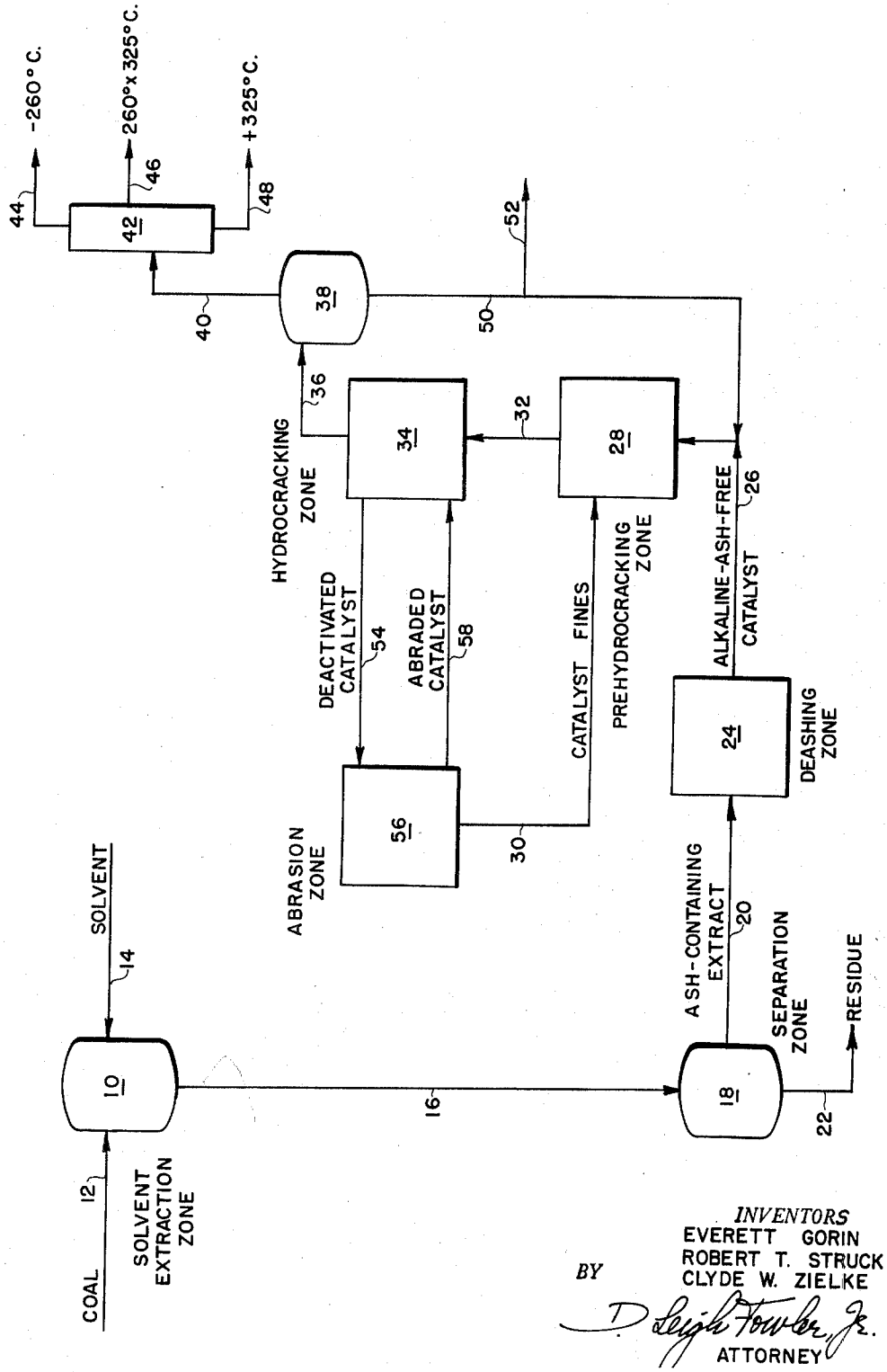
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PROCESS FOR PRODUCING HYDROGEN-ENRICHED HYDROCARBONACEOUS PRODUCTS FROM COAL

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PROCESS FOR PRODUCING HYDROGEN-ENRICHED HYDROCARBONACEOUS PRODUCTS FROM COAL

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This invention relates to an improved process for producing hydrogen-enriched hydrocarbonaceous products from coal. More particularly, this invention relates to a combination process for removing ash, i.e., metallic contaminants and the like, from ash-containing coal extract and from catalysts which have been deactivated during catalytic hydrogenation of ash-containing coal extract. Still more particularly, this invention relates to a process for removing particular ash components from ash-containing coal extract.

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

As described in copending application Serial No. 154,451, filed by Everett Gorin, November 24, 1961, now U.S. Patent 3,143,489; and U.S. Patent No. 3,018,242, which are both assigned to the assignee of this application, valuable liquid products such as gasoline may be derived from coal by initially subjecting the coal to solvent extraction, whereby coal extract and undissolved coal residue are obtained. 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 application Serial No. 154,451, supra.

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

Heretofore, the principal method used for overcoming the above ash-deposition problem was to treat the ash-containing coal extract with acid in a separate deashing step prior to catalytic hydrogenation of the coal extract in order to remove as much ash as possible from the extract. This acid-washing deashing scheme is based on the theory that all of the coal-extract ash is equally harmful to hydrogenation catalyst; therefore, the larger the amount of ash removed from the extract prior to catalytic hydrogenation, the longer the useful life of the hydrogenation catalyst. Unfortunately, the acid-washing deashing scheme has certain disadvantages. Firstly, the cost associated with removing all or even a major portion of the coal-extract ash is prohibitive, not only because of the cost of the acidic reagents, but also because of the cost of the special equipment required when working with such corrosive materials. Secondly, it has been found that coal extract is a highly sensitive material which readily undergoes degradation when it is subjected to

chemical treatments, particularly at elevated temperatures; and as a result, the coal extract is more difficult to hydrogenate and gives poorer hydrogenation yields. The degradation is manifested by the formation of coke and by the increase in the high molecular weight, hydrogen deficient portion of the extract. The benzene-insoluble content of the coal extract is a measure of this undesirable, high molecular weight extract portion, as further explained in copending application Serial No. 167,431, filed by Everett Gorin, January 19, 1962, which is assigned to the assignee of this application.

A more recent method, which was developed to overcome the above ash-deposition problem as well as to overcome the disadvantages associated with the above acid-washing deashing method, is not to remove the ash from the extract prior to catalytic hydrogenation, but to allow the coal-extract ash to deposit on the hydrogenation catalyst and then remove the ash from the catalyst by abrasion. This method is based on the finding that coal-extract ash selectively deposits on the exterior surface of the catalyst, forming a uniform thin outer layer thereon such that it can be removed readily by abrasion. The resulting abraded catalyst has an increased catalytic activity; therefore, it can be reintroduced into the hydrogenation zone for further use, as further explained in copending application by Everett Gorin and Robert T. Struck, filed of even date herewith, which is assigned to the assignee of this application. The disadvantage of the abrasion scheme, however, is that while substantially all of the coal-extract ash deposits on the exterior surface of the catalyst, nevertheless, some ash penetrates into the interior of the catalyst thereby eventually deactivating the catalyst such that it cannot be used for further hydrogenation.

Contrary to the belief of prior investigators, we have found that coal-extract ash is not equally harmful to hydrogenation catalyst, but a certain group of ash contaminants are markedly more harmful to hydrogenation catalyst than the remaining ash contaminants.

Accordingly, the primary object of the present invention is to provide an improved process for overcoming the aforementioned ash-deposition problem such that hydrogen-enriched hydrocarbonaceous products may be obtained more economically from ash-containing coal extracts.

In accordance with our invention, coal extract, which contains both alkaline ash components and inert ash components (as hereinafter more fully explained), is treated in a deashing zone to preferentially remove at least a portion, and preferably all, of the alkaline ash components therefrom. At least a portion of the resulting deashed extract, which contains a lower proportion of alkaline ash to inert ash than the original ash-containing coal extract, is subsequently hydrogenated in a hydrogenation zone in the presence of a hydrogenation catalyst to yield hydrogen-enriched hydrocarbonaceous products. During hydrogenation, coal-extract ash deposits on the catalyst thereby causing the catalyst activity to decrease. At least a portion of the deactivated catalyst is subjected to abrasion to selectively remove a uniform thin outer layer therefrom. The resulting abraded catalyst has an increased catalytic activity.

The essence of our invention is that we are the first to appreciate that coal-extract ash components are not equally harmful to hydrogenation catalyst, but that the alkaline ash components are markedly more harmful to the hydrogenation catalyst than the remaining ash components. By alkaline ash, we main compounds of sodium, potassium, and calcium. The coal-extract ash other than the alkaline ash is sometimes hereinafter referred to as "inert ash."

Unlike the afore-mentioned acid-washing deashing processes which not only remove alkaline ash but also remove a substantial portion of the inert ash, the deashing zone used in our process is designed to preferentially remove alkaline ash components. The cost of removing alkaline ash is much less than the cost of removing an equal portion of inert ash. Furthermore, because alkaline ash is markedly more harmful to hydrogenation catalyst than inert ash, the gain in hydrogenation catalyst life accruing from alkaline ash removal is much greater than the gain in hydrogenation catalyst life accruing from removing an equal portion of inert ash components. However, removing alkaline ash components from the ash-containing coal extract is generally insufficient by itself to enable one to attain the desired economic hydrogenation catalyst life. The remaining inert ash components, if not removed, will deposit on the hydrogenation catalyst and deactivate the catalyst. We have found, however, that by combining alkaline ash removal with catalyst abrasion it is possible to achieve the desired hydrogenation catalyst life.

It is important to keep in mind that coal-extract ash is not similar, nor does it behave similarly, to ash contained in other hydrocarbonaceous materials such as ash contained in petroleum-derived liquids.

The metallic contaminants, i.e., ash, contained in petroleum-derived liquids are generally associated with a porphyrin type of molecule or class of compounds which are to a large extent, if not completely, soluble in the petroleum. In contrast, up to 50 weight percent of the metallic contaminants in coal extract, which contaminants have their origin in the coal feedstock, are insoluble, finely divided particles, substantially all of which have a particle diameter between 0.01 and 2.0 microns, thereby making it difficult, if not impossible, to remove the particles by commercial mechanical separation methods. The remaining metallic contaminants in the coal extract have a particle diameter below 0.01 micron and, frequently, a major portion of these remaining contaminants actually are soluble in the coal extract.

The metallic contaminants found in coal extract are metals which usually appear in the form of compounds, for example, silicates, complex aluminum silicates, sulfates, sulfides, chlorides, and oxides. The metals include sodium, boron, silicon, potassium, iron, calcium, magnesium, aluminum and titanium.

The following Table I contains a typical analysis of the metallic contaminants present in a coal extract. The extract was obtained by subjecting Pittsburgh Seam bituminous coal to solvent extraction with tetrahydronaphthalene solvent under the following conditions:

Temperature, ° C.	380
Pressure, p.s.i.g.	600
Solvent/coal wt. ratio	2
Residence time, minutes	52

The extract was separated (by filtration) from the residue and then analyzed for the metallic contaminants. The contaminants are expressed as oxides. As can be seen from Table I, the alkaline oxide ash compounds comprise less than 40 weight percent of the total metal oxides in the ignited extract ash.

Table I

Metallic contaminants (expressed as oxides):	Percent by weight of the total contaminants contained in the extract
SiO_2	20.4
CaO—alkaline ash component	15.9
TiO_2	15.5
Al_2O_3	10.0
Fe_2O_3	5.5
MgO	1.8
Na_2O—alkaline ash component	1.0
K_2O—alkaline ash component	0.4
Cr_2O_3	0.23
V_2O_5	0.04
Ignition loss [1]	29.23
	100.00

[1] The ignition loss is due to subsequent conversion of metal compounds that are stable at the ashing temperature of 1100° F. to the corresponding oxides.

For a better and more complete understanding of our 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.

Any coal may be used in the process of our invention, non-limiting examples of which are lignite, bituminous coal, and sub-bituminous coal. Preferably, the coal is one having a volatile matter content of at least 20 weight percent, for example, a high volatile bituminous coal such as Pittsburgh Seam coal. A typical composition of a Pittsburgh Seam coal suitable for use in the process of our invention is shown in Table II.

Table II

Proximate analysis:	Wt. percent MF[1] coal
Volatile matter	39.3
Fixed carbon	47.7
Ash	13.0
	100.0
Ultimate analysis:	**Wt. percent MAF[2] coal**
Hydrogen	5.5
Carbon	80.8
Nitrogen	1.4
Oxygen	7.5
Sulfur	4.8
	100.0

[1] MF means moisture-free.
[2] MAF means moisture-free and ash-free.

The feed coal is preferably ground to a finely divided state, for example, minus 14 mesh Tyler Standard screen, and is freed of substantially all extraneous water before introduction into the process.

Coal is introduced into a solvent extraction zone **10** via a conduit **12**. 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, e.g., continuous, batch, countercurrent, or staged extraction, at a temperature in the range of 300 to 500° C., a pressure in the range of 1 to 6500 p.s.i.g., a residence time in the range of 1 to 120 minutes, a solvent to coal ratio in the range of 0.5/1 to 4/1 and, if desired, in the presence of a catalyst and up to 50 standard cubic feet of hydrogen per pound of MAF coal.

Any of the well-known coal extraction solvents may be used in the extraction zone **10**. It is preferred, however, that the solvent be a hydrogen-transferring hydrocarbonaceous liquid. Suitable hydrogen-transferring hydrocarbonaceous liquids are those predominantly polycyclic hydrocarbons which are partially or completely hydrogenated. Polycyclic hydrocarbon mixtures are generally employed and are preferably derived from intermediate or final steps of the process of this invention. Normally, the polycyclic hydrocarbons or mixtures thereof boil above 200° C. and preferably between 260 and 425° C.

Partially hydrogenated polycyclic hydrocarbons are the most active and preferred type of hydrogen-transfer

liquids. Examples of such materials are the di, tetra, and octa hydro derivatives of anthracene and phenanthrene; tetrahydronaphthalene; and alkyl substituted derivatives of the above types of compounds. Completely saturated polycyclic hydrocarbons such as decalin and perhydrophenanthrene are also active as hydrogen-transferring solvents, although less active than the corresponding partially hydrogenated compounds. If desired, non-hydrogen-transferring liquids such as naphthalene, anthracene, biphenyl, and their alkyl substituted derivatives may be present in admixture with the hydrogen-transferring solvents, for example, such is the case when the hydrogen-transferring hydrocarbonaceous liquid is obtained from intermediate or final steps of the process of this invention.

A particularly preferred solvent is a portion of the product obtained from the catalytic hydrocracking zone, as hereinafter more fully explained. This solvent normally comprises a 325 to 425° C. fraction blended with some lower boiling material.

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, at least a portion of the coal. Preferably, between 50 and 80 weight percent of the MAF (moisture-free and ash-free) feed coal is extracted, as further discussed in the afore-mentioned 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 extract and solvent, are withdrawn from the separation zone 18 via a conduit 20. The residue is recovered via a conduit 22. The separately recovered residue subsequently may be used as boiler fuel or subjected to a fluidized low temperature carbonization process such as described in the afore-mentioned U.S. patent and copending application Serial No. 154,451, supra.

The ash-containing coal extract is conducted via the conduit 20 into a deashing zone 24 wherein at least a portion, and preferably all, of the alkaline ash components are removed from the extract. If desired, at least a portion of the extraction solvent may be removed from the extract prior to introduction into the deashing zone 24. Preferably, however, at least a portion of the extraction solvent is left with the extract during deashing in order to minimize degradation of the coal extract, as further explained in copending application Serial No. 167,431, supra.

The extract is treated in the deashing zone 24 to preferentially remove the alkaline ash components, i.e., the compounds of sodium, potassium, and calcium. During deashing, some inert ash components will be removed along with the alkaline ash; however, the resulting deashed extract normally contains a much lower proportion of alkaline ash to inert ash than the ash-containing extract feed.

We have found that a substantial portion of the alkaline ash components can be removed simply by contacting the ash-containing coal extract with water. For example, contacting the extract in one or more stages in any conventional type stirred reaction vessel at a temperature between 25 and 370° C., a pressure between 5 and 3500 p.s.i.g., and a water to extract ratio (volumetric ratio) between 0.5 and 4.0, for 5 to 120 minutes will normally remove between 65 and 90 weight percent of the alkaline ash components (based on the extract feed) while between 20 and 50 weight percent of the total ash contaminants (based on the extract feed) are removed.

A particularly preferred deashing method is to contact the ash-containing coal extract with a slightly acidic aqueous solution, i.e., an aqueous solution containing sufficient acid to neutralize the alkaline ash components contained in the extract. Normally, less than 0.1 weight percent acid and preferably less than 0.05 weight percent acid is added to the water to form this slightly acidic solution. Preferably, the acid is hydrochloric, however, other mineral acids such as halogen acids and nitric acid are generally suitable, but less attractive economically because of their higher cost. Many other mineral acids such as boric, carbonic, hydrofluoric, phosphoric, and sulfuric acids are less suitable because of their basic calcium salts are only slightly soluble in water, if at all. Of course, if an excess of the latter acids is used, the calcium acid salts will be formed which are generally more soluble in water. Certain organic acids such as acetic and benzoic may also be used.

The use of slightly acidic solutions of hydrochloric acid to remove ash from ash-containing coal extract is further discussed in copending application by Clyde W. Zielke, filed of even date herewith, which is assigned to the assignee of this application.

By using a slightly acidic aqueous solution to deash the ash-containing coal extract, the number of deashing stages necessary to remove a given amount of alkaline ash is much less than deashing with water alone. For example, between 90 and 96 weight percent of the alkaline ash (based on extract feed) and between 40 and 60 weight percent of the total ash (based on extract feed) is removed from the ash-containing coal extract by washing the extract with a 0.025 weight percent aqueous solution of hydrochloric acid in a first stage and pure water in a second stage. Both stages may be maintained under similar conditions as above mentioned with respect to water alone. Preferably, however, the slightly acidic water treatment is conducted at a temperature between 200 and 300° C., a pressure between 250 and 1600 p.s.i.g., for 20 to 60 minutes.

The resulting deashed extract, which still contains inert ash components, is separated from the water or acidified water by simple decantation and is withdrawn from the deashing zone 24 via a conduit 26. The deashed extract contains a much lower proportion of alkaline ash to inert ash than the ash-containing extract feed, and preferably contains no alkaline ash components.

It is important to note that even when slightly acidic water solutions are used to deash the coal extract, the cost associated with such reagents as well as the cost of equipment used to handle such reagents is substantially less than the cost associated with the acid-washing deashing schemes used heretofore by prior investigators. Furthermore, the extract normally undergoes little or no degradation due to such water treatment in contrast to the degradation which normally accompanies acid-deashing as used heretofore. Of primary importance, however, is the fact that the increase in catalyst life resulting from removing the alkaline ash components more than overcomes the slight added cost associated with removing the alkaline ash. Such is not the case when a substantial portion of the inert ash is removed by washing with highly concentrated acid solutions.

At least a portion of the alkaline-ash-free extract is conveyed by the conduit 26 into a prehydrocracking zone 28, wherein the extract is hydrocracked in the presence of catalyst fines. These catalyst fines, introduced via a conduit 30, are produced by abrasion of larger hydrocracking catalyst, as is hereinafter more fully explained.

As previously mentioned, it has been found that when ash-containing coal extract is hydrocracked in the presence of a catalyst such as hydrocracking catalyst, substantially all of the ash selectively deposits on the exterior surface of the catalyst such that it can be removed by abrasion. It also has been found that when these ash-laden deactivated hydrogenation catalysts such as hydrocracking catalyst are subjected to an abrasion treatment to remove the

ash layer therefrom, both the ash layer, which is removed in the form of fine particles (referred to as catalyst fines), and the whole abraded catalyst particles, have a substantially higher catalytic activity than the deactivated hydrogenation catalyst from which they were obtained. Therefore, rather than discard these catalyst fines, which are a mixture of catalyst and ash, it is suggested in the copending application filed of even date herewith by Everett Gorin and Robert T. Struck, supra, that the catalyst fines be used to prehydrocrack the coal extract.

The prehydrocracking zone 28 may be any of the conventional type hydrocracking zones, but preferably the zone 28 is one in which the alkaline-ash-free extract is treated for purposes of agglomerating the inert ash which is not removed in the deashing zone 24. The agglomerated ash contained in the resulting prehydrocracking products will have less of a deleterious effect on the larger catalyst particles employed in a subsequent hydrocracking zone, as is further discussed in copending application Serial No. 185,994, filed by Everett Gorin, April 9, 1962, now U.S. Patent 3,162,594, which is assigned to the assignee of this application.

Because the catalyst fines are so small (the catalyst fines normally have a particle diameter below 20 microns), the prehydrocracking zone 28 is operated as a slurry phase or suspensoid type hydrocracking zone. The prehydrocracking products containing the catalyst fines suspended therein are withdrawn from the zone 28 via a conduit 32.

The prehydrocracking zone 28 is preferably maintained at a temperature in the range of 375 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 cubic foot of reaction volume. The catalyst concentration is maintained in the range of 1 to 20 weight percent, and preferably in the range of 3 to 10 weight percent.

The prehydrocracking products, suspended catalyst fines, inert ash components, and any alkaline ash components not removed during deashing, are conveyed via the conduit 32 into a catalytic hydrocracking zone 34.

The catalytic hydrocracking zone 34 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 cubic foot of reaction volume. The catalytic hydrocracking zone 34 may be any one of the conventional type hydrocracking zones used by those skilled in the art wherein catalyst is maintained in the form of a fixed, gravitating, or fluidized bed therein. In addition, the catalyst may also be dispersed within the extract in the form of a slurry and then introduced into a slurry phase, catalytic hydrocracking zone such that the catalyst is introduced into, maintained therein, and withdrawn therefrom in the form of a slurry or a suspensoid. Preferably, the catalytic hydrocracking zone 34 is a dense bed, liquid phase fluidized catalytic hydrocracking zone such as described in copending application Serial No. 31,455, filed by Everett Gorin, May 24, 1960 now abandoned, which is assigned to the assignee of this application. In this manner the hydrocracking catalysts, which normally have a much larger particle diameter than the catalyst fines (1600 microns vs. 20 microns or less), are maintained within the hydrocracking zone, and the catalyst fines are removed with the hydrocracking products.

Suitable hydrocracking 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. The hydrocracking catalyst may be in the form of beads, pellets, cylinders and the like.

Hydrocracking products containing the catalyst fines suspended therein are withdrawn from the hydrocracking zone 34 and conveyed via a conduit 36 into a hot separation zone 38. Distillable hydrocracking products are withdrawn from the hot separation zone 38 via a conduit 40. These distillable products, after removal of non-condensable gases (not shown), are preferably fractionated in a fractionation zone 42 to yield:

(1) A fraction boiling below 260° C., which is subsequently refined to gasoline (recovered via a conduit 44);
(2) A fraction boiling between 260 and 325° C., the major portion of which subsequently is refined to gasoline (recovered via a conduit 46); and
(3) A fraction boiling above 325° C., which is introduced into the extraction zone 10 as make-up solvent (recovered via a conduit 48).

Preferably, a portion of the 260 to 325° C. fraction is introduced into the extraction zone 10 along with the +325° C. fraction (the +325° C. fraction usually boils below about 500° C.). In some instances, it may be desirable to further fractionate the +325° C. fraction such that only the 325 to 425° C. fraction is used as extraction solvent while the +425° C. bottoms are recycled to the hydrocracking zone 34 or, if desired, to a coking zone such as a delayed coker (not shown). Obviously, many other variations in the fractionation of the distillable hydrocarbonaceous liquid may be practiced by those skilled in the art. For example, all of the distillable products may be refined to gasoline, in which case, fresh extraction solvent would be recovered, for example, from one of the refining product streams.

Returning to the hot separation zone 38, the non-distillable hydrocracking product, which contains the catalyst fines suspended therein, is conveyed via a conduit 50 into the prehydrocracking zone 28. By recycling the catalyst fines in the above manner, the catalyst fines concentration in the prehydrocracking zone 28 is maintained at a high level. Without such recirculation of the catalyst fines, excessive abrasion of the hydrocracking catalyst in the abrasion zone may be necessary in order to maintain suitable catalyst concentrations in the prehydrocracking zone 28. If desired, a portion of the catalyst fines may be withdrawn from the system via a conduit 52 and either discarded or regenerated for further use in the prehydrocracking zone.

Returning to the hydrocracking zone 34, ash contained in the prehydrocracking products deposits on the hydrocracking catalyst thereby causing the catalyst to be deactivated. As previously mentioned, it has been found that substantially all of the ash deposits selectively on the exterior surface of the hydrocracking catalyst such that it can be removed by abrasion. Therefore, deactivated catalyst is withdrawn from the hydrocracking zone 34 via a conduit 54 and introduced into an abrasion zone 56. If desired, at least a portion of the deactivated catalyst may be subjected, prior to abrasion, to a conventional type regeneration treatment to remove carbon deposits therefrom.

Preferably, substantially all of the withdrawn deactivated catalyst is introduced into abrasion zone 56, wherein the deactivated catalyst particles are subjected to abrasion in order to remove the ash-laden thin outer layer therefrom. Many variations of abrading the deactivated catalyst will occure to those skilled in the art. However, one convenient method for removing the thin outer layer of ash from the deactivated catalyst is to pass the catalyst into a rotating drum having an abrasive interior surface. Thus, the ash layer, which is a mixture of ash and catalyst, is removed from the catalyst particles by the collision of the particles against the abrasive interior surface as well

as collision of the particles with each other, as further discussed in the copending application by Everett Gorin and Robert T. Struck, filed of even date herewith, supra.

The ash-laden outer layer, which generally is between about 5 and 30 microns in thickness, is removed from the deactivated catalyst particles in the form of fines, referred to as catalyst fines. These catalyst fines, which generally have a particle diameter below about 20 microns, contain the major portion of the ash deposited on the deactivated catalyst. The resulting abraded catalyst particles, which are what remain after the ash layer has been removed, are preferably withdrawn from the abrasion zone 56 via a conduit 58. The catalyst fines are separately withdrawn from the abrasion zone 56 via a conduit 30 and introduced into the prehydrocracking zone 28, as previously discussed.

Substantially all of the abraded catalyst is reintroduced into the hydrocracking zone 34. Eventually, however, the resulting abraded catalyst may be too small for reintroduction into the same hydrocracking unit and thus must be used in another type of hydrocracking unit or in another manner. Obviously, if the particle size of the deactivated catalyst were allowed to become too small, the resulting abraded catalyst particles would be no larger than the catalyst fines, thus they would be withdrawn from the catalyst fines.

EXAMPLE

Two coal extracts were prepared from a Pittsburgh Seam bituminous coal by solvent extraction with tetrahydronaphthalene solvent. The conditions of extraction and filtration were adjusted such that in one case a relatively high ash extract was produced, and in the other, a relatively low ash extract was produced. The conditions of extraction used and the ash content of the extracts are listed in Table III.

Table III

	Extract A	Extract B
Solvent to coal ratio (weight ratio)	2.0	1.5
Extraction temperature (° C.)	380	394
Extraction residence time (mins.)	52	28
Filtration temperature (° C.)	200	264
Extract recovered from filtration (weight percent MAF coal)	57.4	74
Ash content of recovered extract (weight percent of extract)	0.13	0.28

Extract A was partially deashed without selective removal of alkaline ash. Extract B was treated for selective removal of alkaline ash components by washing with slightly acidified water in two stages at 90° C. The extract, dissolved in one part of tetrahydronaphthalene and one part of cresol, was washed at 90° C. with two parts of distilled water containing 0.028 weight percent of hydrochloric acid. This washing was followed by washing the extract solution in a second stage with pure water. The total ash and alkaline oxide ash components contained in the deashed extracts A and B are shown in Table IV.

Table IV

ASH CONTENT OF DEASHED EXTRACTS (WT. PERCENT OF EXTRACT)

Deashed extract	Total ash	Alkaline ash ($CaO+K_2O+NA_2O$)
A	0.085	0.015
B	0.12	0.004

Catalyst life studies were made with deashed extracts A and B by individually passing them through a dense bed, liquid phase fluidized catalytic hydrocracking zone under the conditions shown in Table V. The catalyst used had the following composition:

Catalyst composition:	Weight percent of catalyst
Nickel metal	3.65
Molybdenum metal	3.70
Cobalt metal	0.08
Alumina	92.57
	100.00

Table V

	Deashed extract A	Deashed extract B
Temperature (° C.)	427	427
Pressure (p.s.i.g.)	3,500	3,500
Space rate (gms. extract/gm. catalyst/hr.)	3.1	3.4
Total extract passed over catalyst (gm./gm. catalyst)	393	376

The catalysts used in the above runs were regenerated by burning off the carbon with air at 800° F. They were then tested for activity in an autoclave under the standard test conditions shown in Table VI.

Table VI

Temperature, ° C.	429
Total pressure, p.s.i.g.	4200
Hydrogen partial pressure, p.s.i.g.	3500
Residence time, min.	60
Catalyst/extract (weight ratio)	0.30

The hydrogen consumption is used as a measure of the catalyst activity ass hown in Table VII.

Table VII

	Hydrogen consumption (weight percent of extract)	Activity, percent
Fresh catalyst	5.96	100
Spent catalyst A (used with deashed extract A)	4.65	78
Spent catalyst B (used with deashed extract B)	5.06	85

It is seen in Table VII that in spite of the lower total ash content of deashed extract A, the spent catalyst A showed a significantly lower activity than the spent catalyst B which was used with deashed extract B. This is attributed to a selective poisoning effect of alkaline oxide, i.e., the alkaline oxide content of deashed extract A was significantly higher than the alkaline oxide content of deashed extract B. (Table IV.)

The spent catalysts were then abraded in a rotary drum wherein 5 to 6 weight percent of the outer surface was removed. The activities of the abraded catalysts were again tested under the standard test conditions of Table VI except that a lower catalyst to extract weight ratio of 0.05 was used.

Table VIII

Abraded spent catalyst:	Hydrogen consumption (wt. percent extract)
Abraded catalyst A	3.09
Abraded catalyst B	3.33

As can be seen from Table VIII, the abraded catalyst B which had been exposed to the deashed extract B, which contained high total ash but low alkaline ash, showed a significantly higher activity than abraded catalyst A. Thus selective poisoning of the alkaline oxides is retained even after the outer ash-rich layer is removed by abrasion. Therefore, by alkaline ash removal plus abrasion, an improved economic catalyst life is obtained.

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

We claim:

1. An improved process for producing hydrogen-enriched hydrocarbonaceous products from coal, which process comprises

(a) subjecting said coal to solvent extraction to yield ash-containing extract, said ash comprising alkaline ash components and inert ash components,

(b) treating at least a portion of said ash-containing extract in a deashing zone to preferentially remove alkaline ash from said ash-containing extract so as to yield a deashed extract containing a lower proportion of alkaline ash to inert ash than said ash-containing extract,

(c) subjecting at least a portion of said deashed extract to hydrogenation in a hydrogenation zone in the presence of a catalyst to yield hydrogen-enriched hydrocarbonaceous products, whereby said ash components contained in said deashed extract deposit on the catalyst particles thereby causing said catalyst particles to lose activity, and

(d) subjecting at least a portion of the ash-containing catalyst particles to an abrasion treatment to selectively remove a uniform thin outer layer therefrom such that the resulting abraded catalyst has an increased catalytic activity.

2. The process of claim 1 wherein the ash-containing extract is contacted with water in the deashing zone of step (b) to preferentially remove alkaline ash.

3. The process of claim 1 wherein the ash-containing extract is contacted with slightly acidified water in the deashing zone of step (b) to preferentially remove alkaline ash.

4. The process of claim 1 wherein at least a portion of the ash-containing catalyst particles from step (c) is introduced into an external abrasion zone to selectively remove a uniform thin outer layer therefrom such that the resulting abraded catalyst has an increased catalytic activity.

5. The process of claim 1 wherein substantially all of said alkaline ash components are removed from said ash-containing extract in said deashing zone of step (b).

6. The process of claim 1 wherein said hydrogenation zone of step (c) is a dense bed, liquid phase fluidized catalytic hydrocracking zone.

7. An improved process for producing hydrogen-enriched hydrocarbonaceous products from coal, which process comprises

(a) subjecting said coal to solvent extraction under conditions to yield undissolved coal residue and ash-containing extract, said ash comprising alkaline ash components and inert ash components,

(b) separating at least a portion of said ash-containing extract from said residue,

(c) treating at least a portion of said ash-containing extract in a deashing zone to preferentially remove alkaline ash from said ash-containing extract so as to yield a deashed extract containing a lower proportion of alkaline ash to inert ash than said ash-containing extract,

(d) hydrocracking at least a portion of said deashed extract in a prehydrocracking zone in the presence of catalyst fines as hereinafter produced to yield ash-containing prehydrocracking products,

(e) introducing at least a portion of said prehydrocracking products into a catalytic hydrocracking zone to yield hydrogen-enriched hydrocarbonaceous products, whereby said ash contained in said prehydrocracking products deposits on the catalyst particles thereby causing said catalyst particles to lose activity, and

(f) subjecting at least a portion of the ash-containing catalyst particles to an abrasion treatment to selectively remove a uniform thin outer layer therefrom such that an abraded catalyst having an increased catalyst activity and said catalyst fines are obtained.

8. The process of claim 7 wherein the ash-containing extract is contacted with water in the deashing zone of step (c) to preferentially remove alkaline ash.

9. The process of claim 7 wherein the ash-containing extract is contacted with slightly acidified water in the deashing zone of step (c) to preferentially remove alkaline ash.

10. An improved process for producing hydrogen-enriched hydrocarbonaceous products from coal, which process comprises

(a) subjecting said coal to solvent extraction under conditions such that between 50 and 80 weight percent of the MAF coal is dissolved, whereby ash-containing extract and undissolved residue are obtained, said ash comprising alkaline ash components and inert ash components,

(b) separating substantially all of said ash-containing extract from said residue,

(c) contacting said ash-containing extract with slightly acidified water to yield alkaline-ash-free coal extract,

(d) hydrocracking said alkaline-ash-free extract in a slurry phase prehydrocracking zone in the presence of catalyst fines as hereinafter produced to yield ash-containing prehydrocracking products,

(e) recovering prehydrocracking products containing catalyst fines suspended therein from said prehydrocracking zone,

(f) introducing said prehydrocracking products into a dense bed, liquid phase fluidized catalytic hydrocracking zone wherein inert ash contained in said prehydrocracking products deposits on said hydrocracking catalyst thereby causing said catalyst to lose activity,

(g) recovering hydrocracking products containing said catalyst fines suspended therein from said hydrocracking zone,

(h) reintroducing at least a portion of said catalyst fines into said prehydrocracking zone of step (d),

(i) separately recovering deactivated ash-containing hydrocracking catalyst from said hydrocracking zone of step (f),

(j) subjecting at least a portion of said recovered catalyst to abrasion in an abrasion zone to yield abraded catalyst having an increased catalyst activity and catalyst fines,

(k) reintroducing said abraded catalyst into said hydrocracking zone of step (f), and

(l) introducing said catalyst fines into the prehydrocracking zone of step (d).

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