although, in some cases, it may be desirable to practice this invention in the presence of a vaporized solvent and hydrogen sulfide gas.

EXAMPLE 1

This example illustrates an advantage to having hydrogen sulfide present during the solvent liquefaction of coal. An Eastern Kentucky Stoker Coal having the fol-

lowing properties was crushed to an average particle diameter of less than 100 mesh:

	Weight percent
Ash -----	3.67
Nitrogen -----	1.60
Sulfur -----	1.36
Oxygen -----	6.99
Free H ₂ O -----	1.61
Volatile matter -----	40.30
Carbon -----	79.66
Hydrogen -----	5.55

One (1) part of the crushed coal was mixed with three (3) parts of methylnaphthalene. The mixture was run in a colloid mill for five (5) hours thereby producing coal particles having 99% by weight less than 5 microns diameter.

447 grams of the material from the colloid mill was charged to a racker autoclave, pressure, first, with ten (10) atmospheres of hydrogen sulfide, and, second, with an additional 90 atmospheres of hydrogen thereby obtaining a total pressure of 100 atmospheres. The autoclave was then heated to 390° C. (raising the pressure to 200 atm.). These conditions were maintained for two (2) hours.

The liquefied coal was recovered from the contents of the autoclave by filtration and distillation (including solvent removal). 80 grams of liquefied coal and 17 grams of solid residue was obtained. The conversion of solid coal to liquid coal was determined from the amount of carbon present in the original coal and the amount of carbon left in the recovered solids. Thus, the amount of carbon in the original coal was 89.02 grams and the amount of carbon in the recovered solids was 11.01 grams resulting in a conversion of solid coal to liquid coal of 87.66% by weight.

EXAMPLE 2

The experiment in Example 1 was repeated except that no hydrogen sulfide was added to the autoclave. The results were as follows:

72 grams of liquid coal was recovered,
21 grams of solids were recovered.

Thus, the total carbon present in the original coal sample was 89.02 grams and the amount of carbon present in the recovered solids was 14.32 grams resulting in a conversion of solid coal to liquid coal of 83.9% by weight.

The above data demonstrates the unexpected improvement (increase of about 4%) in conversion level by having hydrogen sulfide present during the coal solvation step. Similar benefits would be expected at other applicable operating conditions and using various other applicable solvents.

PREFERRED EMBODIMENT

From the discussion presented hereinabove and in view of the examples presented, the preferred embodiment of the present invention includes a process for obtaining valuable liquid hydrocarbon from particulate coal which comprises the steps of (a) contacting particulate coal and solvent in an extraction zone under conditions including the presence of hydrogen and added hydrogen sulfide sufficient to convert at least 50% by weight of the m.a.f. coal into liquid coal extract; and, (b) recovering valuable liquid hydrocarbon from said extract.

A still further preferred embodiment of this invention includes the process hereinabove wherein the hydrogen sulfide is added in an amount from 1% to 20% by volume based on the hydrogen present in the extraction zone.

The invention claimed:

1. In a process for producing hydrogen-enriched hydrocarbonaceous products from coal by subjecting said coal to solvent extraction at a temperature from 250° C. to 500° C. and a pressure from 500 to 5,000 p.s.i.g., and subsequently recovering hydrogen-enriched hydrocarbo-

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naceous products, the improvement which comprises introducing hydrogen sulfide into the solvent extraction zone in contact with said coal and solvent.

2. Improvement according to claim 1 wherein hydrogen gas is introduced into the solvent extraction zone.

3. Improvement according to claim 2 wherein said hydrogen sulfide is introduced into the solvent extraction zone in an amount from 1% to 20% by volume based on the volume of hydrogen gas present in said zone.

4. Improvement according to claim 3 wherein said hydrogen sulfide is introduced in an amount from 4% to 8% by volume based on hydrogen gas.

5. Process for obtaining valuable liquid hydrocarbons from particulate coal which comprises the steps of:

(a) contacting particulate coal and solvent in an extraction zone under conditions including the presence of hydrogen and added hydrogen sulfide sufficient to convert at least 50% by weight of the m.a.f. coal into liquid coal extract; and,

(b) recovering valuable liquid hydrocarbons from said extract.

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6. Process according to claim 5 wherein said hydrogen sulfide is added in an amount from 1% to 20% by volume based on the hydrogen present in said zone.

7. Process according to claim 6 wherein said conditions include a temperature from 250° C. to 500° C., pressure from 500 to 5,000 p.s.i.g., solvent to coal ratio from 0.2 to 10, and from 1,000 to 10,000 standard cubic feet of hydrogen per barrel of solvent.

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