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[54] **COAL LIQUEFACTION**
6 Claims, No Drawings

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[50] **Field of Search** 208/10

[56] **References Cited**

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ABSTRACT: Normally solid coal is hydrogenated using certain supported hydrogenation catalysts in the substantial absence of externally supplied liquid slurry medium and in a catalyst/coal weight ratio of from about 0.1/1 to about 2/1.

COAL LIQUEFACTION

BACKGROUND OF THE INVENTION

Heretofore normally solid, subdivided coal has been converted into a combination of gaseous hydrocarbonaceous and liquid hydrocarbonaceous products by subjecting the coal to hydrogenation under elevated temperatures and pressure in the presence of a liquid slurry medium (solvent).

The hydrogenation slurry medium (hereinafter slurry medium) is normally a hydrocarbonaceous liquid oil previously obtained from the liquefaction of coal but can be other hydrocarbonaceous liquids as desired and as well known in the art.

A particularly useful coal liquefaction process is fully and completely disclosed in U.S. Pat. Re. 25,770, the disclosure of which is incorporated herein by reference. Generally, the slurry medium is a complex hydrocarbonaceous liquid having a boiling range within the range of from the boiling temperature of butane to about 1,500° F. and contains one or more of naphtha boiling in a range of from the boiling point of butane to about 400° F., light distillate boiling in the range of from about 400° to about 650° F., heavy distillate boiling in the range of from about 650° to about 975° F., and residual fuel oil boiling in the range of from about 975° to about 1,500° F.

The hydrogenation medium medium normally employed in a slurry medium/coal weight ratio of from about 0.1/1 to about 4/1 so that there is always substantial amounts of liquid slurry medium present in the hydrogenation operation.

Various catalysts have been used, generally in catalyst/coal weight ratios of 0.01/1 to 0.02/1.

Generally, in coal liquefaction processes it is most desirable from an economic point of view to maximize the production of gaseous and liquid hydrocarbonaceous products and to minimize the production of coke forming materials such as asphaltenes. This is so because a gaseous or liquid hydrocarbonaceous product will generally bring a higher return per unit of product than coke and the like.

In addition, it is desirable to minimize the amount of asphaltenes present in a hydrocarbonaceous product which must undergo subsequent processing such as fractionation, solvent extraction, and the like because the asphaltenes themselves are difficult to process. Asphaltenes therefor render the material in which they are contained more difficult to process into the desired liquid hydrocarbonaceous products such as naphtha, light distillate, and the like. This is also true because asphaltenes tend to coke under normal processing temperatures.

Therefore, in many situations it is highly desirable to minimize the asphaltenes content of the products of the coal hydrogenation operation, thereby simplifying the subsequent processing steps required for these products while at the same time maximizing the amount of higher return gaseous and liquid products produced.

SUMMARY OF THE INVENTION

It has now been found that the quantity of asphaltenes present in coal liquefaction products is substantially reduced when the hydrogenation operation is carried out using certain solid catalysts in the substantial absence of slurry medium and certain catalyst/coal weight ratios.

It was surprisingly found that by hydrogenating normally solid coal according to this invention the asphaltenes content of the liquid product was more than 50 percent reduced while at the same time the amount of gaseous product and liquid light oil product and the overall conversion were all substantially increased.

Accordingly, it is an object of this invention to provide a new and improved method for carrying out a coal hydrogenation process. It is another object to provide a new and improved method for reducing the amount of asphaltenes contained in products from a coal liquefaction operation. It is another object to provide a new and improved method for liquefying coal without a slurry medium. It is another object to provide a new and improved method for producing liquid hydrocarbonaceous products from normally solid coal which products contain substantially reduced amounts of asphaltenes as compared to similar materials produced by the liquefaction of coal in the presence of a liquid medium.

Other aspects, objects, and advantages of this invention will be apparent to those skilled in the art from this disclosure and the appended claims.

DETAILED DESCRIPTION OF THE INVENTION

According to this invention there is provided a method wherein normally solid coal is hydrogenated under conditions to liquefy at least a portion thereof with the significant difference that the coal hydrogenation operation itself is carried out using certain supported solid catalysts in the substantial absence of any externally supplied slurry medium whereby the production of asphaltenes is reduced.

The coal hydrogenation operation generally involves mixing subdivided coal (e.g., at least 90 weight percent of the coal passing an eight mesh (Tyler) sieve) with molecular hydrogen in an amount sufficient to provide a hydrogen partial pressure of from about 400 to about 8,000, preferably from about 500 to about 3,000, p.s.i.a. The overall hydrogenation operation is carried out under a temperature of from about 500 to about 1,000° F. and under a total pressure of from about 400 to about 10,000 p.s.i.g. The operation is carried out for a time sufficient to at least partially liquefy the coal, the normal reaction time being such that a major amount of the solid coal is converted to gaseous and/or liquid hydrocarbonaceous products, the minor amount remaining in the solid form being unconverted coal, ash, char, coke, and the like.

The coal hydrogenation operation is carried out in the presence of an effective catalytic amount of a supported, solid hydrogenation catalyst.

Suitable hydrogenation catalysts include the metals, preferably in subdivided form such as powders, of iron, cobalt, nickel, vanadium, molybdenum, or tungsten, or compounds of these metals such as the halides, oxides, sulfides, molybdates, sulfates, or oxalates. Mixtures and other combinations of two or more of these metals and/or compounds of these metals can be employed as desired. Exemplary materials that have heretofore been employed as hydrogenation catalysts include the chlorides of nickel, iron, and cobalt. There can also be used sulfates of iron, cobalt, and nickel, molybdates of cobalt, nickel, and iron, sulfides of tin, tungsten, molybdenum, or nickel, and combinations thereof, powders of metals such as nickel, cobalt, or iron. Oxides or combinations thereof can also be used such as oxides of iron alone or in combination with nickel oxide, oxides of tungsten alone or in combination with nickel oxide, oxides of nickel, oxides of cobalt alone or in combination with nickel oxide, vanadium oxide, and the like.

The catalyst is supported on a carrier material such as alumina, magnesia, silica, titania, zirconia, fullers earth, kieselghur, clay such as kaolin (Kaolinite, Halloysite, Dickite, Nacrite, and Endellite) or bentonite (Montmorillonite, Beidellite, Nontronite, Hectorite, and Saponite), attapulgite, and sepiolite, carbon, and the like. For example, combinations of iron oxide, alumina, and/or silica and/or titania can be employed. Also, oxides of molybdenum, oxides of tungsten, oxides of magnesium, sulfides of tungsten, and the like can be combined with alumina and/or silica and/or fullers earth, and the like. When carbon is employed as a support it can be in the form of wood char, coal char, activated carbon, or any other carbonaceous material containing a major amount of carbon.

In the above examples the iron, cobalt, and nickel can have valences of two or three, the vanadium a valence of five, four, three, or two, and the molybdenum and tungsten a valence of six, five, four, three, or two.

Each support material can be employed alone or in combination with other support materials and is used in an amount which supports substantially all of the catalyst present.

Substantially any coal can be employed in this invention. For example, semianthracite, bituminous, semibituminous, subbituminous, lignite, peat, and the like can be used.

The amount of catalyst used will be an effective hydrogenation catalytic amount. The catalyst is used in a catalyst/coal weight ratio of from about 0.1/1 to about 2/1, preferably from about 0.5/1 to about 1.5/1.

EXAMPLE I

Two identical hydrogenation runs were carried out with the only difference between the two being that one employed an externally supplied hydrocarbonaceous liquid slurry medium while the other employed no such added slurry medium. In each run a commercially available hydrogenation catalyst was used which contained 3.4 weight percent CoO, 13.2 weight percent MoO_3, 83.4 weight percent Al_2O_3, and 4.1 weight percent sulfur based on the total weight of the catalyst and which was subdivided to be in the particle size range of minus 100 and plus 200 mesh (U.S. sieve). The catalyst was employed in the amount of 100 weight percent based on the total weight of the coal. The catalyst was mixed with Pittsburgh 08 coal subdivided to be in the same particle size range as the catalyst. The catalyst/coal weight ratio was 1/1.

In both runs the coal-catalyst mixture was exposed to molecular hydrogen at a total pressure of 3,000 p.s.i.g., a temperature of 800° F. and for 30 minutes. In run No. 1 there was also present 100 weight percent, based on the total weight of coal, of hydrocarbonaceous coal oil having a boiling range of from 675° to 775° F. which had been previously obtained from the hydrogenation of the same type of coal under the same hydrogenation conditions as set forth above. In run No. 2 no coal oil or other externally supplied slurry medium was employed and the dry mixture of solid coal and solid catalyst was exposed to the hydrogen.

The gaseous and liquid products were analyzed and the results, reported in weight percent based upon MAF coal charged, were as follows:

TABLE I

Products	Run 1 (With slurry medium)	Run 2 (Invention, no slurry medium
Gas	4	7.2
Light Hydrocarbonaceous liquid (boiling range under 500° F.)	3	12.2
Heavy hydrocarbonaceous liquid (boiling range greater than 500° F.)	49.3	40.9
Asphaltenes	20.3	3.8
Water	5.1	10.9
Percent Conversion	70.1	73.8

It can be seen from the above data that the asphaltenes content was substantially reduced, while the overall conversion and the amount of gas and light coal oil were all increased.

EXAMPLE II

Pittsburgh 08 coal (minus 100/plus 200 U.S. sieve mesh) was hydrogenated with molecular hydrogen in the absence of hydrogenation catalyst and with no added slurry medium. The coal was heated to 812° F. for 25 minutes under a maximum hydrogen pressure of 2,940 p.s.i.g. The products were analyzed and the results, reported in weight percent based upon MAF coal charged, were as follows:

TABLE II

Gas	6.3
Light Oil (boiling range under 500° F.)	2.1
Heavy Oil (boiling range over 500° F.)	16.5
Asphaltenes	17.5
Water	3.8
Percent Conversion	47.9

It can be seen from this example that a combination of presence of supported solid catalyst and absence of externally supplied slurry medium is necessary to substantially reduce the asphaltenes content in the manner done in run 2 of example I.

EXAMPLE III

Pittsburgh 08 coal (minus 100/plus 200 U.S. sieve mesh) was hydrogenated with molecular hydrogen in the presence of a 1/1 weight ratio of tabular alumina particles (minus 3/plus 100 U.S. sieve mesh) but in the absence of any added hydrogenation catalyst or slurry oil. The coal was heated to 810° F. for 30 minutes under a maximum hydrogen pressure of 2,650 p.s.i.g. The products were analyzed and the results, reported in weight percent based on MAF coal charged, were as follows:

TABLE III

Gas	6.2
Light Oil (boiling range under 500° F.)	1.4
Heavy Oil (boiling range over 500° F.)	19.4
Asphaltenes	25.0
Water	2.1
Percent Conversion	48.0

It can be seen from this example that the substitution of inert solids for the solid catalyst does not achieve the asphaltenes reduction of this invention (run 2, example I).

Reasonable variations and modifications are possible within the scope of this disclosure without departing from the spirit and scope of this invention.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. In a method for hydrogenating normally solid coal to liquefy at least a portion thereof, the improvement comprising carrying out the coal hydrogenation operation in the presence of an effective catalytic amount of a solid, supported hydrogenation catalyst using a catalyst/coal weight ratio of from about 0.1/1 to about 2/1, and in the substantial absence of externally supplied liquid slurry medium, whereby the production of asphaltenes is reduced.

2. A method according to claim 1 wherein said hydrogenation operation comprises mixing subdivided coal with at least one of molecular hydrogen in an amount sufficient to provide a hydrogen partial pressure of from about 400 to about 8,000 p.s.i.a., and maintaining the mixture under a temperature of from about 500° to about 1,500° F. and a total pressure of from about 400 to about 10,000 p.s.i.g. for a time sufficient to at least partially liquefy at least part of the coal.

3. A method according to claim 1 wherein said catalyst is one of Fe, Co, Ni, V, Mo, or W, or the halide, oxide, sulfide, molybdate, sulfate, or oxalate of said metals or combinations of two or more of said metals and/or said compounds thereof.

4. A method according to claim 3 wherein said catalyst is supported on at least one of alumina, silica, magnesia, zirconia, titania, clay, carbon, fullers earth or kieselghur.

5. A method according to claim 1 wherein said catalyst is sulfided CoO and MoO_3 supported on alumina.

6. A method according to claim 1 wherein said catalyst/coal weight ratio is from about 0.5/1 to about 1.5/1.

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