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**COAL LIQUEFACTION PROCESS**

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6 Claims

**ABSTRACT OF THE DISCLOSURE**

Process for liquefying coal by subjecting bituminous coal particles to microwave energy and recovering valuable liquid hydrocarbon products from the resulting liquid coal extract.

**BACKGROUND OF THE INVENTION**

This invention relates to a process for liquefying coal using wave energy having a frequency above 1,000 megacycles. It particularly relates to a process for liquefying coal using a selective solvent and subjecting the solvent-coal mixture to microwave energy.

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 valuable liquid hydrocarbon 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.

However, the aforementioned prior art procedures have not been substantially commercially attractive or feasible to warrant widespread commercial exploitation of converting coal into valuable normally 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 normally liquid products from coal.

**SUMMARY OF THE INVENTION**

Therefore, it is an object of this invention to provide an improved process for the liquefaction of coal whereby valuable normally 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 normally liquid hydrocarbons.

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

Therefore, in accordance with the practice of one embodiment of this invention, there is provided a process for liquefying coal which comprises subjecting coal particles to wave energy having a frequency above 1,000 megacycles under conditions including a temperature from 100° C. to 500° C. and pressure from 1 atmosphere to 10,000 p.s.i.g. sufficient to convert at least 50% by weight M.A.F. coal into normally liquid products.

Another embodiment of the invention includes the presence of hydrogen gas during the liquefying step.

Another specific embodiment of the invention includes the presence of a selective solvent during the liquefying step.

**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 use of wave energy having a frequency above 1,000 megacycles to convert solid particulate coal into normally liquid coal products. It is believed that one of the reasons the practice of this invention produces such a desirable result is that, for example, microwave energy activates the inherently present small amount of volatile matter in the coal which begins dissolving the coal and provides the nucleus for the formation of a solvent material to continue the conversion of solid coal into liquid products. Furthermore, as will be evident from the description presented herein, the use of wave energy permits the liquefaction of coal at significantly lower temperatures than normally utilized by the prior art and significantly reduces the time required to convert solid coal into liquid products.

Additional benefits may also accrue in the practice of this invention by utilizing a selective solvent, hydrogen gas, and/or a hydrogenation catalyst in the liquefaction zone.

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) and, typically, from 25% to 35% by weight volatile content. Although the present invention will be described with reference to the conversion of bituminous coal to valuable normally liquid hydrocarbons, it is within the concept of the present invention to apply the inventive process to bituminous coal, 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.

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 the crushing and grinding of coarse materials, so no detailed discussion of the apparatus need be presented herein. Preferably, the coarse coal usually having an average particle diameter in excess of 0.8 inch and, typically, from 0.25 to 2.0 inches, is processed through the crushing and grinding apparatus sufficient to reduce in size the average particle



diameter to at least -8 Tyler screen size and, preferably, reduce to an average particle size of -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 particle, $D_{avg}$ 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 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 coal particles are then passed into a liquefaction zone which, in effect, is a reaction zone for the substantial conversion of the coal into normally liquid hydrocarbonaceous products.

In accordance with this invention, the pulverized coal is subjected to wave energy having a frequency above 1,000 megacycles. Preferably, this wave energy is of microwave frequency.

Apparatus and equipment for generating the wave energy are standard and well known to those skilled in the art. Typically, for example, such equipment might include an oscillator such as a Magnetron, an amplifier such as a Klystron, and a radiation device for transmitting the wave energy to the material to be treated. Since these items are conventional, those skilled in the art from the teachings presented herein will know how to accumulate and assemble the stock components necessary to generate the required wave energy and apply it to the coal in the manner described herein.

Operating conditions during the liquefaction step include a temperature from 100° C. to 500° C. and a pressure from 1 atmosphere to 10,000 p.s.i.g. sufficient to convert at least 50% by weight M.A.F. coal into normally liquid products

In a preferred embodiment of this invention, a selective solvent is utilized as an integral part of the liquefaction process. In operation, the coal is admixed with the selective solvent either during the pulverization step previously described or in the liquefaction zone or in both instances.

Suitable solvents for use in the practice of the preferred embodiment of this invention are those of the hydrogen-donor type and are at least partially hydrogenated and include naphthalenic hydrocarbons. Other hydrocarbons, such as naphthalene, methylnaphthalene, etc. may also be used if added hydrogen gas is also used in the extraction zone. Preferably, the solvent is one which is in liquid phase at the recommended temperature and pressure for extraction. Mixtures of the 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 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 still further 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 utilization of wave energy of the type described herein will clearly enhance the efficiency and effectiveness of the conversion of solid coal to liquid coal extract. Specifically, it was found that the time required for liquefaction was considerably reduced, the amount of solvent utilized in the preferred embodiment was significantly reduced and the temperature at which liquefaction was possible was significantly reduced. In fact, in some cases, depending upon the volatile content of the coal utilized as feed, it was found possible to eliminate the need for an added solvent.

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.

Type of aromatic hydrocarbon:	J-factor number
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 liquefaction 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.

For the preferred embodiment, utilizing the presence of a selective solvent, the operating conditions for the liquefaction step include a temperature from 200° C. to 500° C., a pressure from 500 p.s.i.g. to 5,000 p.s.i.g., a solvent-to-coal ratio of from 0.2 to 10, and a residence time in the liquefaction zone from 30 seconds to 5 hours and, still more preferably, include the presence of hydrogen sufficient to dissolve coal such that a total in excess of 50% by weight of the coal feed into the liquefaction zone has been liquefied into normally liquid products.

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 palladium on an alumina 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. The amount of hydrogen which may be added to the liquefaction zone can be varied over an extremely wide range. For example, hydrogen in an amount from 1,000 to 10,000 standard cubic feet of hydrogen per barrel of selective solvent and, typically, about 5,000 s.c.f./b. may be used with satisfactory results. Similarly, in the embodiment wherein no added solvent is utilized in the liquefaction zone, the amount of hydrogen may vary from 100 to 10,000 standard cubic feet per 100 pounds of solid coal particles introduced into the liquefaction zone. By way of emphasis, as used herein, the term "liquefaction zone" or "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 liquefaction of the coal utilizing wave energy, preferably with added 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 solvent and hydrogen gas.

As previously mentioned, it may be desirable to utilize solvent during the pulverization step. The conditions during the pulverization step, of course, may be varied widely according to the desires of those skilled in the art and the teachings of this invention. The temperature may be varied over a relatively broad range from essentially ambient temperature to a relatively high temperature. In the event a solvent is used during the pulverization step, it is preferred 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.

#### EXAMPLE 1

A Pittsburg Seam Coal is pulverized to an average particle diameter of about -14 Tyler screen size. The crushed coal is mixed with Tetralin on a 1:1 weight basis and passed into a reaction zone maintained under a temperature of 300° C. and a pressure of 1,000 p.s.i.g. The admixture is then subjected to a microwave energy for a period of about 3 hours. Approximately 80% by weight of the M.A.F. coal is converted to C<sub>6</sub>+ hydrocarbonaceous product.

#### EXAMPLE 2

The reaction of Example 1 is repeated except that 5,000 s.c.f./barrel of solvent of hydrogen is introduced into the reaction zone. Approximately 85% by weight of the M.A.F. coal is converted to C<sub>6</sub>+ hydrocarbonaceous products in significantly less time than in Example 1, e.g. 2 hours.

The experiments are again repeated and similar results are experienced by substituting ultraviolet light for the microwave energy.

#### EXAMPLE 3

The reaction of Example 1 was repeated except that no wave energy was imposed on the solvent-coal mixture. In order to convert 80% by weight M.A.F. coal to C<sub>6</sub>+ products required significantly longer time, e.g. 3+ hours, but also required significantly higher temperature, e.g. 400° F. to 450° F.

#### PREFERRED EMBODIMENT

From the discussion presented hereinabove and in view of the illustrative examples presented, the preferred embodiment of the present invention includes a process for liquefying coal which comprises subjecting bituminous coal particles to microwave energy above 1,000 megacycles under conditions including a temperature from 200° C. to 500° C., pressure from 500 to 5,000 p.s.i.g., and the presence of a selective solvent sufficient to convert at least 50% by weight M.A.F. coal into normally liquid products.

What is claimed is:

1. Process for liquefying coal which comprises subjecting coal particles to wave energy having a frequency



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above 1,00 megacycles and in the microwave frequency range under conditions including a temperature from 100° C. to 500° C. and pressure from one atmosphere to 10,000 p.s.i.g. sufficient to convert at least 50% by weight M.A.F. coal into normally liquid products.

2. Process according to claim 1 wherein said conditions include the presence of added hydrogen gas.

3. Process for liquefying coal which comprises subjecting bituminous coal particles to microwave energy above 1,000 megacycles under conditions including a temperature from 200° C. to 500° C., pressure from 500 p.s.i.g. to 5,000 p.s.i.g., and the presence of a selective solvent sufficient to convert at least 50% by weight M.A.F. coal into normally liquid products.

4. Process according to claim 3 wherein said conditions include the presence of added hydrogen gas.

5. Process according to claim 3 wherein said coal comprises high volatile content bituminous coal having a volatile content greater than 20% by weight of the M.A.F. coal.

6. Process according to claim 5 wherein said condi-

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tions include the presence of from 1,000 to 10,000 standard cubic feet of added hydrogen per barrel of solvent, a solvent to coal ratio from 0.2 to 10, and a residence time from 30 seconds to 5 hours.

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