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COAL LIQUEFACTION PROCESS

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4 Claims

ABSTRACT OF THE DISCLOSURE

Process for liquefying coal utilizing a dual solvent system of a polycyclic aromatic hydrocarbon primary solvent and a halogenated hydrocarbon secondary solvent having 6–20 carbons which minimizes ash contamination of the coal extract. Valuable liquid hydrocarbon products are recovered from the resulting coal extract.

BACKGROUND OF THE INVENTION

This invention relates to a solvent extraction process. It also relates to a method for liquefying coal using at least two selective solvents. 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/or 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 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, such as a polynuclear aromatic compound, which acts as a hydrogen-donor to the coal to aid in converting it into a liquid state.

Subsequent to the solvent extraction step the prior art schemes have utilized various recovery and treatment procedures, such as hydrogenation of the liquid coal extract followed by distillation for increasing its value and utility. Combination processes have also been developed which coke and/or thermally crack the residue material obtained from the solvent extraction step.

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

In addition, these contaminants are extremely difficult to remove via filtration techniques since the particle size

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distribution of the ash is extremely small and, in fact, approaches colloidal dimensions in many cases. However, the prior art has utilized filtration as one method of removing ash from the 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 more valuable liquid products. Generally, the difficulties in the prior art schemes have not only involved capital investment problems and disposal problems of the residue or waste 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 coal (particularly 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 particular 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 specific object of this invention to provide an improved process for producing hydrogen-enriched hydrocarbonaceous products from coal utilizing a dual solvent extraction technique 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 primary solvent extraction at a temperature from 250° C. to 500° C. and a pressure from 500 p.s.i.g. to 500 p.s.i.g. and subsequently recovering hydrogen enriched hydrocarbonaceous products which comprises introducing a secondary solvent into the extraction zone, said secondary solvent being selective as an ash agglomerating agent.

A particular embodiment of this invention includes the improvement hereinabove wherein said secondary solvent comprises a halogenated hydrocarbon having from 6 to 20 carbon atoms per molecule.

A further embodiment of this invention includes the improvement hereinabove wherein hydrogen gas is also introduced into the solvent extraction zone in addition to the secondary solvent.

Thus, it is to be noted from the description presented thus far that the benefits to be derived from the practice of this invention are predicated on the presence of an ash agglomerating agent in the solvent extraction zone. Such an agent is for convenience purposes herein referred to as a "secondary solvent." It is believed that one of the reasons the present invention produces such desirable results is that the secondary solvent acts in some way as an initiator for agglomerating the micro-size particles of ash into large solid particles which are then more amenable

to separation from the liquid coal extract via centrifugation, decantation, filtration, etc. The ultimate effect of the secondary solvent, in addition to rendering the ash more readily removable is to produce a liquid coal extract of higher quality and in many cases of higher hydrogen content than would otherwise be obtained, for example, via the prior art techniques. Additional benefits may also accrue in the practice of this invention by utilizing a finely divided hydrogenation catalyst in the solvent extraction zone, as well as hydrogen gas in conjunction with secondary solvent, more fully described hereinafter.

DETAILED DESCRIPTION OF THE INVENTION

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 should have a high volatile content, such as 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 primary solvents for use in the practice of this invention are those which are of the hydrogen-donor 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 primary solvent hydrocarbons or mixtures or hydrocarbons boil between about 175° C. and 425° C. Examples of suitable primary solvent include tetrahydronaphthalene (Tetralin), Decalin, biphenyl, methyl-naphthalene dimethylnaphthalene, etc. Other types of solvents which may be added to the preferred primary solvents of this invention for special reasons include phenolic compounds, such as phenol, cresols, and xylenols. As used herein, however, it is to be understood that the "primary solvent" includes all materials added to the extraction zone as solvents except the hereinbelow defined secondary solvent. In other words, a primary solvent might include a mixture of Tetralin and phenol and still be referred to and included in the term "primary solvent." Additionally, the primary solvent may also contain the subsequent addition of an anti-solvent to the liquid coal extract, such as saturated paraffinic hydrocarbons like hexane, to aid in the precipitation of tarry and solid residue from the coal extract of the invention. However, this latter situation is not to be interpreted as the addition of a secondary solvent within the concept of this invention. Only those secondary solvents hereinafter defined should be included in the broad concept of dual solvent extraction to which this invention is directly applicable.

However, in the selection of a suitable primary 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 zone having coal dissolved therein must have a reduced hydrogen content compared to the hydrogen content of the lean primary solvent which is added to the extraction zone.

The essence of the present invention is based on the discovery that the presence of from 0.1% to 40% by volume of an agglomerating agent (based on the volume of primary solvent present) will considerably enhance the separation of ash from the solvent coal extract produced from the conversion of solid coal to liquid. Preferably,

the amount of secondary solvent or ash agglomerating agent will be from 1% to 10% by volume based on the volume of primary solvent.

In a preferred embodiment of this invention there is embodied the selective hydrogenation of the primary solvent during extraction in order to increase its hydrogen content so that hydrogen may be more easily transferred from the solvent to the coal and/or directly from the hydrogen gas 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 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 known, 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, Tetralins.
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.

Broadly, the critical feature of the present invention is in the use of an ash agglomerating agent in the extraction zone as an adjunct to the primary solvent. It is intended that this invention be wide in scope in that any agent which has the ability to agglomerate ash as herein defined from smaller particles into larger particles in a manner sufficient to render such ash more readily separable from the liquid coal extract is to be included within the concept of this invention. Particular agglomerating agents include halogenated hydrocarbons having from 6 to 20 carbon atoms per molecule. More particular agglomerating agents include aromatic hydrocarbons, such as mono- and di-chronophthalene; mono- and dibromonaphthalene; chlorobenzenes; chloro- and bromo-Tetralins and Decalins; and the like.

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 pre-

sented 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 of at least -8 Tyler screen size (or equivalent U.S. Sieve Series) and, preferably, would be reduced to an average particle size for -14 Tyler screen size. In many cases, it is desirable to use colloidal size coal, e.g. less than 2 microns. As used herein the term "Tyler screen" refers in all instances to the commercial Tyler Standard Screens. The correlation between Tyler screen mesh (and approximate U.S. Sieve Series) and average particle diameter is as follows:

U.S. Sieve Series (approximate)	Tyler Screen Mesh	Average diameter of Particles, Davq in.
4	-8+10	0.0791
5	-10+14	0.0555
8	-14+20	0.0394
14	-20+28	0.0280
20	-28+35	0.0198
30	-35+48	0.0140
45	-48+65	0.0099
60	-65+100	0.0077
80	-100+150	0.00496
120 etc.	-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 over-sized 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 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 weight ratio from 0.2 to 10, a residence time from 30 seconds to 5 hours, the presence of secondary solvent (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 heterogeneous 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 step, 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 and a bottoms fraction comprising residue material which is suitable for fuel. The secondary solvent may also be separated from the liquid coal extract by conventional means, such as distillation, either before, during or subsequent to the separation of the extract into desired products. In essence, therefore, the valuable liquid hydrocarbons recovered from the liquid coal extract include, for example, gasoline boiling range products and/or chemical, 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 secondary solvent 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 primary solvent.

The invention may be more fully understood with reference to the following examples:

EXAMPLE 1

A sample of bituminous coal was crushed to 100 mesh size, mixed with Tetralin, and colloided on an Eppenbach Colloidal Mill. The particle size after five hours of operation was reduced to less than two microns. (95% by weight of the coal was less than two microns with none larger than 100 microns.) This mixture was then subjected to the following conditions:

Temperature	0.5.
Pressure	430° C.
Tetralin/coal ratio, wt.	2000 p.s.i.g.
Secondary solvent	3/1.
Hydrogen gas rejection	None.
Residence time, hours	Yes (also H ₂ S).

A coal extract having the following properties was recovered:

Molecular weight	503
Wt. percent sulfur	1.29
Percent benzene insolubles, wt.	12.12
Percent hydrogen, wt.	7.18

The solids were filtered from the extract and were analyzed with the following results:

U.S. Sieve Series—	Particle size, wt. percent
On No. 4	5.4
On No. 10	16.8
On No. 20	14.4
On No. 50	16.3
On No. 100	21.8
On No. 200	13.5
On No. 270	5.0
Thru 270	6.8

EXAMPLE 2

Example 1 was repeated except that 10 grams of dichloronaphthalene (i.e. 2.5% by volume based on Tetralin volume) was added as a secondary solvent to the extraction zone. All other conditions were maintained substantially the same as in Example 1. A cone extract having the following properties was recovered (on a secondary solvent-free basis):

Molecular weight	396
Sulfur, wt. percent	0.72
Benzene insolubles, wt. percent	8.04
Hydrogen, wt. percent	7.07

The filtered and recovered solids had the following analysis:

U.S. Sieve Series—	Particle size, wt. percent
On No. 4	26.8
On No. 10	45.5
On No. 20	12.5
On No. 50	6.4
On No. 100	4.5
On No. 200	2.5
On No. 270	1.2
Thru 270	0.6

¹ Includes 6 wt. percent of 0.5 inch pieces.

The data clearly shows the agglomerating effect of the secondary solvent. In addition, the extract of Example 2 is also enhanced by reduced sulfur content and reduced benzene insolubles content.

Similar results would be expected from the use of the other secondary solvents hereinabove described.

PREFERRED EMBODIMENT

The preferred embodiment of the present invention comprises a process for obtaining valuable liquid hydrocarbons from particulate coal which comprises the steps of: (a) contacting particulate coal and a primary solvent comprising polycyclic aromatic hydrocarbons in an ex-

traction zone under conditions including the presence of added hydrogen gas and a secondary solvent comprising halogenated hydrocarbons having from 6 to 20 carbon atoms per molecule in an amount from 1% to 10% by volume based on the volume of said primary solvent sufficient to convert at least 50% by weight of the m.a.f. coal into liquid coal extract, and to agglomerate ash particles; (b) separating the agglomerated ash particles from the said extract; and (c) recovering valuable liquid hydrocarbons from said separated extract.

The invention claimed is:

1. A process for producing hydrogen-enriched hydrocarbonaceous products from particulate coal by subjecting particulate coal, at a temperature from 250° C. to 500° C. and a pressure from 500 to 5000 p.s.i.g., to solvent extraction in an extraction zone with a primary solvent comprising a polycyclic aromatic hydrocarbon which is liquid at said temperature and pressure and a secondary solvent comprising a halogenated hydrocarbon having from 6 to 20 carbon atoms per molecule, said secondary solvent being selective as an ash agglomerating agent.

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

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

(a) contacting particulate coal and a primary solvent comprising polycyclic aromatic hydrocarbons in an extraction zone under conditions including a temperature from 250° C. to 500° C. and a pressure from 500 to 5000 p.s.i.g. and the presence of added hydrogen gas and a secondary solvent comprising halogenated hydrocarbons having from 6 to 20 carbon atoms per molecule in an amount from 1% to 10% by volume based on the volume of said primary solvent sufficient to convert at least 50% by weight of the m.a.f. coal into liquid coal extract, and to agglomerate ash particles;

(b) separating the agglomerated ash particles from said extract; and

(c) recovering valuable liquid hydrocarbons from said separated extract.

4. Process according to claim 3 wherein said primary solvent comprises tetrahydronaphthalene and said secondary solvent comprises chloronaphthalene.

References Cited

UNITED STATES PATENTS

1,822,349	9/1931	Jannek et al.	208—8
1,925,005	8/1933	Rose	208—8
2,596,793	5/1952	Schabelitz	208—8
2,681,300	6/1954	Ruidisch	208—8
3,162,594	12/1964	Gorin	208—8
2,133,280	10/1938	Burk	208—8

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