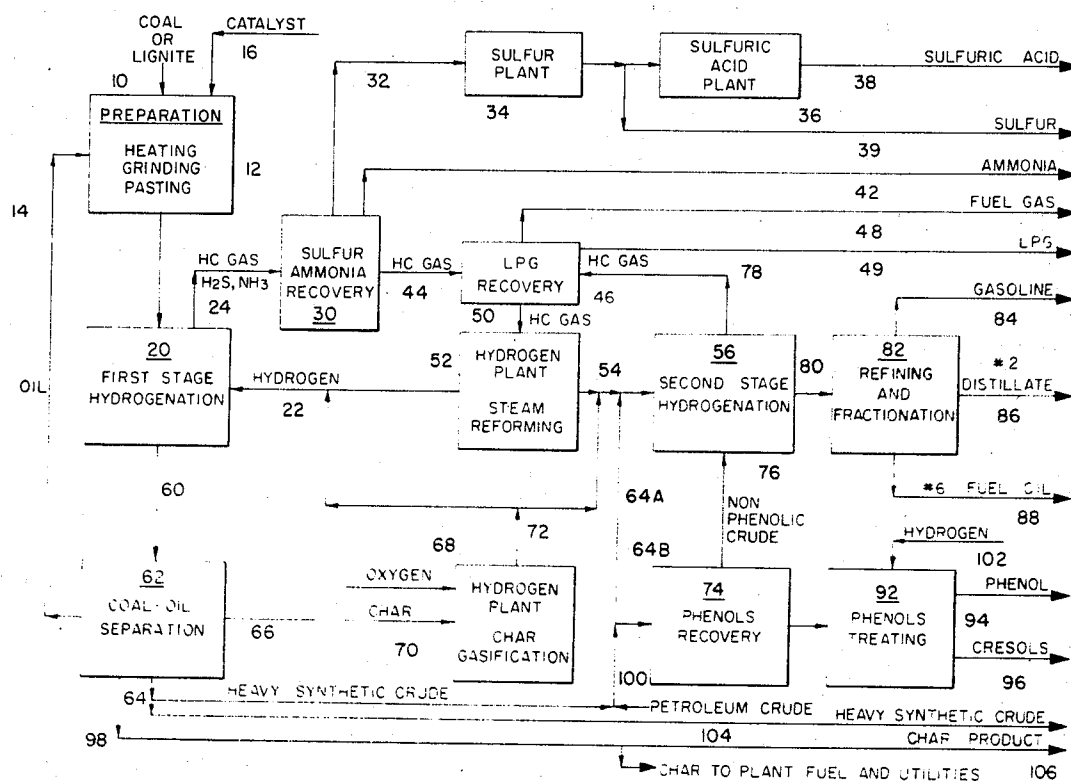
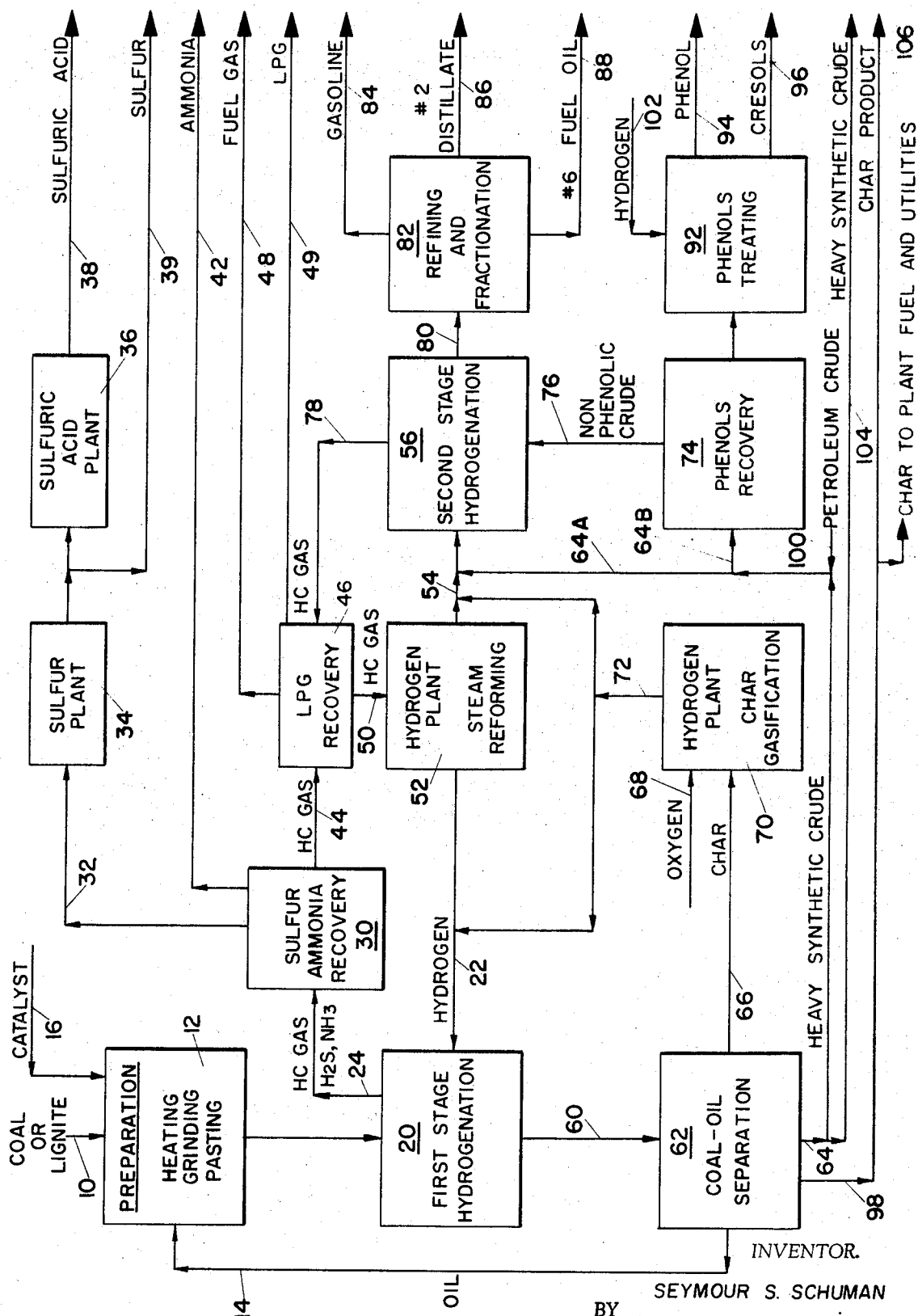






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MULTI-STAGE EBULLATED BED COAL-OIL HYDROGENATION AND HYDROCRACKING PROCESS

The application is a continuation of applications Ser. No. 18,383 filed Feb. 13, 1970; Ser. No. 784,967 filed Sept. 5, 1968; Ser. No. 638,663 filed May 15, 1967 and Ser. No. 410,485 filed Nov. 12, 1964; now all abandoned.

This invention relates to the conversion of solid carbonaceous solids such as bituminous, semi-bituminous and sub-bituminous grades of coal as well as lignites for the production of more valuable products including solid, liquid and gaseous fuels and chemical by-products. The invention comprises a process system, substantially based on hydrogenation, which yields products similar to those obtained in oil refineries; in this sense, the system may be called a "coal refinery".

The history of efforts to produce more valuable products from coal illustrates the formidability of the task. Although technical work dates from Bergius in 1914, and although the Germans produced oil from coal during World War II at a rate of about 100,000 barrels per day, the conversion of coal to liquid fuels has never attained real commercial status. It is obvious that before coal can be commercially utilized to produce liquid fuels, the following requirements must be met:

1. An operable, economic coal hydrogenation process must be available.
2. The cost of the hydrogen necessary to hydrogenate the coal must be low.
3. Optimum value products must be obtained, possibly including gaseous fuels, solid fuels and for petrochemicals as well as liquid fuels.

It is considered that these basic requirements for the utilization of coal to produce liquid fuels will be met and satisfied in accordance with this invention. The following describes a process which can bring about such utilization of coal, and provides several cases which illustrate the application of the process in specific coal "refineries".

FIRST STAGE HYDROGENATION

In the operation of German plants during World War II, the primary coal hydrogenation step was carried out at pressures between 5,000 to 10,000 psig, with complete conversion of solids to liquids, and with the liquid products sufficiently low in boiling range so that they could be further processed in a secondary hydrogenation stage in the vapor phase. New concepts and technology make it highly desirable to modify the German hydrogenation practice in the following major ways:

1. Reduction of hydrogenation pressures to a level wherein capital costs are drastically reduced, more or less conventional equipment can be employed, and operating safety greatly increased.
2. Incomplete conversion of the coal with low hydrogen-containing, difficultly hydrogenatable char either used as a source of hydrogen or as process fuel, or sold as a product.
3. Primary conversion of the coal to products which are not necessarily in the vapor phase in the subsequent secondary hydrogenation stage.

These basic requirements are obtained in the following process as a further improvement of technology developed for the hydrogenation process for the production of lighter liquid fuels from petroleum residuums.

The basic feature of the hydrogenation process is the use of the catalyst in an ebullated bed, with the suspended catalyst in a random motion with respect to the flowing mixed phase of liquid oil and gaseous hydrogen. Relatively small sized particles of catalyst can be used in the ebullated bed system; yet a liquid product is withdrawn from the system which is essentially catalyst-free.

The use of relatively fine, highly active catalyst allows a drastic reduction in operating pressure. Where, previously, petroleum residuums were hydrogenated at pressures of 5,000 pounds or higher, the hydrogenation process has been operated effectively at as low as 800 pounds. It should be noted that the catalyst in the hydrogenation process is relatively low in cost, and of sufficiently long life so that it does not have to be regenerated.

A feature of such a hydrogenation process is that the reactor heat release problems which plagued German work have been completely eliminated.

In a 30 barrel per day pilot plant, the hydrogenation process has upgraded low hydrogen content tars containing up to 3 percent ash, with no difficulties from the high ash. In this operation the ash passes through the ebullating bed and is removed from the reactor without losing catalyst. Furthermore, a clean pumpable liquid can be made available from the reactor for recycle or other purposes.

This work indicates the essential feasibility of a primary coal hydrogenation step in which the charge, ground somewhat finer than the catalyst, is fed as a slurry into a reactor containing an ebullated bed of catalyst and passes through the coarser catalyst, which remains in the reactor. Residual coal solids are then removed and a relatively clean oil product made available to transport the coal feed. It has been confirmed that sufficient conversion of coal for a workable process can be obtained by hydrogenation at about 400-500°C at pressures as low as 1,500-3,000 psig using a catalyst that has not been ground or impregnated into the coal as in the German practice.

The optimum extent of conversion to be effected in such a first stage coal hydrogenation step is complex and depends on many factors. In all cases, it seems desirable to produce some char; this char may be used as a source of hydrogen, or used for fuel, or sold as such. Similarly, the liquid products from my first stage operation may vary considerably in boiling range; depending on the ultimate products to be sold, the availability of excess capacity in the subsequent refining operations required, and many other factors. In the cases presented below, char is produced from the first stage in varying amounts as will be seen. The liquid product from the first stage has the boiling range of a heavy petroleum crude (but is of a much higher specific gravity because of a high content of aromatic hydrocarbons). After topping off naphtha, this oil would have the essential properties of No. 6 fuel oil and/or Bunker C fuel oil.

SECONDARY HYDROGENATION STAGES

In cases where lighter products are desired, additional hydrogenation stages are required. For these cases, a residuum-containing fraction from the first stage is then additionally converted in an intermediate hydrogenation stage. It is conceivable that continued development of the process will permit this additional

conversion to be effected in the primary stage; in this case, elimination of the intermediate stage will further significantly reduce overall costs.

The intermediate hydrogenation stage would be similar in all respects to operations now practiced commercially. Pilot plant and commercial operations have proved that very high conversions can be obtained in this stage with little or no No. 6 fuel oil production if desirable. Thus, the liquid products after this intermediate hydrogenation stage are substantially naphtha, furnace oil and heavy gas oil. Here again the product can be considered to be a synthetic crude and fed to an existing refinery as such.

However, in many of the cases of interest, it would be desirable to convert this light synthetic crude to marketable products. This requires an additional secondary conversion stage. In converting the heavy gas oil, an additional hydrocracking stage is more satisfactory than catalytic cracking, because of the aromatic nature of the heavy gas oil to be cracked and because of the low cost of hydrogen attained in a large integrated coal refinery. As practiced by the Germans, such a hydrocracking operation was carried out in the vapor phase. This necessitated a deep conversion in earlier stages, with highly inefficient utilization of hydrogen, and the production of large quantities of gas and relatively low octane gasoline. As practiced herein, the hydrocracking stage can be carried out in the liquid phase, thus decreasing the conversion required in the relatively less efficient prior stages. Catalysts may be utilized which are far more active and selective than those previously used by the Germans. Most importantly, a high throughput efficiency may be obtained at pressures of the order of 1,000–2,000 psig, as compared with the 5,000 psig operations of the Germans. Full realization of these advantages is obtained using an ebullated bed, as in the primary and intermediate stages. Among the many advantages of the ebullated bed hydrocracking process is that it can handle the highest boiling heavy vacuum gas oils without temperature control or coking problems.

HYDROGEN PRODUCTION

The inexpensive production of hydrogen is a collateral essential element in the economic conversion of coal to liquid fuels. Such hydrogen may be derived from char produced in the first stage; in this case the plant gas product is either sold as a methane-equivalent fuel gas, or used as fuel within the overall plant. Alternatively, the gas may be employed to produce hydrogen, with char used as fuel or sold. Obviously many intermediate possibilities exist.

It is obvious that hydrogen-deficient char obtained from the hydrogenation operation, is a more economical fuel for gasification than coal itself. However, possibly more important, the char is a much more satisfactory feed to a fluid bed gasification process, because of its much lessened tendency to cake or agglomerate. Such caking problems have badly plagued fluid bed gasifiers in the past, particularly when operations have been carried out on some highly agglomerating coals obtained from the Pittsburgh seam.

In a typical case, such a fluid bed gasifier can be operated with thermal efficiencies of the order of 75 percent including oxygen power requirements at good space rates corresponding to about 350,000 SCFD per square foot of gasifier cross-section. This process

would be highly suitable for an integrated coal refinery such as that described here.

However, alternatively, the large amount of hydrogen required for the coal conversion plant may be obtained by steam reforming of the light gas produced in the hydrogenation stages. Considerable economies have been obtained at this time in the overall cost of steam reforming operations. Thus, it is highly problematic at the present time whether the conversion of coal to liquid fuels will ultimately be practiced with hydrogen obtained from the intrinsically cheaper gasification of char, or with hydrogen obtained from steam reforming. Examples of both of these possibilities are presented below.

Thus, it is an object of this invention to develop a process for the economic conversion of coal to more valuable products.

It is a further object of this invention to accomplish such conversion substantially by a hydrogenation process which is considerably more economic than that used heretofore.

A further object of this invention is to provide a means for obtaining inexpensive hydrogen for the purpose of said hydrogenations.

It is still a further object of this invention to convert coal substantially by hydrogenation to a range of marketable petroleum products and chemical byproducts, such that said conversions may be economically practiced.

A further object is to accomplish said economic conversion using a wide range of different coals or ash-containing, non-petroleum derived, solid carbonaceous substances.

Further objects and advantages of my invention will appear from the following description of preferred forms of embodiment thereof as more particularly shown in the attached drawing illustrative thereof, such drawing being a block diagram of the various steps in converting solid carbonaceous materials to valuable liquid and gaseous end products.

As shown, the solid carbonaceous material such as coal or lignite, or any similar carbonaceous material containing ash, enters the system at 10 and is first passed through a preparation unit generally indicated at 12. In such a unit it is desirable to dry the coal of all surface moisture and to grind the coal to a desired mesh and then to screen it for uniformity. In the case of lignite, it is particularly desirable to conduct the drying operation at a temperature in the range of 300–700°F. in order to remove easily destroyable oxygen in the form of carbon dioxide, carbon monoxide or water.

For my purpose it is desirable that the coal have a fineness of about 100 mesh and is preferably of relatively close sizing, i.e., all passing 50 mesh and not less than 80 percent retained on 200 mesh. However, it will be observed that the preciseness of size may vary between different type of solid carbonaceous materials which may be treated.

In the preparation unit which may consist of several physical pieces of apparatus, an essential step is the slurring of the finely ground solids with a pasting oil, the source of which is hereinafter to be discussed. To establish an effective transferable slurry, it is found that the ground solids should be mixed with roughly an equal weight or more of pasting oil. In addition, a catalyst or contact agent may be added at 16 in the ratio of

about 0.01 to 0.20 pound of catalyst per ton of carbonaceous solids. Such a catalyst, known as a hydrogenation catalyst, is from the class of cobalt, molybdenum, nickel, tin, iron and the like, usually deposited on a support of the class of alumina, magnesia, silica and the like.

The coal-oil slurry is then passed into the first stage hydrogenation reactor, generally indicated at 20 and preferably passes upwardly from the bottom together with hydrogen in line 22 at a rate, and under temperature and pressure conditions to accomplish the desired hydrogenation.

By concurrently flowing streams of liquid and gasiform materials upwardly through a vessel containing a mass of solid particles of a contact material which may be a specific catalyst as above indicated, and expanding the mass of solid particles at least 10 percent over the volume of the stationary mass, the solid particles are placed in random motion within the vessel by the upflowing streams. A mass of solid particles in this state of random motion in a liquid medium may be described as "ebullated". The characteristics of the ebullated mass at a prescribed degree of volume expansion can be such that a finer, lighter solid will pass upwardly through the mass so that the particles constituting the ebullated mass are retained in the reactor and the finer, lighter material may pass from the reactor.

The contact material (herein catalyst) is preferably in the form of beads, pellets, lumps, chips or like particles at least 1/32 inch and more frequently in the range of 1/16 to 1/4 inch (i.e., between about 3 and 20 mesh screens of the Tyler scale). The size and shape of the particles used in any specific process will depend on the particular conditions of that process, e.g., the density, viscosity and velocity of the liquid involved in that process.

It is a relatively simple matter to determine for any ebullated process the range of throughput rates of upflowing liquid which will cause the mass of solid particles to become expanded and at the same time placed in random motion. The gross volume of the mass of contact particles expands when ebullated without, however, any substantial quantity of the particles being carried away by the upflowing liquid and, therefore, a fairly well-defined upper level of randomly moving particles establishes itself in the upflowing liquid. The upper level above which few, if any, particles ascend will hereinafter be called the upper level of ebullation.

In contrast to processes in which fluid streams flow downwardly or upwardly through a fixed mass of particles, the spaces between the particles of an ebullated mass are thus large with the result that the pressure drop of the liquid flowing through the ebullated mass is small and remains substantially constant as the fluid throughput rate is increased. Thus, a considerably smaller consumption of power is required for a given throughput rate. Moreover, the ebullated mass of particles promotes much better contact between the coal fines and gasiform streams than with any fixed bed process. Under these conditions, a significantly greater fluid throughput rate carrying the coal fines may be used without impairing the desired degree of contact than if conventional downflow or upflow through a fixed bed of contact particles is used.

Moreover, solid material will pass through an ebullated bed where it would otherwise plug a fixed bed. Additionally, the random motion of particles in an

ebullated mass caused these contact particles to rub against each other and against the walls of the vessel so that the formation of deposits thereon is impeded or minimized. The scouring action helps to prevent agglomeration of the contact particles and plugging up of the vessel. This effect is particularly important where catalyst particles are employed and maximum contact between coal fines, hydrogen and the catalytic surfaces is desired, since the contact surfaces are exposed to the reactants for a greater period of time before becoming fouled or inactivated by foreign deposits.

The process of this invention may be carried out under a wide variety of conditions. To obtain the advantages of this invention it is only necessary that liquid, coal fines, and gasiform materials flow upwardly through a mass of solid particles of a contact material at a rate causing the mass to reach an ebullated state. In each ebullated system, variables which may be adjusted to attain the desired ebullation include the flow rate, density and viscosity of the liquid and the gasiform material, and the size, shape and density of the particulate material. However, it is a relatively simple matter to operate any particular process so as to cause the mass of contact material employed to become ebullated and to calculate the percent expansion of the ebullated mass after observing its upper level of ebullation through a glass window in the vessel, or by radiation or acoustic permeability, or by other means such as liquid samples drawn from the vessel at various levels. In general, the gross density of the stationary mass of contact material will be between about 25 and 200 pounds per cubic foot, the flow rate of the liquid will be between about 5 and 120 gallons per minute per square foot of horizontal cross section of the ebullated mass, and the expanded volume of the ebullated mass usually not more than about double the volume of the settled mass and preferably only about 80 percent.

Preferred reactor operating conditions are in the range of 750 to 950°F. and from 1,000 to 4,000 psig. Coal throughput is at the rate in excess of 15 pounds per hour per cubic foot of reactor space and usually in the range of 15-150 pounds per hour per cubic foot of reactor space so that the yield of unreacted coal as char is not greater than 50 percent and usually between 15 and 50 percent of the quantity of moisture and ash free coal feed. The relative size of the coal and catalyst particles and condition of ebullation are such that the catalyst is retained in the reactor while the unreacted char is carried out with the reaction products and the slurry oil solid. As indicated previously, makeup catalyst may be added to the slurry at 16, or directly to the first stage reactor.

The products from the first stage 20 include a gaseous product, shown schematically as removed in line 24, and a liquid product similarly shown as line 60.

Particularly with certain coals, there is sufficient justification for the recovery of sulfur as well as ammonia which can be accomplished in the sulfur-ammonia recovery unit 30. In such case, hydrogen sulfide goes overhead at 32 and passes through Claus sulfur plant 34. Part or all of the sulfur may pass through a sulfuric acid plant 36 to produce sulfuric acid at 38. Sulfur at 39 may also be an end product. Ammonia will be removed at 42 also as an end product. The net hydrogen and hydrocarbon gas pass by line 44 to the liquefied petroleum gas (LPG) recovery unit 46. The LPG being recovered at 49. Fuel gas product may be removed at

48. Alternatively part or all of the fuel gas with hydrogen may pass through line 50 to a hydrogen plant 52.

This hydrogen plant 52 is conveniently one operating under the usual conditions of steam reforming to produce the hydrogen 22 for the first stage hydrogenation as well as by line 54 for the second stage hydrogenation 56. This is particularly effective when the conversion of coal in the first stage hydrogenation is substantially 100 percent.

Returning to the first stage hydrogenation, the liquid effluent through line 60 conveniently passes to a coal-oil separation unit 62 from which a heavy synthetic crude is removed at 64, together with char removed at 66. If desired, the pasting oil 14 may be removed from the coal-oil separation unit 62. Pasting oil is also removed from the bottoms of a fractionation of the effluent of the second stage hydrogenation.

As a supplemental or alternative means for the production of hydrogen, the char 66 together with oxygen at 68 may be introduced to a char gasification unit 70 from which hydrogen may be removed at 72 both for the first stage hydrogenation as well as for the second stage hydrogenation 56.

It will be recognized that the heavy synthetic crude 64 contains desirable hydrocarbons which may pass by line 64A to the second stage hydrogenation at 56 as well as phenols and cresols which are diverted to the phenols recovery unit 74 by means of the line 64B. The phenols recovery unit 74 separates a non-phenolic crude at 76 which also goes to the second stage hydrogenation from the remaining phenols and cresols that pass to phenols treating unit 92.

The second stage hydrogenation unit is also preferably of the upflow ebullated bed type such as described in the Johanson Patent, No. 2,987,465, and from which the hydrocarbon gas and hydrogen are removed overhead at 78 with a high grade hydrocarbon-like material product removed at 80. This, in turn, will be passed through the usual refining and fractionation stages 82 to produce, as an example, gasoline of 95 CFRR octane rating at 84; a No. 2 distillate of 32°API gravity at 86; and a No. 6 fuel oil of 0°API gravity at 88. Such conventional refining is preferably effected by hydrocracking the heavy gas oil (again utilizing hydrogen from steam reforming unit 52 or from char gasification unit 70). Where very high yields of gasoline are desired, the furnace oil may be similarly hydrocracked.

In some cases, the yield of cresol may be excessive for the market and in such case a hydrodealkylation unit at 92 may be employed to convert cresols substantially to phenol. By operating at a temperature in the range of 1,000–1,500°F., either catalytically or non-catalytically, it is possible to hydrodealkylate the higher cresols, utilizing hydrogen from line 102 again available from 52 or 70.

In some cases where excess conventional refining capacity is available, part of the heavy synthetic crude from the first stage, after separation from solids in 62 may be withdrawn as product in line 104.

In some cases, where a satisfactory market for char exists, this material may be removed as product through 106. Another possibility, not shown, is to remove a mixture of char and heavy oil as feed to an electric power plant.

Another possibility is to produce hydrogen from gas in the summer, storing char, the latter then used to pro-

duce hydrogen in the winter with the gas then sold as peak load fuel gas commanding premium prices.

Another possibility is to supplement plant output by feeding in a petroleum crude to the H-Coal refinery shown schematically by line 100. Such a practice may also be desirable in that gasoline produced from coal alone may be excessively aromatic.

It is obvious that many other modifications exist in the design and operation of a coal refinery such as that described herein. However, such modifications are combinations of existing art with the basic scheme presented. I desire a broad interpretation of the invention within the scope and spirit of the description herein and of the claims appended hereinafter.

I claim:

1. The process of conversion of coal to liquid petroleum-like hydrocarbons and gas by a liquid phase catalytic hydrogenation wherein the coal is pretreated to render it amenable to hydrogenation, which pretreatment includes grinding said coal so that all coal particles will pass 50 mesh (Tyler) and slurring said coal particles with a liquid carrier pasting oil subsequently recovered from the process and said slurry is passed continuously upwardly through a first stage hydrogenation zone in the presence of a particulate hydrogenation catalyst and hydrogen under ebullating bed conditions to the extent that the catalyst is maintained in random motion in the liquid and yet is largely retained in the reaction zone, the reaction zone being under hydrogenation conditions of pressure in the range of 1,000 to 4,000 pounds per square inch gauge, and a temperature in the range of 750° F. to 950° F with a coal solids throughput between 15 and 150 pounds of coal per hour per square foot of reaction space with a partial conversion of the coal of at least 50 percent to produce a first stage effluent the improvement which comprises:

- a. withdrawing a gaseous fraction from the first stage effluent;
- b. withdrawing a solids containing liquid fraction boiling in the range of heavy synthetic crude, the solids comprising unreacted coal, ash and char, from the first stage effluent;
- c. passing said liquid fraction to a coal-oil separation stage for the removal of char, pasting oil and heavy synthetic crude;
- d. separating the phenolic compounds from part of the heavy synthetic crude oil;
- e. passing a blend of said synthetic crude oil together with said phenol free synthetic crude oil and supplemental petroleum crude oil, said supplemental petroleum crude oil added in an amount whereby the final product boiling in the gasoline range is rendered less aromatic, together with hydrogen upwardly through a second stage hydrogenation zone in the presence of particulate hydrogenation catalyst under ebullating bed conditions to the extent that the catalyst is maintained in random motion in the liquid and yet is largely retained in the second stage reaction zone, the second stage reaction zone being under hydrogenation conditions of pressure and temperature and coal throughput to accomplish a further hydrogenation of the liquid fraction containing desirable hydrocarbons to produce a second stage effluent;

- f. fractionating the second stage effluent to remove a pasting oil from the bottom fraction of said effluent;
- g. hydrocracking liquid effluent of the second stage hydrogenation zone in the presence of catalysts 5 under liquid phase ebullated bed conditions at pressures in the order of 1,000-2,000 psig to recover gas and to produce a crude boiling range liquid;
- h. fractionating said crude boiling range liquid into 10 gasoline boiling range material, light distillates,

- heavy distillates and bottoms, and
- i. producing hydrogen to supply the requirements for said process by gasification of product char and steam reforming said gasification products, and by steam reforming normally gaseous products of the process hydrogenation stages.
2. The process of claim 1 wherein phenols removed from the first stage effluent prior to second stage hydrogenation are hydrodealkylated to phenol at a temperature between 1,000° and 1,500° F.
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