

United States Patent

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[54] **COAL LIQUEFACTION PROCESS
USING ASH AS A CATALYST**

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[58] Field of Search **208/10, 9**

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[57]

ABSTRACT

A method for the liquefaction of coal using a solvent extraction process in which finely-divided coal, a solvent, and a catalyst-acting ash derived from coal are admixed and subjected to solvent extraction conditions. The ash utilized in the solvent extraction process is a substantially carbon-free residue resulting from the decarbonization of coal.

7 Claims, No Drawings

COAL LIQUEFACTION PROCESS USING ASH AS A CATALYST

BACKGROUND

This invention is related to a process for the conversion of carbonaceous materials such as coal to liquid products. More specifically, this invention is related to a process for the conversion of coal to liquid products by solvent extraction of the coal using a suitable liquid as the solvent and employing a catalyst-acting ash which improves the yield of valuable hydrocarbon products from solvent extraction processes.

Solid reserves of carbonaceous substances such as coal, lignite, etc., are abundant relative to petroleum reserves and represent a valuable source of hydrocarbons to supplement or replace those conveniently derived from petroleum. As reserves of crude oil continue to be used up 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 could be 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. High pressure hydrogenation and solvent extraction techniques have been developed, the latter of which is related to the process of the present invention. In the processes of solvent extraction known to prior art, finely-divided coal or other particulate carbonaceous material is placed in contact with a solvent at solvent extraction conditions, usually in the presence of hydrogen gas, and the liquified part of the solid is subsequently separated from the remaining solid material by filtration, centrifugation or a similar operation. The liquified material is generally separated from the solvent and is further processed by conventional means such as hydrocracking or distillation, while the solvent is conventionally recycled to the extraction process. 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.

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 palladium or homogenous catalysts such as compounds of tin, nickel, molybdenum, tungsten, or cobalt have been proposed for these processes. Such catalysts and the schemes for their use suffer from the economic and technical difficulty imposed on them by the desirability of separating the catalyst 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 difficult and expensive. The elimination of this separation step in using a catalyst to aid solvent extraction would thus be both an economic and technical advancement of processes known to prior art.

Another difficulty encountered in the use of catalysts in solvent extraction processes is the rapid decline in effectiveness undergone by catalysts under the process conditions necessary for solvent extraction and product separation. The swift deterioration in catalyst activity is due partly to the high content in coal and similar solids of metallic and other substances which poison the catalyst upon exposure thereto. Catalysts in processes known to prior art are deactivated also by the unavoidable presence thereon of coke and are separated from this coke for reuse only with difficulty and expense. A means for eliminating the above described difficulty would overcome an important barrier to an effective and efficient process for solvent extraction utilizing a catalyst material.

SUMMARY OF THE INVENTION

Therefore, it is an object of this invention to provide a method for the liquefaction of solid carbonaceous materials whereby valuable liquid hydrocarbons are obtained as the product. It is a specific object of this invention to provide an effective and efficient method for the solvent extraction and hydrogenation of carbonaceous materials by utilizing a catalyst to aid in liquefaction and to improve the products of the process. In accordance with these objectives, this invention provides a method for obtaining valuable liquid hydrocarbons from solid carbonaceous materials which, in a general embodiment, comprises: (a) subjecting a solid carbonaceous material in admixture with a suitable solvent and a catalyst-acting ash, the latter being an ash resulting from the decarbonization of coal or similar carbonaceous material, to solvent extraction conditions including the presence of hydrogen gas; and, (b) separating the liquid hydrocarbon residuum from the resultant mixture.

The above-stated steps constitute those essential to the inventive process, and may be combined with methods for the reuse of hydrogen gas, solvent, or the solid part of the resultant mixture. The inventive process may be used in combination with the same general schemes for solvent extraction of coal as have been disclosed in prior art. Among the benefits to be derived from the inventive process are three important ones. First, the separation of the catalyst from the residual undissolved coal in order to reuse it is no longer required. Second, catalysts may be produced by the process itself. Third, the poisoning and coking which inactivate other catalysts are irrelevant in this process.

The present invention is based on the discovery that the ash produced from coal when it is decarbonized possesses catalytic properties. When commingled with a carbonaceous solid and a solvent, and subjected to solvent extraction conditions, this ash produces an increase in the fraction of valuable hydrocarbon liquid products obtainable through solvent extraction.

DETAILED DESCRIPTION

Although the process of this invention will be described in terms of the utilization of bituminous coal to form liquid hydrocarbonaceous products, it is within the concept of the present invention to apply the inventive process to the solvent extraction of bituminous coal, sub-bituminous coal, lignite, oil shale, tar sand, and other solid carbonaceous materials.

Many solvents have been disclosed for processes of solvent extraction. Some solvents, which tend to give up hydrogen to the carbonaceous solid, including for example, Decalin, Tetralin and Biphenyl, are known as hydrogen donors. Other solvents disclosed, which are often used in the presence of hydrogen gas under pressure, include naphthalene, methyl-naphthalene, etc. Any of the above mentioned solvents, which are noted as examples, may be used in the present inventive process as well as any other solvents which will perform the same function.

Particular embodiments of solvent extraction in the process of the present invention will depend upon the particular carbonaceous solid to be liquified, the particular solvent utilized, and the type of extraction zone employed. The advantages of particular solvents, and the advantages of particular solvent extraction conditions to be utilized in the extraction of particular coals are well known to those skilled in the art. The typical range of solvent extraction conditions includes a temperature of about 150° F. to about 900° F., a pressure of about one atmosphere to about 300 atmospheres, and the presence of hydrogen gas. The catalyst-acting ash may be added to the mixture of solvent and coal, to the coal, or to the solvent, prior to, or after the coal and solvent enter the reaction zone. Typically, the solvent and coal are combined at weight ratios in the range of from about 1 part solvent to 1 part coal up to about 5 parts solvent to 1 part coal. The amount of catalyst-acting ash added to the coal and the solvent should be between 2 percent

and 25 percent of the weight of the combined coal and solvent. When the mixture of coal, solvent and ash has been subjected to solvent extraction conditions for a length of time sufficient to extract the maximum amount of valuable hydrocarbon liquid from the coal, the hydrocarbon residuum to be recovered as the product may be separated from the solid residuum by methods familiar to those skilled in the art. Various procedures are known to those skilled in the art for utilizing the liquid residuum resulting from subjection of the solvent, coal, and ash to solvent extraction conditions. It is usual but not necessary to the present process to separate the solvent from the hydrocarbons obtained from the coal in the solvent extraction, and to recycle the solvent for further use. The coal-derived hydrocarbons may be processed further by fractionation, hydrogenation and other means, to increase their utility. The means of separating the liquid residuum from the solid residuum in the mixture resulting from solvent extraction are well known. Examples of typical means suitable within an embodiment of this invention are centrifugation and filtration.

One method, suitable within the scope of the present process, for decarbonization of coal or other suitable material to be used as the catalyst-acting ash in the present inventive process, would be to burn coal in the conventional manner, as fuel and to recover the ash as the decarbonized product. In another suitable example of decarbonization, coal is subjected to solvent extraction and the solid residuum is employed as the catalyst-acting ash. In a third method of decarbonization, coal which has been solvent extracted is subjected to low temperature coking or carbonization. The products of coking include a liquid component and a solid component. Coking conditions include a temperature sufficient to drive off a large fraction of the volatile material from the charge to the coking zone and the absence, in the coking zone, of oxygen. In a method of coking preferred for use in decarbonization within the scope of the present process, the temperature of the coking zone should not exceed about 1,150° F. This temperature will determine the greatest fraction of volatile material which can

present inventive process include anthracite coal, bituminous coal, lignite, oil shale, tar sand, or other solid carbonaceous materials from which a suitable solid residuum may be obtained for use as a catalytic ash. Decarbonization comprises essentially the separation of the non-carbonaceous materials in the solid to be decarbonized from a substantial fraction of the carbon therein.

Decarbonized catalytic ash is the result of the application of a method of decarbonization to a carbonaceous solid, the means of said decarbonization being dependent upon a particular embodiment of decarbonization, as exemplified by the above-described methods but not limited thereto.

In a preferred method of decarbonization in the present inventive process, substantially complete decarbonization of the catalyst-acting ash would be effected by subjecting a coal, in turn, to solvent extraction, low temperature coking and burning. The energy obtained in burning the residue from a coking operation could be used to maintain the necessary high temperature in the solvent extraction and coking operations. The decarbonization effected by burning in the preferred method requires that a temperature below about 1,150° F. be maintained in the decarbonization zone and that sufficient oxygen be present therein to combine with essentially all of the carbon thereon. The solid remainder of a coal which has been subjected to substantially complete decarbonization is preferred for use in the process of the present invention. The particular source of the ash used is not essential to a general embodiment of the present invention excepting that said ash must be derived from some naturally occurring carbonaceous substance such as coal. Such an ash would normally contain a variety of minerals, the relative proportions of which in the composition of the ash will depend on the particular coal which is to be utilized to form said ash in a particular embodiment of the present invention. Typical constituents of coal ash and the approximate limits of the fraction in which they occur in the ash of coals mined in the United States is shown as follows:

TYPICAL CONSTITUENTS OF U.S. COAL ASH

Constituent.....	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	TiO ₂	Na ₂ O+K ₂ O
Usual range of percent.....	30-60	10-40	3-30	1-20	0.5-4	0.5-3	1-4

be driven off as a vapor under coking conditions. The liquid effluent from a cracking zone is composed of the volatile material driven off under said coking conditions. This liquid component may be admixed with a liquid resulting from solvent extraction of a carbonaceous material and processed therewith, or may be further processed in a number of ways well known to those skilled in the art of hydrocarbon processing. Some fraction of a liquid product from solvent extraction, a liquid product from coking, or both, may be utilized as the solvent, or a fraction thereof, within the scope of the present invention in the present solvent extraction process. The liquid component recovered and the solid component recovered from a coking zone may be separated from one another by methods well known to previous art. The solid which results from coking the solid residuum of a solvent extracted coal is composed of ash and coke. It has been known that the solid which results from coking a coal may be burned as fuel. Within the scope of the present inventive process, burning the resultant solid from coking would comprise a method of decarbonizing the catalytic ash to be utilized. Decarbonization may comprise solvent extraction of a coal. Decarbonization may also comprise coking a coal or coking the solid residuum from solvent extracting a coal. Decarbonization may also comprise burning a coal in air, burning the solid residuum from solvent extracting a coal in air, or burning the solid resulting from coking a coal, or the solid residuum of a solvent extracted coal, in air. Decarbonization may also comprise the partial or complete destructive distillation of a coal. Materials which may suitably be decarbonized to yield the catalytic ash contemplated within the scope of the

An ash used as catalyst-acting ash may be treated, within the scope of the present invention, to increase its catalyst activity with water, steam, acids, bases, or other means. The shape and form of the catalyst may be changed after the ash is decarbonized within a general embodiment of the inventive process. For example, the ash may be crushed, ground, piled, extruded, filtered etc.

PREFERRED EMBODIMENTS

A preferred embodiment of the present inventive process comprises the following procedure. A United States mined bituminous coal with a 20 percent, by weight, content of volatile materials is pulverized to particles small enough to pass through a 14 mesh Tyler screen, or smaller, mixed with Tetralin on a 5:1 weight basis of solvent to coal and to this is admixed about 5 percent, by weight, of catalyst-acting ash. This mixture of coal, Tetralin and ash is continuously passed into an upflow slurry extraction zone under solvent extraction conditions, including about 2,000 psig. hydrogen pressure and a temperature of about 850° F., sufficient to liquify about 80 percent of the coal entering the process. The effluent residuum from the extraction zone is separated into two components, one of which comprises the solid residuum in the effluent. The solid residuum in the effluent is subjected to conventional low temperature coking conditions including a temperature below 1,150° F. during which substantially all of the volatile content of the solid residuum is driven off and recovered. The resultant coke and ash is burned in a conventional decarbonization zone to provide heat for the prior steps of the process, and, from the substantially carbon-free ash, a

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part thereof, sufficient to provide 5 percent, by weight, of the subsequent feed to the solvent extraction process, is retained and utilized therein as described above. The liquid residuum separated from the solid residuum in the effluent from the solvent extraction zone is further processed by distillation and fractionation, and a solvent is thereby recovered and recycled to provide a continuous supply of solvent for the solvent extraction process.

I claim as my invention:

1. A process for converting a solid carbonaceous material to normally liquid hydrocarbons which comprises the steps of:
 - a. solvent extracting said solid material with a hydrocarbonaceous solvent, at solvent extraction conditions, and in contact with a decarbonized catalytic ash; and
 - b. separating the resultant mixture into a liquid residuum and a solid residuum and recovering said liquid residuum as said liquid hydrocarbons.

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2. The process of claim 1 further characterized in that said catalytic ash is derived from said solid residuum.

3. The process of claim 1 further characterized in that said catalytic ash is derived from the decarbonization of said solid residuum.

4. The process of claim 1 further characterized in that said solvent extraction conditions include a hydrogen atmosphere.

5. The process of claim 1 further characterized in that said solid carbonaceous material is coal.

6. The process of claim 1 further characterized in that said solid residuum is subjected to coking at a temperature below about 1,150° F. to produce said catalytic ash.

7. The process of claim 1 further characterized in that said solid residuum is burned in air at a temperature below about 1,150° F. to produce said catalytic ash.

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