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HYDROCRACKING PROCESS USING A COAL-DERIVED ASH

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7 Claims

ABSTRACT OF THE DISCLOSURE

A process for hydrocracking heavy hydrocarbonaceous oils utilizing a coal-derived ash as a catalyst. The process is particularly applicable to the hydrocracking of oils derived from the solvent extraction of coal.

BACKGROUND OF THE INVENTION

This invention concerns a process for hydrocracking heavy hydrocarbonaceous oils. This invention also concerns a novel catalytic material which is used in a hydrocracking process. More specifically, this invention concerns a process for hydrocracking heavy hydrocarbonaceous oils utilizing a catalytic ash derived from the decarbonization of a natural carbonaceous substance such as coal. Hydrocracking refers to the hydrogenation or cracking, in the presence of hydrogen, of a heavier hydrocarbon to produce a lighter, more valuable hydrocarbon.

Hydrocracking processes have been used for some time to improve the properties and utility of heavy hydrocarbon stocks. An alternative to hydrocracking stocks containing non-distillables (hydrocarbons which boil above about 1050° F.) is to use these heavy oils to charge a coking unit from which distillable hydrocarbons and coke are produced. In view of the ever-increasing demand for distillable hydrocarbons as motor and jet fuels, etc., hydrocracking must be preferred to coking because of its higher yields. Hydrocracking produces a change in the molecular structure of the hydrocarbons processed, as evidenced by the lower boiling points of the products, the consumption of hydrogen in the process and the decontamination of products from the usual high concentration of contaminants in heavy charge stocks. A variety of heavy residual petroleum oils, tars, and coal- and oil shale-derived oils have been processed to produce lower boiling saturated products such as gasolines, diesel fuels and gas oils. A problem generally encountered in the use of catalysts to hydrocrack such stocks is the poisoning or contamination of the catalyst by the high contaminants content of the charge stocks and the rapid deposit of coke that occurs in hydrocracking. Charge stocks often contain relatively large amounts of nitrogenous and sulfurous compounds which have a negative effect on the activity of most catalysts, and many such stocks contain organometallic complexes which have a serious adverse effect on most catalyst when present in quite low concentrations. Heavy oils obtained from coal, lignite, oil shale, tar sand, and some petroleum crude oils are particularly difficult to process because of the high concentration of these contaminants found in them. These oils usually contain a relatively large fraction of asphaltenes, which are non-distillable, paraffin-insoluble coke precursors, and which are particularly uneconomical and technically difficult to process. Asphaltenes are often complexed with the above-discussed contaminants and cause rapid deposit of coke on catalyst when processed.

Various catalysts have been used to facilitate hydrocracking processes. Commonly used as basic catalytic materials are refractory oxides such as silica, alumina, zirconia, magnesia, etc. Many conventional catalysts em-

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ploy metals from Group VIII and/or Group VI, in conjunction with a refractory oxide. Various zeolites and combinations of zeolites with the above-mentioned oxides and metals have also been used. These catalysts all suffer from the effects of the contaminants noted above, as well as from deactivation by coke formation on them and the required treatment to remove it.

It is well known in the art that heavy hydrocarbon oils, suitable as charge stocks to hydrocracking processes, may be obtained by the solvent extraction of natural carbonaceous materials such as coal. Such stocks may also be obtained from the destructive distillation and/or coking of these natural materials or of the solid residue which results from solvent extracting them. In general, the separation of non-carbonaceous residue, or ash, from the carbonaceous and hydrocarbonaceous materials has been a major difficulty in attempts to process the carbon-containing portions to obtain valuable liquid products from them. A process which obviated the need for such a separation would provide a beneficial improvement in attempts to process natural carbonaceous materials. It is well known that the coke, admixed with non-carbonaceous material, obtained from destructive distillation or coking may be burned for its fuel value. The ash which results from complete combustion of such a solid in air, has not heretofore been considered valuable, and has not been thought useful in hydrocracking processes. The use of the non-carbonaceous, oil-insoluble ash from a natural carbonaceous substance as a catalyst would simplify and make more economical a process for hydrocracking heavy hydrocarbon oils, particularly those oils which are derived from the same natural substance as the ash used to facilitate their hydrocracking.

SUMMARY OF THE INVENTION

It is an object of this invention to provide a process for hydrocracking a hydrocarbon to produce more valuable products. It is another object of this invention to provide a novel catalyst which may be utilized in a hydrocracking process. More specifically, it is an object of this invention to provide a process for hydrocracking a hydrocarbon to produce more valuable products by utilizing in the process a catalyst which comprises an ash derived from coal. The present invention is based on the discovery that the ash produced from coal, when it is decarbonized, possesses catalytic properties. When utilized as a catalyst in a hydrocracking process, this ash produces an increase in the fraction of valuable hydrocarbon products obtainable.

The process of this invention is particularly applicable to a hydrocracking process wherein the heavy hydrocarbon to be cracked is derived from solvent extracting a carbonaceous material such as coal, in that the inventive process obviates the need for the strict separation of liquids from solids in the mixture which results from such a solvent extraction process. In processes for hydrocracking coal-derived oils in prior art, it has been taught that the separation of the oils from the remaining solid materials in them is necessary, while in the present process, any fraction of the solids which remains in an oil may pass through the hydrocracking zone and may further be utilized by recovering it along with the catalyst ash, decarbonizing it, and employing it as a catalyst.

In a broad embodiment, this invention relates to a process for hydrocracking a hydrocarbon charge stock by subjecting the charge stock to hydrocracking conditions in contact with a catalyst-acting ash which has been derived by the decarbonization of coal. In a more particular embodiment, this invention relates to a process for hydrocracking a high-boiling hydrocarbon oil in a hydrocracking zone under hydrocracking conditions including a temperature of about 200° F. to about 1,200° F., a pressure

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from about 1 atmosphere to about 200 atmospheres, the presence of hydrogen gas at concentrations of about 2,000 standard cubic feet per barrel of charge stock to about 30,000 s.c.f./bbl. and in contact with an ash which is derived from the decarbonization of coal. In yet another embodiment, this invention relates to a process for hydrocracking a heavy hydrocarbonaceous oil derived from a natural carbonaceous substance such as coal which comprises the steps of:

(1) Solvent extracting a natural solid carbonaceous substance;

(2) Separating a part of the material which has remained solid from the material which has been liquefied;

(3) Subjecting the separated solid to low temperature coking conditions to produce a char and a liquid;

(4) Burning the char to produce an ash which is substantially carbon free; and

(5) Subjecting the material liquified in step (1) and the liquid produced in step (3) to hydrocracking conditions in contact with the ash produced in step (4).

This latter embodiment of the inventive process has a particular advantage in that it obviates the need for a strict separation of the liquid from the solid in step (2), as has been taught in prior art, before further processing of the liquid. The solids which remain in the solvent extracted oil may be admixed with the catalyst utilized in step (5) and subjected to decarbonization with the catalyst when it is burned to free it from coke formed in hydrocracking.

DETAILED DESCRIPTION

The process of this invention may be utilized to hydrocrack any suitable hydrocarbon hydrocracking charge stock. Among the charge stocks which may be suitably used within an embodiment of the inventive process are crude oils, crude distillation tower bottoms products, atmospheric distillation bottoms products, vacuum distillation tower bottoms products, topped crude oils, slurry oils, light cycle oils, straight run gas oils, and heavy cycle oils, etc. Also suitable as charge stocks within an embodiment of the present process are hydrocarbons derived from coal, lignite, oil shale, tar sand, and other natural carbonaceous materials. Particularly preferred as charge stocks in the present process are hydrocarbons derived from a carbonaceous material from which an ash, suitable as the decarbonized ash utilized as a catalyst in the present process, may also be derived. Such materials include, for example, coal, lignite and oil shale. The process of the present invention is particularly effective in hydrocracking charge stocks containing high boiling non-distillable coke precursors such as asphaltenes. Heavy, contaminated charge stocks which are normally difficult to process can be treated in the present process without some of the difficulties encountered in treating such stocks in prior art hydrocracking processes.

Hydrocracking conditions suitable in the present process include a temperature of about 500° F. to about 1200° F., a pressure of about 25 atmospheres to about 300 atmospheres, a hydrogen concentration of about 1,000 s.c.f./bbl. of charge to about 30,000 s.c.f./bbl. Preferably, the temperature of the hydrocracking conditions does not exceed about 1150° F., and the hydrogen pressure of the hydrocracking conditions is greater than about 135 atmospheres.

Although the process of the present invention will be described in terms of an ash derived from a coal, this invention is also applicable using ash derived from any other natural carbonaceous substance, such as lignite, tar sand, oil shale, etc., which forms a suitable ash when freed from substantially all of the carbon contained therein.

The ash which is employed in the process of this invention is derived by recovering the carbon-free residue which is left by substantially complete decarbonization of a natural carbonaceous substance such as coal lignite, or oil shale. Preferred for use in this process is an ash

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derived from coal and in particular bituminous coal. The composition of the ash in a particular embodiment of the inventive process will depend on the particular source of the ash. The components of typical coal ash and the range of weight percent with which they occur in coals mined in the United States is shown below:

WEIGHT PERCENT OF COMPONENTS IN COAL ASH

Component:	Range of wt. percent
SiO ₂ -----	30-60
Al ₂ O ₃ -----	20-30
Fe ₂ O ₃ -----	4-19
TiO ₂ -----	1-2
CaO -----	2-12
MgO -----	0.1-4
Na ₂ O+K ₂ O -----	1.5-3

Any suitable method for decarbonizing the ash may be employed. Typically suitable methods of deriving the ash, to be utilized in the present process, include burning a coal or other natural carbonaceous material in air, solvent extracting, destructive distillation, coking, and burning the solid residuum from solvent extracting, destructive distillation or coking. It is preferred that the temperature of the decarbonization procedure does not exceed about 1150° F. Particularly preferred is a method of decarbonizing the ash whereby a coal solvent is extracted, the solid residue is at least partially separated from the liquid residue, the solid residue separated is subjected to low temperature carbonization in a coking process, and the solid residue from coking is burned to obtain the ash utilized as the catalyst in the present invention. Methods of coking the solid residue from a coal solvation process are well known to the art of coal processing and these methods may suitably be used in the scope of the decarbonization method herein described. Burning the solid residue from coking processes has also previously been practiced, and is a source of heat energy which may be utilized in the practice of the inventive process. A method of decarbonizing the ash utilized as the catalyst in the inventive process, preferred for use where the charge stock to be hydrocracked is derived from solvent extraction of a carbonaceous solid, may also be utilized to regenerate ash which has been previously employed as a catalyst in the inventive process. In this method, ash, which has been employed as a catalyst to hydrocrack an oil derived from solvent extraction of a carbonaceous solid, is commingled with the solid residuum remaining in said oil after solvent extraction and hydrocracking, and said ash and said solid residuum are burned and the commingled newly formed and previously formed ash are indistinguishably utilized subsequently as the catalyst.

The ash to be utilized in the practice of the invention may be subjected to any suitable treatment or combination with other catalysts or inert materials before or during use. For example the physical form of the ash may be changed by crushing, grinding, extruding, pelleting, pilling, etc. The ash may be treated with an acid, a base, with steam or with a hydrocarbon solvent. The catalyst may also be combined with and/or treated with water or steam. The ash may also be heated before use or aged in contact with an acid or with a base. The ash may be commingled with previously known catalysts such as refractory oxides of metals, Group VIII metals, or Group VI metals before or during use as a catalyst in a hydrocracking process. The ash may be impregnated with catalytic metals including metals from Groups V, VI, and the iron group of the Periodic Table of Elements.

PREFERRED EMBODIMENT

In a preferred embodiment of the inventive process, a bituminous coal is solvent extracted using a suitable solvent. The liquid extract and solvent are partially separated from the material which remains solid. The amount of solid material remaining in the mixture of solvent and

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liquid extract should not exceed about 1%, by weight, of the total coal charged. The undissolved residue, which may be separated from the liquefied portion by any suitable means known to prior art, is then subjected to a low temperature coking process. The temperature of this process should not exceed about 1150° F. The low temperature coking process may be effected in any suitable way known to prior art. The hydrocarbons driven off in the low temperature coking process are admixed with the liquid produced in the solvent extraction step, after the solvent has been separated from the mixture by a suitable means, such as distillation or fractionation, for reuse in solvent extraction. The solid residue, or char, from the coking procedure should contain not more than about 5% volatiles by weight, the exact weight percent being determined by the temperature of coking. This char is burned in air until substantially complete combustion of the remaining carbon is effected. The conditions of the combustion procedure should be regulated to keep the temperature below about 1150° F. The hydrocarbons obtained from the solvent extraction and coking procedures, together with the fraction of undissolved coal remaining therein, are admixed with a portion of the ash recovered from the combustion procedure and are charged continuously to a hydrocracking zone wherein they are maintained at hydrocracking conditions which include a temperature of about 900° F. and a hydrogen gas pressure of about 135 atmospheres or greater. Hydrogen gas is simultaneously passed to the hydrocracking zone to maintain a concentration of about 10,000 standard cubic feet per barrel of hydrocarbons charged. The ash is admixed with the hydrocarbon charge stock in an amount of about 25 wt. percent of the charge stock. The solids in the effluent from the hydrocracking zone are separated from the liquids. These solids comprise the undissolved coal and the ash added as catalyst. The solids are subjected to combustion in air which frees the used catalyst from carbon deposited thereon in the hydrocracking zone and converts the undissolved coal into the ash suitable as a catalyst. The renewed and newly formed ash are then charged to the hydrocracking zone as ash in the manner described above.

The above-described process has several advantages over processes known to prior art. First, the strict separation of solids from liquids is not necessary in order to effect further processing of hydrocarbons derived from natural carbonaceous substances. Second, the catalyst may be continuously produced in large quantities by solvent extraction and burning, which makes economically possible the discarding of the catalyst as it becomes poisoned, thus obviating the negative effects of poisoning on the catalyst.

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Third, the ash produced by combustion of coal may be utilized in a novel and highly practical manner, heretofore unknown, while the asphaltene content of a hydrocarbon is reduced in the process.

I claim as my invention:

1. A process for the conversion of a high boiling hydrocarbon charge stock into lower-boiling hydrocarbons which comprises hydrocracking said charge stock in contact with a substantially carbon-free ash derived from the decarbonization and burning of a solid carbonaceous substance.

2. The process of claim 1 further characterized in that said charge stock is derived, at least in part, from said solid carbonaceous substance.

3. The process of claim 1 further characterized in that said solid carbonaceous substance is coal.

4. The process of claim 1 further characterized in that the conditions of said hydrocracking include a temperature of from about 250° F. to about 1150° F. and a hydrogen gas pressure of from about one atmosphere to about 300 atmospheres.

5. The process of claim 1 further characterized in that said ash is derived by solvent extraction of said solid carbonaceous substance, coking a part of the solid residue from said solvent extraction, burning the solid residue from said coking, and recovering the resultant solid as a part of said ash.

6. The process of claim 1 further characterized in that said ash is placed in contact with said charge stock by admixing said ash with said charge stock as a slurry.

7. The process of claim 1 further characterized in that said charge stock is a heavy hydrocarbonaceous oil containing asphaltenes.

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