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# SOLVENT EXTRACTION OF COAL UTILIZING A HETEROPOLY ACID CATALYST

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## ABSTRACT OF THE DISCLOSURE

A process for solvent extracting solid carbonaceous materials in which a heteropoly acid of a Group V–B or Group VI–B metal is employed as a catalyst and the heteropoly acid catalyst or the Group V–B or Group VI–B metal component thereof is recovered in heteropoly acid form from the solid residue resulting from solvent extraction and the heteropoly acid recovered is recycled to the solvent extraction operation.

## BACKGROUND OF INVENTION

This invention relates to a process for liquefying a solid carbonaceous material such as coal to provide liquid hydrocarbons. More specifically, this invention concerns a process for solvent extraction of coal and the like, utilizing a heavy hydrocarbonaceous solvent, and employing as a catalyst a heteropoly acid of a Group V–B or Group VI–B metal.

Reserves of solid carbonaceous substances such as coal, lignite, etc., are quite abundant relative to reserves of petroleum and represent a valuable source of hydrocarbons to supplement or replace the hydrocarbons conventionally derived from petroleum. As reserves of crude oil continued to be used up very rapidly, the need for an economical substitute becomes greater. The energy requirements in industrial countries have created a shortage in the supply of hydrocarbons which can be at least partially alleviated by the supplementation or substitution of solid fuel-derived hydrocarbons for those derived from petroleum. Several processes for converting coal to valuable liquid products are known to those skilled in the art of coal liquefaction. Among the older processes is destructive distillation. High pressure hydrogenation and solvent extraction techniques have more recently been developed, the latter of which is related to the process of the present invention. In general, in a process for solvent extraction, finely divided coal or other particulate carbonaceous material is placed in contact with a solvent at solvent extraction conditions, usually including the presence of hydrogen gas, and the liquefied portion of the material and the solvent are subsequently separated from the remaining solid material by filtration, centrifugation or a similar operation. The liquefied material is generally separated from the solvent, usually by fractionation, and is further processed by conventional means such as hydrocracking or distillation, while the solvent is conventionally recycled to the extraction operation. In some solvent extraction processes which have been developed, the solid residue in the effluent from solvent extraction is also subjected to further processing in order to recover all possible valuable hydrocarbon products therefrom. Such treatments of the residual solids include, for example, destructive distillation and coking. Solvent extraction of solid carbonaceous materials is, in several ways, unlike the older method of obtaining liquid hydrocarbons which comprises destructive distillation of the solid. The product of destructive distillation is gaseous at distillation conditions, while the product of solvent extraction is a heavy liquid, so that separation of the product from the ash and remaining solid carbonaceous material is a completely different type of operation in each case. Similarly, no hydrocarbonaceous solvent material is utilized in order to remove the product of destructive distillation from the residual solid material, so that separation of the solvent from the ash and other residual solids and from the liquefaction product is not encountered as it is in solvent extraction. For the above reasons and others, use of catalysts in destructive distillation operations is generally considered to be of less technical difficulty than in solvent extraction. Moreover, the object of destructive distillation is to break down the carbonaceous and hydrocarbonaceous constituents of the solid to provide volatile liquids and gases while the object of solvent extraction is to hydrogenate and remove selected constituents from the solid structure of the material in the form of a solution in a hydrocarbonaceous solvent, so that catalysts perform different functions in the two operations.



Schemes for the use of catalysts to promote the liquefaction and hydrogenation of coal in solvent extraction processes have been disclosed in prior art. Various conventional hydrogenation catalysts such as Group VIII metals and others, including compounds of tin, nickel, molybdenum, tungsten, or cobalt have been proposed for such processes. Typically, these catalysts and the schemes for their use suffer from the economic and technical difficulty posed by the necessity of separating the catalysts from the finely divided solid residue of coal left by solvent extraction in order that the catalyst may be used more than once. These catalysts are relatively expensive to create, and the separation of a catalyst from the particulate residue resulting from solvent extraction is quite difficult and expensive. The elimination of such a separation step for recovering a solid catalyst would thus be an economic and technical advancement in the solvent extraction art.

In general, catalytic metals have been utilized in coal liquefaction in the form of a dispersion on the surface of, or within, a refractory solid such as silica, alumina, etc. Such a method of use has been found necessary in order to provide a sufficient surface area of active catalytic material without the use of excessive amounts of the relatively expensive catalytic metals. An obvious drawback inherent in the use of supported catalysts has been the large increase in the amount of difficultly handled solid materials which must necessarily be passed through the extraction and separation operations and recycled. The present invention is directed, in part, to providing a method for using a desirable catalytic metal in a solvent extraction operation, wherein the catalytic metal is present in a form having a very high active surface area without the use of undesirable and bulky refractory supports.

Another difficulty encountered in the use of catalysts in solvent extraction operations is the rapid decline in activity and effectiveness undergone by catalysts at the process conditions necessary for operability of solvent extraction and product separation. The swift deterioration which has been noticed in catalyst activity may be due in part to the high content, in coal, of metallic and other substances which can poison the catalyst upon exposure thereto. Catalysts are also known to be deactivated by the deposition thereon of coke and similar highly carbonaceous materials. The catalysts are generally separated from such coke for reuse only with difficulty and expense. A means for eliminating such difficulties would overcome a significant barrier to the effective and efficient use of metal-containing catalysts in a process for solvent extraction of coal.

## SUMMARY OF INVENTION

It is an object of the present invention to provide a method for solvent extraction of a solid carbonaceous material to produce vaulable hydrocarbon products utilizing a metal-containing catalyst. Another object of this invention is to provide a method for employing a highly dispersed metallic catalyst in a solvent extraction process. Yet another object of this invention is to provide a solvent extraction process employing a heteropoly acid as a catalyst. A still further object of the present invention is to provide a solvent extraction process utilizing a catalytic metal which is recovered subsequent to the extraction operation and recycled for further catalytic use.

In an embodiment, the present invention relates to a process for converting a solid carbonaceous material to a hydrocarbonaceous liquefaction product which comprises the steps of: (a) solvent extracting said solid carbonaceous material with a hydrocarbonaceous solvent at solvent extraction conditions utilizing a catalyst comprising a heteropoly acid containing a Group V–B or Group VI–B metal component; (b) separating the resultant mixture into a liquid residuum and a solid residuum; and (c) recovering said hydrocarbonaceous liquefaction product from said liquid residuum.

In another embodiment, the present invention relates to a process for converting a solid carbonaceous material to a hydrocarbonceous liquefaction product which comprises the steps of: (a) solvent extracting said solid carbonaceous material with a hydrocarbonaceous solvent at solvent extraction conditions utilizing a catalyst comprising a first heteropoly acid containing a Group V–B or Group VI–B metal component; (b) separating the resultant mixture into a liquid residuum and a solid residuum, said solid residuum containing said metal; (c) recovering said hydrocarbonaceous liquefaction product from said liquid residuum; (d) contacting said solid residuum with a liquid solution of an acid selected from phosphoric or silicic to produce a liquid solution of a heteropoly acid containing said metal component; (e) separating said heteropoly acid solution from said solid reesiduum; and (f) recovering a second heteropoly acid containing said metal component from said heteropoly acid solution and passing said second heteropoly acid to solvent extraction Step (a).

In still another embodiment, the present invention relates to a process for converting a solid carbonaceous material to a hydrocarbonaceous liquefaction product which comprises the steps of: (a) solvent extracting said solvent carbonaceous material with a hydrocarbonaceous solvent at solvent extraction conditions utilizing a catalyst comprising a first heteropoly acid containing a Group V–B or Group VI–B metal component; (b) separating the resultant mixture into a liquid residuum and a solid residuum, said solid residuum containing said metal component; (c) recovering a first portion of said hydrocarbonaceous liquefaction product from said liquid reesiduum; (d) heating said solid residuum to produce a distillate fraction and a solid char fraction, said char fraction containing said metal component, and recovering a second portion of said hydrocarbonaceous liquefaction product from said distillate fraction; (e) oxidizing said char fraction to produce an oxide of said metal component therein; (f) contacting the oxidized char fraction of Step (e) with a liquid solution of an acid selected from phosphoric and silicic to produce a liquid solution of a heteropoly acid containing said metal component; (g) separating said heteropoly acid solution from said oxidized char fraction; and (h) recovering a second heteropoly acid containing said metal component from said heteropoly acid solution and passing said second heteropoly acid to solvent extraction Step (a).

I have found that heteropoly acids of metals from Group V–B and Group VI–B of the Periodic Table, particularly molybdenum, tungsten, and vanadium, may be employed as effective catalysts in a process for solvent extraction of coal and similar solid carbonaceous materials. I have also found that, surprisingly, the heteropoly acid form of these metals is a more effective catalyst than other forms, and that the catalyst can be recovered from the solid residue resulting from solvent extraction in heteropoly acid form, and may thus be recycled to the extraction step for further use through the method herein disclosed.



## DETAILED DESCRIPTION

The process of the present invention may be applied to the conversion of any available carbonaceous solid. Among the naturally occurring carbonaceous materials which are readily available and are suitable for use in the present process are coal, lignite, peat, oil shale, tar sand, etc. The present invention is particularly applicable to the conversion of bituminous coals, and especially those having a relatively high volatiles content. For example, a bituminous coal having a volatiles content of about 20 wt. percent or greater is particularly preferred. Conventionally, in a solvent extraction operation, the coal, or other material, is pulverized prior to the extraction. In a preferred embodiment of the present process, the solid carbonaceous material is pulverized to a size sufficiently fine to pass through a 100 mesh Tyler sieve, or finer. When the preferred bituminous coal is utilized, it is preferred that the coal be ground sufficiently fine to pass through a 200 mesh Tyler sieve.

Hydrocarbonaceous solvents suitable for use in the solvent extraction operation generally include those known in the art. Hydrogen donor solvents such as dehydroanthracene, tetrahydroanthracene, dihydrophenanthrene, tetrahydrophenanthrene, tetrahydronaphthalene, decanhydronapthalene, etc., are among the solvents preferred for use in the present process. Typically, the solvents employed in prior art comprises hydrocarbonaceous compounds or fractions boiling between about 200° C. and about 450° C., which are liquid at the temperatures and pressures employed in the extraction operation. Generally, at least a portion of such solvents is provided by recycling a portion or fraction of the liquefied hydrocarbons produced from the coal in the extraction operation. It may be necessary to catalytically hydrogenate or otherwise treat the recycled portion of the coal extract before it is suitable for use as a solvent. In general hydrogen donor solvents are preferred for use in the present process.

Also suitable for use as the solvent in the solvent extraction operation are such heavy oils as crude oil, residual fractions resulting from the refining of petroleum, etc. I have found that use of such relatively low value residual stocks as solvents in the extraction step can result in an improvement in the value of the solvent as well as in the extraction of valuable hydrocarbons from the coal. Thus, one preferred method for performing the extraction operation in the present process is to employ a heavy residual oil, containing such undesirable impurities as sulfur, nitrogen, metals, etc. The solvent which is recovered after the extraction step is often found to be improved by reduction in its sulfur, nitrogen and metals content and by a desirable decrease in its specific gravity, e.g. as characterized by an increase in the API number in degrees API (where deg. API=141.5/specific gravity at 25° C.–131.5).

The heteropoly acid catalysts which are employed in the process of the present invention include those containing metals from Group V–B and Group VI–B of the Periodic Table. The preferred heteropoly acids are those containing molybdenum, tungsten and vanadium. Especially preferred are phosphomolybdic acid, phosphotungstic acid, phosphovanadic acid, silicomolybdic acid, silicotungstic acid and silicovanadic acid. The heteropoly acids may also be used in combinations of two or more of the acids described above.

The catalyst can be contacted with the coal or other solid carbonaceous material in any suitable manner. A

preferred method for distributing the catalyst is to pulverize the coal and subsequently impregnate the coal particles with a liquid solution of the heteropoly acid. The impregnated coal is then preferably dried to deposit the heteropoly acid catalyst uniformly throughout the coal. The catalyst may be employed in solution in, for example, water, alcohols, acetone, ethyl acetate, etc. Water is particularly preferred. For example, a water solution containing about 1 wt. percent to about 25 wt. percent heteropoly acid can be contacted with comminuted coal to form a paste or slurry. The water is evaporated at a temperature of about 25° C. to about 300° C. and the impregnated coal is then ready for the solvent extraction operation. The heteropoly acid is employed in a concentration of about 0.01 wt. percent to about 100 wt. percent, based on the amount of coal or other carbonaceous solid to be solvent extract. Preferably, the concentration of catalyst is about 0.1 to about 50 wt. percent of the coal. In another embodiment, the heteropoly acid may be impregnated on relatively large coal particles which are subsequently pulverized to, e.g., 100 mesh or smaller. Alternatively, the heteropoly acid may be distributed, as a solid, in the larger size coal before pulverization or in the previously pulverized coal. The heteropoly acid may also be charged to the liquefaction reactor or vessel separately and contacted initially with the coal therein. Impregnation of the previously pulverized coal with an aqueous solution of the heteropoly acid and subsequent evaporation of the water is the preferred method for combining the heteropoly acid with the coal.

Regardless of the method employed to contact the heteropoly acid catalyst with the solid carbonaceous material, the heteropoly acid, the solid material and the hydrocarbonaceous solvent are contacted in a suitable liquefaction reactor at solvent extraction conditions in order to extract valuable hydrocarbonaceous components from the solid. Solvent extraction conditions in the present process include a temperature of about 100° C. to about 500° C. and a pressure of about 10 atmospheres to about 300 atmospheres or more. The amount of hydrocarbonaceous solvent employed is about 10 wt. percent to about 1000 wt. percent of the coal or other solid material. Preferably, hydrogen gas is also employed in the solvent extraction operation. A suitable amount of hydrogen is about 2 s.c.f. to about 250 s.c.f. per pound of coal. It is especially advantageous to utilize hydrogen gas in the extraction operation when a solvent is employed which is low in hydrogen donor properties, e.g. aromatics, residual oils, crude oils, etc. The present process may be embodied in a batch type operation or a continuous operation. In a batch type operation, a quantity of coal, heteropoly acid, hydrocarbonaceous solvent, and preferably hydrogen, are charged to a suitable reactor, such as, for example a conventional autoclave. The solids, catalyst, solvent and hydrogen are contacted at a suitable pressure and temperature for about 1 minute to about twenty-four hours. The resultant mixture is then removed from the reactor and any unconsumed hydrogen is preferably recovered for further use. The resulting mixture of liquids and solids is separated by conventional methods such as filtration, centrifugation or extraction. The liquid residuum thus separated contains the hydrocarbonaceous product of the solvent extraction operation in solution in the solvent or in admixture therewith. In a continuous type operation, the coal, heteropoly acid, solvent, and preferably hydrogen, are continuously passed into a conventional continuous reactor and the liquefaction product, solvent, hydrogen, and solids such as catalyst and ash, are continuously removed from the reactor and the liquefaction product separated. A suitable contact time in a continuous operation is about 1 minute to about 24 hours. A variety of reactors suitable for use in either a batch solvent extraction operation or a continuous operation are well known in the art. A suitable reactor may contain agitation or stirring means or other conventional equipment.

The liquefaction product may be separated from the coal ash, undissolved coal, other solids, and the heteropoly acid catalyst, or the metal component thereof, in any suitable manner. Methods employed in prior art include filtration of the solvent extraction reactor effluent, centrifugation of the reactor effluent or extraction of the desired product from the reactor effluent utilizing a selective solvent. The latter method is preferred in the present process. Suitable solvents for use in this separation operation include $C_3$–$C_{12}$ saturated hydrocarbons, such as, for example, paraffins, cycloparaffins, isoparaffins, etc. Other solvents which may be used in recovering the liquefaction product include aromatics and alkylaromatics. Preferred for use in the present process are pentane, hexane and particularly heptane. It is known in the art that these conventional aliphatic solvents have no substantial effect on the conversion of solid coal to a liquid coal extract. The solvents employed in the present process to separate the hydrocarbonaceous liquefaction product from the undissolved coal, ash and catalyst, or metal component thereof, are intended to include particularly the solvents, such as, for example, heptane, which separate hydrogen-rich, and therefore more desirable, components from the solids and hydrogen-lean, undesirable asphaltene components produced in the solvent extraction operation. It has been found that the preferred light aliphatic solvents, e.g. heptane isomers, are selective for the hydrogen-rich components and reject undesirable asphaltenes as well as the catalyst, or metal component thereof, and undissolved coal and ash. The extraction of the liquefaction product from the liquefaction reactor effluent is typically performed at a temperature of about 50° C. to about 300° C. and preferably about 50° C. to about 150° C. A pressure of about 10 atmospheres to about 100 atmospheres is preferred, but not essential, and the presence of hydrogen gas may aid in the separation procedure. When a light aliphatic solvent such as heptane is employed in the separation procedure, the solvent is generally employed at about 0.5 to about 5 parts, by weight, per part of the liquid-solid mixture resulting from the solvent extraction operation. As stated, this liquid-solid mixture can alternatively be separated into a liquid residuum and a solid residuum by such equivalent methods as centrifugation or filtration, and the liquid residuum recovered as the product of the solvent extraction process. When the above described extraction procedure is employed to separate the liquid residuum from the solid residuum after the solvent extraction operation, it has the additional advantage of rejecting the undesirable asphaltenes in the mixture resulting from the solvent extraction operation. When the liquefaction product is separated using a solvent, e.g. heptane, it can conveniently be recovered, and the solvent can be recycled for further use by flashing off the relatively low boiling solvent and recovering the hydrocarbonaceous liquefaction product as a bottoms product. The separation operation can be performed as a batch type operation or a continuous operation, and generally depends on the type of operation preferred for the solvent extraction step.

## EXAMPLE I

In this run, coal was solvent extracted in accordance with the process of the present invention utilizing phosphomolybdic acid as a catalyst. A sample of bituminous coal was pulverized sufficiently to pass through a 100 mesh Tyler sieve. A solution of phosphomolybdic acid in methanol was made up, which contained 7.9 grams of molybdenum. 100 grams of the pulverized coal was impregnated with the methanol solution of the heteropoly acid, and the methanol was evaporated from the coal. The coal was then placed in a rocking autoclave, and 213 grams of a crude oil was also placed in the autoclave. The autoclave was then sealed and sufficient hydrogen was charged to the autoclave to provide a pressure of 65 atmospheres. The mixture in the autoclave was heated to

400° C. and the pressure was observed to be 135 atmospheres. The mixture was maintained at this temperature and pressure for 4 hours and then cooled to room temperature. The excess pressure was released and the remaining contents of the autoclave were removed. The mixture taken from the autoclave was extracted with heptane at a pressure of atmosphere and a temperature of 25° C. The heptane-soluble materials and heptane solvent were separated from the solid, insoluble materials. The heptane-soluble materials were separated from the heptane solvent and recovered and a portion of this hydrocarbonaceous liquefaction product of the process was analyzed. It was found to contain 87.10 wt. percent carbon, 11.23 wt. percent hydrogen, 0.83 wt. percent sulfur and 0.38 wt. percent nitrogen. The API gravity was found to be 19.2 degrees. The solid, insoluble materials left as the residue after extraction of the autoclave effluent with heptane, and containing the catalyst, were placed in the autoclave. A second 100 grams of the pulverized coal was also placed in the autoclave, and 214 grams of the same crude oil was also charged. The autoclave was again sealed and sufficient hydrogen was charged to provide a pressure of 65 atmospheres. The contents of the autoclave were maintained at a pressure of 135 atmospheres and a temperature of 400° C. for 4 hours, and then cooled to room temperature. Excess pressure was released and mixture remaining in the autoclave was removed and extracted with heptane in the same extraction procedure previously utilized. The heptane solvent and the materials dissolved therein were then separated from the solid, heptane-insoluble residue. The weight of this solid residue remaining after heptane extraction of the autoclave effluent was found to be 82.5 grams. The heptane solvent was separated from the extracted materials, and this extracted fraction was recovered and analyzed. It was found to contain 86.51 wt. percent carbon, 11.02 wt. percent hydrogen, 1.39 wt. percent sulfur and 0.43 wt. percent nitrogen. The gravity of the extracted fraction was found to be 16.5.

## EXAMPLE II

In order to compare the heteropoly acid catalyst to a conventional molybdenum-containing catalyst, a run was undertaken using molybdic acid in place of the heteropoly acid employed in Example I. A 100-gram sample of the same pulverized bituminous coal used in Example I was obtained. A solution of molybdic acid in water was made up, which contained 7.9 grams of molybdenum. The coal sample was impregnated with the solution and the water was evaporated from the coal. The coal was then placed in the same autoclave used in Example I, and 212 grams of the same crude oil was also placed in the autoclave. The autoclave was then sealed and pressurized to 65 atmospheres with hydrogen. The mixture in the autoclave was heated to 400° C. and held at this temperature and at a pressure of 135 atmospheres for 4 hours. The mixture was then cooled to room temperature and excess pressure in the autoclave was released. The mixture was removed from the autoclave and extracted with heptane in a manner identical to that used in Example I. The heptane solvent and materials dissolved therein were separated from the remaining solid residuum and the extracted fraction was recovered. Analysis of this extracted fraction showed that it contained 86.52 wt. percent carbon, 10.94 wt. percent hydrogen, 1.89 wt. percent sulfur and 0.59 wt. percent nitrogen. The gravity of this fraction was found to be 15.7 °API. The solid residuum remaining after the heptane extraction was placed in the autoclave along with another 100-grams sample of the coal. 220 grams of the same crude oil was also placed in the autoclave. The autoclave was sealed and sufficient hydrogen was introduced to provide a pressure of 65 atmospheres. The mixture in the autoclave was maintained at a temperature of 400° C. and a pressure of 135 atmospheres for 4 hours and then cooled to room temperature. Excess pressure was released and the remaining mixture in the autoclave was removed and extracted with heptane in the same manner as previously employed. The heptane solvent and dissolved fraction were separated from the remaining solid materials, and the extracted fraction was recovered. The solid materials remaining after the heptane extraction weighed 94.9 grams. Analysis of the extracted fraction showed that it contained 86.36 wt. percent carbon, 10.85 wt. percent hydrogen, 2.13 wt. percent sulfur and 0.57 wt. percent nitrogen. The gravity of the extracted fraction was found to be 15.5.

Comparison of the results obtained in Example I with those in Example II shows that the method of the present invention, as used in Example I, provided a surprisingly superior liquefaction product and resulted in an unexpected increase in the fraction of the autocalve effluent which was heptane-soluble. Particularly significant were the strikingly lower sulfur and nitrogen contents of the heptane-soluble fractions obtained in Example I. The heptane-soluble product of the first extraction operation in Example I contained only 0.83 wt. percent sulfur, while the heptane-soluble product of the first extraction operation in Example II contained 1.89 wt. percent sulfur, i.e. more than twice as much sulfur as the product of Example I. A similar improvement in the nitrogen content is also apparent, the first extraction product of Example I having a nitrogen content of 0.37 wt. percent and the first extraction product of Example II having 0.59 wt. percent, or more than 50% more nitrogen in Example II. Those skilled in the art will recognize that the lower sulfur and nitrogen content of the product obtained by the method of the present invention in Example I is a significant improvement in the quality and utility of the liquefaction product. Similarly, comparison of the gravity of the product obtained in Example I with that of Example II shows that the liquefaction product of Example I had a significantly lower specific gravity than that of Example II and, as is well known in the art, is thereby demonstrated to be a more desirable hydrocarbonaceous product. For example, the API gravity of the first extraction operation in Example I was 19.2°, while the API gravity of the first extraction operation in Example II was 15.7°. Another unexpected beneficial result obtained using the heteropoly acid catalyst of the present process was the significant reduction in the amount of heptane-insoluble solid material remaining after heptane extraction of the autoclave effluent. For example, at the end of the heptane extraction in the second solvent extraction operation in Example I, 82.5 grams of solid materials remained, while in Example II, 94.9 grams of solids remained after the second extraction operation.

In the present process, the heteropoly acid catalyst remains in the solid residuum which is separated from the hydrocarbonaceous liquefaction product after the solvent extraction operation. In prior art processes employing a metallic or metal-containing catalyst in the solvent extraction of coal, one of the most difficult operations was in recovering all, or a portion of, the catalyst from admixture with ash, undissolved coal, and, often, asphaltenes. In the present process, the heteropoly acid catalyst, or the metal component thereof, may be recovered conveniently from admixture with the other components of the solid residuum. It is believed that the metallic component of the catalyst is generally converted to the reduced form or to an oxide form during the solvent extraction and separation operations. Irrespective of whether the metallic component of the heteropoly acid catalyst remains in the heteropoly acid form after the extraction and separation steps or is converted to another form and the heteropoly acid is destroyed, the metallic component of the catalyst is easily recovered, for further use, in heteropoly acid form.

One preferred method for recovering the heteropoly acid catalyst, or metallic component thereof, from admixture with the solid residuum resulting from the extrac-

tion and separation operations is by contacting the solid residuum with a solution of an acid which forms a heteropoly acid with the metal employed. The acids preferred for use in the recovery are phosphoric acid and silicic acid. Phosphoric acid is particularly preferred. The acid is employed in solution in an appropriate solvent, such as water, at a concentration of about 0.5 wt. percent to about 5 wt. percent, depending on solubility of the particular acid used in the particular solvent which is employed. The solid residuum is contacted with the acid solution at a temperature of about 20° C. to about 300° C. for a contact time of about 1 minute to about 24 hours. A particularly preferred operation employs an aqueous solution of phosphoric acid of a concentration of about 1 wt. percent to about 3 wt. percent. When this preferred phosphoric acid solution is utilized, a contact time of about 5 minutes to about 6 hours and a temperature of about 30° C. to about 200° C. are preferred. When higher temperatures are employed, it is preferred to conduct the recovery operation at elevated pressures sufficient to maintain a liquid phase acid solution. The solid residual materials may be contacted with the acid solution, e.g. aqueous phosphoric acid, in a batch type operation, utilizing a suitable reactor, such as an autoclave.

Alternatively, a continuous operation may be employed, in which the solid materials and acid solution are continuously contacted and separated. A continuous operation may employ cocurrent or countercurrent contact between the solids and the acid solution. After the acid solution and the residual solids have been contacted for a suitable time, sufficient to dissolve the metallic component of the original heteropoly acid catalyst, the acid solution is separated from the remaining solids and the solids may be discarded, if desired. The metallic component of the original catalyst is converted, by the foregoing recovery operation, into a component of a heteropoly acid in solution in the solvent. Any of the original heteropoly acid catalyst not destroyed in the extraction and separation steps is also recovered in solution in the solvent; however, as stated, it is believed that the metallic component of the original catalyst is primarily converted to other forms or compounds, such as the reduced form or the oxide, in the extraction and separation steps, Consequently, the recovery operation is directed primarily toward forming a new heteropoly acid which includes the metallic component of the original heteropoly acid used previously as the catalyst in the extraction step. The metal in the solid residuum forms the new heteropoly acid when contacted with the acid solution, and is thereby solubilized. The liquid solution of the newly formed heteropoly acid, containing the metal, is then separated conveniently from the remaining residual solids by, for example, decantation, filtration, etc. Subsequent evaporation of the liquid provides a new heteropoly acid which can be employed as a catalyst in further solvent extraction operations. The heteropoly acid solution formed in the foregoing recovery operation can also, in an alternative mode of operation, conveniently be employed to impregnate coal without separating the heteropoly acid from the solvent. The solvent is then evaporated from the coal as taught in the foregoing description of the use of the catalyst.

## EXAMPLE III

The solid residual materials which remained after heptane extraction of the autoclave effluent in Example I are recovered after the separation operation. 40 Grams of the solids are placed in a rocking autoclave. 50 cc. of a 1 wt. percent solution of phosphoric acid in water is also placed in the autoclave. The autoclave is sealed and pressurized to 50 atmospheres with nitrogen. The contents of the autoclave are agitated at 200° C. for 4 hours. The mixture is then cooled to room temperature and removed from the autoclave. The aqueous solution is analyzed and found to contain phosphomolybdic acid. This aqueous solution is admixed with 100 grams of pulverized bituminous coal and the water is evaporated. The impregnated coal is then solvent extracted with tetrahydronaphthalene by contacting the coal and solvent in an autoclave under the extraction conditions employed in Example I.

An alternate method for recovering the metallic component of the heteropoly acid catalyst from the solid residuum remaining after the solvent extraction step and separation step in the present process includes low temperature carbonization of the residual solids to produce a liquid distillate and a solid char. The liquid distillate is recovered and may be included as a portion of the hydrocarbonaceous product of the liquefaction process. The solid char is then burned or otherwise oxidized in order to convert substantially all of the metallic component of the original heteropoly acid catalyst into the oxide form. The oxidized char fraction is treated with an acid solution, e.g. of phosphoric acid in water, as described above, to recover the metallic component in solution in the form of a new heteropoly acid.

Low temperature carbonization, i.e., conventional destructive distillation of the solid residuum at about 400° C. to about 800° C., produces a solid fraction called "char" which contains primarily carbon, ash and the metal component of the original heteropoly acid catalyst. The carbonization step also produces an overhead, distillate fraction which contains substantially all the volatile materials left in the solid residuum after the solvent extractions and separation operations. The distillate fraction comprises primarily high boiling hydrocarbons which are generally further refined, e.g. by hydrocracking, to produce valuable hydrocarbons such as gasoline, aromatic chemicals, etc., and, in general, are utilized in a manner similar to the solvent extracted hydrocarbonaceous materials which are the primary product of the present process. The low temperature carbonization operation is performed in a manner well known in the art, and generally includes agitation of the solids during the heating thereof using, for example, rotary kilns, moving belts or fluidized beds. The distillate fraction is withdrawn and condensed into liquid form before further treatment in the preferred mode of operation. Some normally gaseous products are also generally recovered in the carbonization step. After the volatile materials have been driven off at the carbonization temperature, there remains a solid, hydrogen-deficient material comprising carbon and ash, and termed "char." In the present process, this char material also contains the metal component of the original heteropoly acid catalyst. The char is recovered and oxidized in order to convert this metal component to its oxide form.

The char can be oxidized in any conventional manner. Preferably, it is burned in air to provide at least a portion of the heat energy requirements of the solvent extraction operation and carbonization operation. The temperature and pressure of the oxidation procedure are not critical. It is preferred that the carbon content of the char be reduced by burning to the greatest possible extent in order to reduce the amount of solids which must subsequently be processed to recover the metal component. The char can also be conveniently oxidized by heating in air at a temperature of about 300° C. to about 650° C.

After the char is oxidized, preferably by burning off its carbon content as fuel, the oxidized char is treated with a liquid solution of an acid which forms a heteropoly acid with the metal component of the original heteropoly acid catalyst. This acid solution treatment, and the subsequent recovery and use of the new heteropoly acid thereby formed, are in accordance with the method described above, wherein the acid solution is used to treat the solid residuum from the solvent extraction and separation operations. Similarly, in the present operation which includes acid treatment of the oxidized char to recover the metal component in heteropoly acid form, a solution of phosphoric acid in water is the preferred acid solution. Generally, the acid treatment of the oxidized char need not be conducted at as high temperatures and pressures as

the acid treatment of the solid solvent extraction residuum. For example, a temperature of about 20° C. to about 150° C. is preferred when the aqueous phosphoric acid solution is utilized. The metal component reacts to form a heteropoly acid solution in the liquid solvent. The solvent is then separated from the remaining solid portion of the oxidized char, and the heteropoly acid is separated from the solvent, e.g., by evaporation of the solvent. Alternatively, the heteropoly acid solution, as separated from the remaining oxidized char, e.g. by decantation, is used to impregnate coal to provide a heteropoly acid catalyst for use in solvent extraction of the coal.

I claim as my invention:

1. A process for converting a solid carbonaceous material selected from the group consisting of coal, lignite, peat, oil shale and tar sand to a hydrocarbonaceous liquefaction product which comprises the steps of:

(a) solvent extracting said solid carbonaceous material with a hydrocarbonaceous solvent comprising hydrocarbonaceous compounds or fractions boiling between about 200° and about 450° C. at solvent extraction conditions utilizing a catalyst comprising a first heteropoly acid containing a component selected from the group consisting of molybdenum, tungsten and vanadium;

(b) separating the resultant mixture into a liquid residuum and a solid residuum, said solid residuum containing said metal component;

(c) recovering said hydrocarbonaceous liquefaction product from said liquid residuum;

(d) contacting said solid residuum with a liquid solution of an acid selected from phosphoric acid or silicic acid to produce a liquid solution of a heteropoly acid containing said metal component;

(e) separating said heteropoly acid solution from said solid residuum; and,

(f) recovering a second heteropoly acid containing said metal component from said heteropoly acid solution.

2. The process of claim 1 wherein said hydrocarbonaceous solvent comprises a hydrocarbon selected from tetrahydronaphthalene, decahydronaphthalene, biphenyl, methylnaphthalene, dimethylnaphthalene and dihydroanthracene.

3. The process of claim 1 wherein said hydrocarbonaceous solvent comprises a portion of said hydrocarbonaceous liquefaction product or a fraction of said hydrocarbonaceous liquefaction product.

4. The process of claim 1 wherein said hydrocarbonaceous solvent comprises a petroleum crude oil.

5. The process of claim 1 wherein said first and said second heteropoly acids are selected from phosphomolybdic acid, silicomolybdic acid, phosphotungstic acid, silicotungstic acid, phosphovanadic acid and silicovanadic acid.

6. The process of claim 1 wherein said liquid residuum is separated from said solid residuum by extraction with a $C_3$–$C_{12}$ aliphatic solvent.

7. The process of claim 6 wherein said aliphatic solvent is a $C_5$–$C_7$ saturated hydrocarbon.

8. A process for converting a solid carbonaceous material selected from the group consisting of coal, lignite, peat, oil shale and tar sand to a hydrocarbonaceous liquefaction product which comprises the steps of:

(a) solvent extracting said solid carbonaceous material with a hydrocarbonaceous solvent comprising hydrocarbonaceous compounds or fractions boiling between about 200° and about 450° C. at solvent extraction conditions utilizing a catalyst comprising a first heteropoly acid containing a metal component selected from the group consisting of molybdenum, tungsten and vanadium;

(b) separating the resultant mixture into a liquid residuum and a solid residuum, said solid residuum containing said metal component;

(c) recovering said hydrocarbonaceous liquefaction product from said liquid residuum;

(d) carbonizing said solid residuum at about 400° C. to about 800° C. to produce a liquid distillate fraction and a solid residual char fraction, said char fraction containing said metal component, and recovering said distillate fraction;

(e) oxidizing said char fraction to produce an oxide of said metal component therein;

(f) contacting the oxidized char fraction of Step (e) with a liquid solution of an acid selected from phosphoric acid and silicic acid to produce a liquid solution of a heteropoly acid containing said metal component;

(g) separating said heteropoly acid solution from said oxidized char fraction; and,

(h) recovering a second heteropoly acid containing said metal component from said heteropoly acid solution.

9. The process of claim 8 wherein said hydrocarbonaceous solvent comprises a hydrocarbon selected from tetrahydronaphthalene, decahydronaphthalene, biphenyl, methylnaphthalene, dimethylnaphthalene and dihydroanthracene.

10. The process of claim 8 wherein said hydrocarbonaceous solvent comprises a portion of said hydrocarbonaceous liquefaction product or a fraction of said hydrocarbonaceous liquefaction product.

11. The process of claim 8 wherein said hydrocarbonaceous solvent comprises a petroleum crude oil.

12. The process of claim 8 wherein said first and said second heteropoly acids are selected from phosphomolybdic acid, silicomolybdic acid, phosphotungstic acid, silicotungstic acid, phosphovanadic acid and silicovanadic acid.

13. The process of claim 8 wherein said liquid residuum is separated from said solid residuum by extraction with a $C_3$–$C_{12}$ aliphatic solvent.

14. The process of claim 13 wherein said aliphatic solvent is a $C_5$–$C_7$ saturated hydrocarbon.

15. The process of claim 1 wherein the second heteropoly acid of Step (f) is passed to solvent extraction Step (a).

16. The process of claim 8 wherein the second heteropoly acid of Step (f) is passed to solvent extraction Step (a).

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