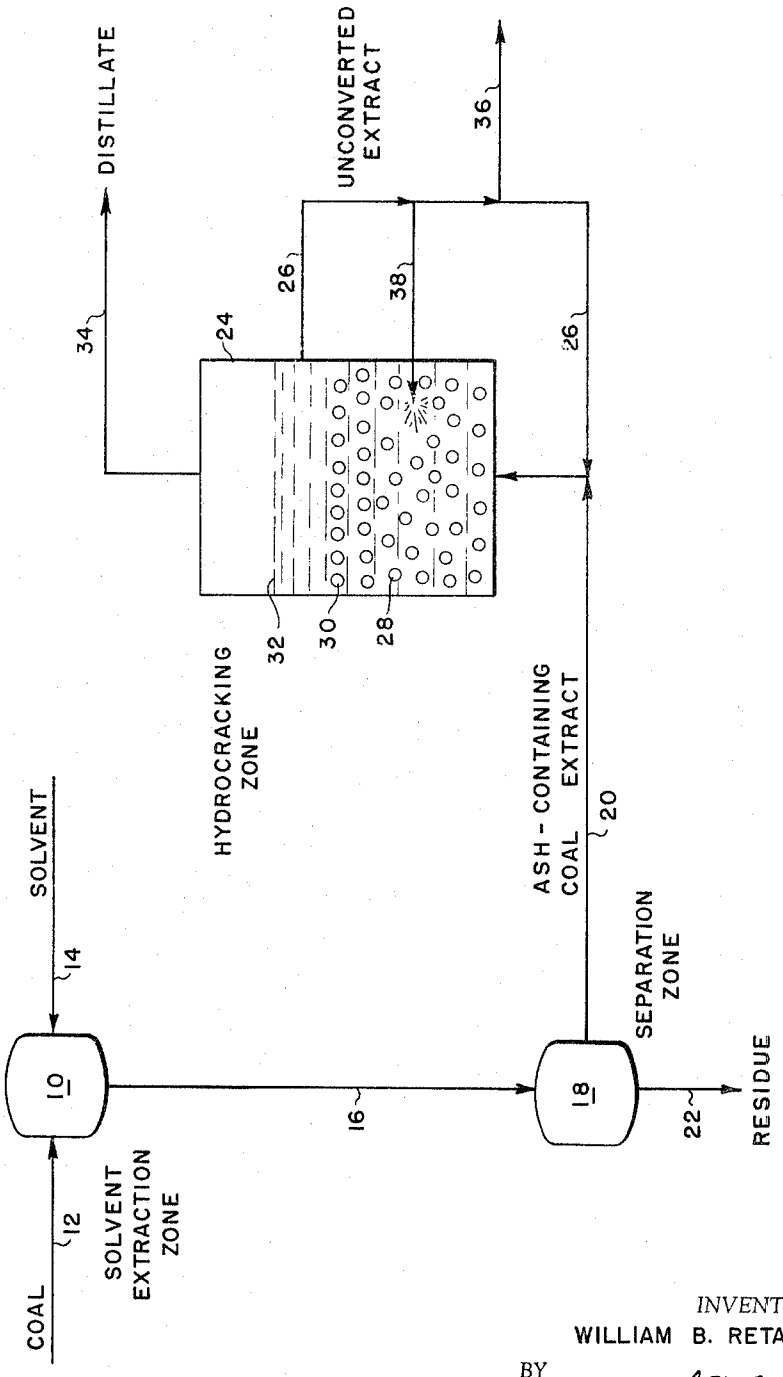
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METHOD OF ATTRITING SOLIDS IN A HYDROCRACKING PROCESS

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METHOD OF ATTRITING SOLIDS IN A HYDROCRACKING PROCESS

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This invention relates to a method of attriting solids. More particularly, this invention relates to a method of attriting liquid-phase fluidizable solids. Still more particularly, this invention relates to a method of removing a thin outer layer of ash from a catalyst, which has been used to catalytically hydrogenate ash-containing hydrocarbonaceous liquids.

The term catalytic hydrogenation, as hereinafter used, means any catalytic process wherein hydrogenation takes place, for example, hydrogenation, hydrocracking, hydrofining, and hydroforming.

The terms "attrition" and "abrasion" are sometimes hereinafter used interchangeably, both terms meaning to remove a portion of the surface from a solid by the act of rubbing against another solid.

In copending application Serial No. 154,451, filed by Everett Gorin, November 24, 1961, now U.S. Patent No. 3,143,489, and U.S. Patent No. 3,018,242, which are both assigned to the assignee of this application, processes are described for the production of valuable liquid products such as gasoline from coal. The coal is initially subjected to solvent extraction to yield coal extract and undissolved coal residue. After separating the extract from the residue, the extract is catalytically hydrocracked to yield an ash-free, distillable hydrocarbonaceous liquid, sometimes hereinafter referred to as a hydrogen-enriched hydrocarbonaceous liquid. The distillable liquid is suitable for refining to gasoline, for example, by a refining scheme such as described in copending application Serial No. 154,451, supra.

The extract obtained by the solvent extraction of coal, after being separated from the undissolved coal residue, contains a minute, unfiltrable amount of metallic contaminants, commonly referred to as ash. If this ash is not removed from the coal extract prior to a catalytic hydrocracking treatment, the ash tends to deposit on the catalysts contained in the hydrocracking zone. The ash deposit causes a more rapid decrease in the activity of the catalyst than otherwise would be experienced. More importantly, the ash deposit causes a more rapid decrease in the useful life of the catalyst. Such decrease in activity forces resort to more frequent replenishment of the catalyst with fresh catalyst.

It has been found that when ash-containing coal extract is contacted with catalyst, the coal-extract ash preferentially deposits on the catalyst surface and forms a thin outer layer thereon. In fact, the ash deposition is so selective that when a used hydrogenation catalyst is halved, a distinct thin outer layer, which has a different color than the interior of the catalyst, is readily discernible. Generally, the so-called "thin outer layer," which comprises a mixture of ash and catalyst, is between about 1 and 30 microns in thickness. This is a very small portion of the whole hydrogenation catalyst, which is normally more than 1000 microns in diameter. In addition, it has been found that the thin outer layer, which contains the major portion of the ash which has deposited on the catalyst, may be selectively removed from the deactivated catalyst. Furthermore, when the outer layer is removed the resulting abraded or attrited catalyst frequently possesses substantially pristine activity.

Many methods may be used for removing the thin outer layer from the catalyst. Normally, the catalyst is withdrawn from the hydrocracking zone and passed into a rotating drum so that the ash deposits are removed by collisions of the catalyst particles with one another and with the inner walls of the drum. Vibrating equipment may also be used to rub off the thin outer layer. The attrited catalyst is preferably reintroduced into the hydrocracking zone for further use.

It is desirable to remove the ash-laden thin outer layer from the catalyst as it forms during the hydrocracking treatment. In this manner the expense involved in withdrawing the deactivated catalyst from the hydrocracking zone, separating the deactivated catalyst from any occluded liquid, attriting the deactivated catalyst, and then reintroducing the attrited, reactivated catalyst into the hydrocracking zone is obviated. Such internal attrition, i.e., attrition within the catalytic reaction zone, is readily achieved in a gaseous-phase fluidized catalytic reaction zone. For example, it is well known that in conventional gaseous-phase fluidized catalytic cracking zones, the cracking catalyst particles are continuously attrited by the numerous collisions of the particles with one another. In fact, frequently the major problem in a gaseous-phase fluidized system is not in obtaining enough attrition, but in obtaining too much attrition.

Unfortunately, coal extract is not similar nor does it behave similarly to other hydrocarbonaceous materials such as petroleum-derived liquids. This dissimilarity exists primarily because coal extract has a different chemical structure from that of other hydrocarbonaceous materials. Moreover, coal extract, a solid at room temperature, contains very little (in general, less than about 5 weight percent) material boiling below 400° C. The remainder of the extract is essentially nondistillable without decomposition. In contrast, other hydrocarbonaceous materials are substantially completely distillable without decomposition. Because of the above characteristics coal extract generally is not catalytically treated in a gaseous-phase type system, but is catalytically treated (catalytically hydrocracked) in a liquid-phase type system.

Recently, it has been suggested to accomplish liquid-phase hydrocracking of the coal extract in a dense bed, liquid-phase fluidized catalytic hydrocracking zone. This type system is similar in some ways to gaseous-phase fluidization. However, one important difference is that in a liquid-phase fluidized system essentially no catalyst attrition occurs. It is believed the catalyst attrition is prevented because the catalyst particles, in motion in the liquid-phase fluidized bed, are cushioned by an envelope of liquid.

It would be highly desirable if some means were developed for attriting catalyst particles within a dense bed, liquid-phase fluidized catalytic reaction zone. In short, this is exactly what I have accomplished by the present invention.

Accordingly, the primary object of the present invention is to provide a method of attriting liquid-phase fluidizable solids.

In accordance with my invention, attritable solids (that is, solids which are capable of having a portion of their surface removed by attrition), which are of a liquid-phase fluidizable size, are introduced into a treating zone. Liquid is introduced upwardly into the treating zone such that the velocity of the liquid is sufficient to establish and to maintain the attritable solids as a liquid-phase, dense fluidized bed. An energizing means is introduced into at least one local region of the dense fluidized bed of solids so as to cause the solids to contact each other with sufficient force to attrit at least a portion of the exterior surface therefrom.

The essence of my invention is that I am the first to appreciate that solids may be attrited in a liquid-phase fluidized system. Heretofore, it was known that little, if any, inherent attrition occurred in a liquid-phase fluidized system. The contrary is true in a gaseous-phase fluidized system wherein excessive, inherent attrition is the usual case. As stated above, my invention in its broad concept is applicable to attriting any attritable solid of liquid-phase fluidizable size. Preferably, however, my invention is designed to remove the thin outer layer of ash and catalyst from catalyst particles, which have been used to hydrocrack ash-containing hydrocarbonaceous liquids such as ash-containing coal extract.

In addition to finding a method for attriting solids in a liquid-phase fluidized system, I have also found that the attrition may be achieved without destroying the dense fluidized bed of solids. For example, the energizing means is only introduced into local regions of the dense fluidized bed. The turbulence caused by the energizing means in the local regions is sufficient to cause attrition, but insufficient to destroy the dense fluidized bed. Obviously, if excessive energizing means were used, then the dense fluidized bed may very well be destroyed. Moreover, I have also found that the energizing means may be controlled so that substantially no breakage of the attritable solids occurs.

When my process is used for removing the thin outer layer of ash from catalyst which has been used in the presence of ash-containing materials such as ash-containing coal extract, the following advantages are obtained:

(1) Ash may be immediately and continuously removed from the catalyst particles as the ash deposits thereon;

(2) The deactivated catalyst particles do not have to be removed from the liquid-phase, dense fluidized bed to be attrited;

(3) The dense fluidized bed is not substantially affected by the energizing means, and thus the advantages of the liquid-phase fluidized system are not lost; and

(4) The thin outer lay may be removed without substantial breakage of the catalyst particles.

Energizing means

The energizing means may be any means which will cause the attritable solids to contact each other with sufficient force to cause attrition, but with insufficient force to cause substantial breakage. The energizing means must also be one which may be introduced into local regions of the dense fluidized bed so as to cause only turbulence. In this manner, the energy introduced by the energizing means is expended in causing attrition and does not substantially disrupt the liquid-phase, dense fluidized bed.

Suitable energizing means are jets of liquid or gas. These fluid jets are introduced at a higher velocity than the velocity of the fluidizing means, i.e., the upwardly flowing liquid which is used to fluidize the attritable solids. Simple experimentation will enable one to determine how many fluid jets are needed and the proper fluid velocity which must be used. The number of jets and the proper velocity will vary with the rate of attrition desired, the number of attritable solids present, and the hardness of the exterior surface of the attritable solids. For example, when ash-containing coal extract (containing between about 0.01 and 0.5 weight percent ash) is catalytically hydrocracked with a catalyst having a size between about 1000 and 2000 microns, the fluidizing liquid usually has a velocity between 0.05 and 1.0 foot per second. I have found that the ash deposits which form on the catalyst may be removed by introducing a jet of liquid having a velocity between 5 and 50 feet per second. The catalysts in the liquid-phase, dense fluidized bed are continually moving within the dense fluidized bed so that essentially all of the catalyst particles eventually find their way into the so-called "local regions of turbulence."

It is to be understood that the energizing means is extraneous to the fluidizing means, as it has been previously stated that the fluidizing liquid imparts insufficient energy to cause attrition. However, the energizing means may comprise the same type liquid which is introduced as the fluidizing means.

For a better and more complete understanding of my invention, its objects and advantages, reference should be had to the following description and to the accompanying drawing which is a diagrammatic illustration of the preferred embodiment of this invention.

Preferred embodiment

The following, with reference to the drawing, is a description of the preferred embodiment of the present invention.

Coal is introduced into a solvent extraction zone **10** via a conduit **12**. Any conventional type hydrocarbonaceous solvent is introduced into the extraction zone **10** via a conduit **14**. The coal and the solvent react therein to yield the desired coal extract. The solvent extraction process may be any of the processes commonly used by those skilled in the art.

The coal and the solvent are maintained in intimate contact within the extraction zone **10** until the solvent has extracted, i.e., converted or dissolved, up to 80 weight percent of the MAF (moisture-free and ash-free) coal. Preferably, between 50 and 80 weight percent of the MAF feed coal is extracted, as further discussed in the aforementioned copending application Serial No. 154,451, supra.

Following extraction, the mixture of solvent, extract, and residue is conducted through a conduit **16** to a separation zone **18** wherein, preferably, substantially all of the residue is separated from the extract and solvent. Normally, the separation zone **18** is a filtration zone. However, if desired, a centrifuge, sedimentation zone, hydroclone and the like may be used.

The liquid extraction products (filtrate), comprising ash-containing coal extract and solvent, are withdrawn from the separation zone **18** via a conduit **20**. The residue is recovered from the zone **18** via a conduit **22**. The separately recovered residue may be used as boiler fuel or subjected to a fluidized low-temperature carbonization process such as described in the aforementioned U.S. patent and copending application Serial No. 154,451, supra.

The ash-containing coal extract, which normally contains below about 0.50 weight percent ash, is preferably introduced into a dense bed, liquid-phase fluidized catalytic hydrocracking zone **24**. If desired, prior to introducing the coal extract into the hydrocracking zone, portions of the extraction solvent may be removed, e.g., in a flash still (not shown), and recycled to the solvent extraction zone **10** for further use.

The ash-containing coal extract in combination with any recycle unconverted liquid product (conduit **26**) is introduced into the hydrocracking zone **24**. The upward flow of the extract and recycle liquid is controlled such that the liquid velocity is sufficient to maintain catalyst particles in the form of a liquid-phase, dense fluidized bed **28** in the zone **24**. The fluidized catalyst has an upper bed level **30**.

The catalytic hydrocracking zone **24** is maintained at a temperature in the range of 400 to 550° C., a pressure in the range of 1000 to 10,000 p.s.i.g., a hydrogen feed rate in the range of 5 to 100 standard cubic feet per pound of feed, and a liquid feed rate in the range of 10 to 150 pounds per hour per cubic foot of reactor volume. The catalyst has a size consisting between about 500 and 2000 microns and preferably about 1600 microns. The velocity of the upwardly flowing fluidizing liquid (extract plus recycle liquid) is preferably between 0.05 and 1.0 foot per second, but may be between 0.01 and 1.0 foot per

second. The size of the catalyst that is used in the zone **24** is the primary determinant of the fluidizing velocity.

Suitable catalysts are, for example, metals of Groups 5 to 8 of the Periodic Chart, preferably oxides or sulfides and combinations thereof. A preferred catalyst is one containing a metal oxide or sulfide of Group 6 of the Periodic Chart, e.g., molybdenum combined with a relatively minor amount of a transition group metal oxide or sulfide such as cobalt or nickel. The active metals are preferably supported on a hydrous oxide support such as alumina gel or gamma alumina substantially free of water of hydration. The catalyst may be in the form of beads, pellets, cylinders and the like.

As the extract reacts with the hydrogen under the above conditions, substantially ash-free vaporous products are formed. The vaporous products collect in the zone **24** above a liquid level **32**. The vaporous products are withdrawn from the hydrocracking zone **24** via a conduit **34**. The vaporous products are then conveyed to a condenser (not shown) wherein noncondensable gases and a condensed vaporous product, i.e., an ash-free, distillable hydrocarbonaceous liquid product, are separately recovered.

Returning to the hydrocracking zone **24**, the coal extract which is not converted to a distillable product therein is withdrawn from the zone **24** aia the conduit **26** and a portion is preferably reintroduced into the hydrocracking zone **24** in order to supply a portion of the fluidizing liquid. Some of the unconverted liquid may be withdrawn from the hydrocracking system via a conduit **36**, for example, to prevent ash build-up in the zone **24** or to treat the unconverted liquid extract in another hydrocracking zone under different conditions.

During the passage of the ash-containing coal extract through the hydrocracking zone **24**, a portion of the ash deposits on the catalyst forming a thin outer layer of ash thereon. Actually, the ash penetrates into the catalyst interior such that the thin outer layer comprises ash and catalyst. The ash penetration is not very deep; therefore, the thin outer layer is formed. This outer layer generally has a thickness between about 1 and 30 microns. As previously mentioned, when the thin outer layer is removed the resulting abraded catalyst frequently has substantially pristine activity.

Preferably, a portion of the recycle unconverted extract is introduced into the liquid-phase, dense fluidized bed **28** in the form of a liquid jet **38**. The velocity of the liquid jet is between 5 and 50 feet per second, but preferably is between 10 and 30 feet per second. The liquid jet causes turbulence in only a portion of the dense fluidized bed. Thus, in the local region of turbulence the catalyst particles are caused to contact one another and thereby are attrited. The turbulence is sufficient to cause attrition of the catalyst particles, but is insufficient to substantially disrupt the dense fluidized bed.

The thin outer layer is removed from the catalyst particles in the form of "fines." These fines which generally are below 20 microns in diameter flow through the catalyst bed and pass out of the hydrocracking zone **24** with the unconverted extract via the conduit **26**. To prevent an excessive build-up of these fines in the zone **24** a portion of the unconverted liquid is withdrawn from the hydrocracking system via the conduit **36**.

According to the provisions of the patent statutes, I have explained the principle, preferred construction, and mode of operation of my invention and have illustrated and described what I now consider to represent its best embodiment. However, I desire to have it understood that, within the scope of the appended claim, the invention may be practiced otherwise than as specifically illustrated and described.

I claim:

The process for catalytically hydrocracking ash-containing coal extract which comprises

(a) establishing and maintaining a bed of catalyst in a catalytic hydrocracking zone,

(b) introducing ash-containing coal extract in a liquid state into the hydrocracking zone,

(c) maintaining the flow of liquid through the bed of catalyst under hydrocracking conditions at a velocity between 0.01 and 1 foot per second to maintain the catalyst as a liquid-phase, dense fluidized bed, whereby a portion of the ash-containing extract is converted to distillate products and at least a portion of the ash in the extract is deposited upon the catalyst, and

(d) recycling at least a portion of the unconverted coal extract in the liquid state into a local region of the liquid-phase, dense fluidized bed at a velocity between 5 and 50 feet per second, whereby a zone of relatively high turbulence is created in a portion of the bed wherein the ash-laden catalyst is attrited and thereby reactivated.

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