The present invention relates to the hydrogenation of coal, such as bituminous coal and lignite, whereby engine fuels, such as gasoline, diesel fuel, jet fuel and the like, are produced together with valuable chemicals, such as phenols and aromatics.

As known to the art, the process of obtaining such products from coal involves subjecting a paste of ground coal, heavy oil (recycled from the process) and catalyst to high pressure hydrogenation in the liquid phase under conditions of contact time (or space velocity), temperature and pressure such that most of the oil formed, generally from 90 to 95 percent, from the coal is gasoline and middle oil (as used herein, the term, middle oil, refers to oil boiling in the range of about 350° to 625° F.). (All references to the conversion of coal herein, except where otherwise noted, are based on moisture and ash-free coal, commonly referred to as m. a. f. coal.) The middle oil, gas and gasoline are separated from the heavy oil and any non-volatile portion of the converted coal, the mineral portion of the coal (ash), the unconverted coal and catalyst, all of which form a slurry or liquid-containing residue. The middle oil and gasoline, together with any material produced in other phases of the process, is subjected to vapor phase hydrogenation under conditions that convert the middle oil to gasoline.

In order to recover the heavy oil (as used herein, the term, heavy oil, refers to oil boiling above about 625° F. up to non-volatile compounds, such as asphalt), the liquid residue or slurry from the liquid phase hydrogenation is subjected to filtration, extraction, centrifuging, low temperature carbonization, such as in worm or ball ovens, or steam flashung. Irrespective of the manner in which the heavy oil, generally referred to as the H.O.I.D. or heavy oil let down, is separated from the inorganic and unconverted organic solids (hereinafter referred to as the solid residue), it is essential that this oil be recovered in order to have the overall process commercially feasible. The economic necessity of efficient oil recovery from the H.O.I.D. is capably discussed by Peter W. Sherwood in "High-pressure hydrogenation of carbonaceous matter," part V, "The liquid phase in industry," an article that was published in the "Chemical Reformer," vol. 29, page 123, May 1950. In order to reduce the losses in H.O.I.D. recovery, the liquid phase hydrogenation is generally effected under conditions which yield products containing the minimum amount of heavy oil (i.e., the amount lost in recovering the H.O.I.D.) which is of the order of 5 to 10 percent of the total products from the coal.

When the heavy oil of the H.O.I.D. is recovered, it is recycled to the liquid phase hydrogenation step for use as pasting oil. The solids remaining after separation of the heavy oil of the H.O.I.D. are used as a low grade fuel, being unsuitable for most purposes because of the high ash content (generally from 50 to 60 weight percent).

The present invention overcomes the difficulties inherent in the above described type of process, and at the same time, achieves important economies in the consumption of hydrogen and in the consumption of coal for the entire plant, including the requisite power facilities. Furthermore, because of the manner in which the liquid phase operation is more efficient and less reaction volume is necessary, with resultant savings in the capital investment necessary for the plant. Additionally, the process of the present invention produces a good grade of coke, suitable for the manufacture of hydrogen so that hydrogen can be produced without the necessity of the expensive operation of importing coke to the plant.

In accordance with the present invention, the liquid phase hydrogenation of coal paste is effected under conditions such that the major portion of the fraction boiling above gasoline of the normally liquid products is heavy oil and only a minor portion is middle oil. Therefore, in one or more operations, heavy oil and solid residue or ash are separated from the middle oil and lower boiling products and a slurry of heavy oil and solid residue and/or the heavy oil separately is thermally decomposed under conditions that convert the heavy oil and/or any asphalt present into substantial quantities of middle oil, gasoline and gaseous products with the attendant production of substantial quantities of relatively low ash content coke (below about 20 weight percent, including any catalyst present, for most coals although high ash coals, such as those containing 8 weight percent ash, may produce coke having ash contents, including catalyst, of about 30 weight percent). When the heavy oil is thermally decomposed separately an ash-free coke is produced. Coincidentally some heavy oil is vaporized and/or produced by the thermal decomposition. Such heavy oil is separated from the middle oil and lower boiling products of gasoline and normally vaporous products and used for pasting the ground coal fed to the liquid phase hydrogenation. Middle oil and gasoline, produced by both the liquid phase hydrogenation and by the thermal decompositions, are fed to a vapor phase hydrogenation zone wherein the middle oil is converted into gasoline and the quality of the pre-existing gasoline is improved.

Specifically, in the hydrogenation of coal, a coal paste is generally preheated and conducted under pressure to a plurality of converters in series, four or five of which make up a stall. After the coal paste has been reacted by passage through the converters the products pass to a separating vessel, a hot catchpot where unreacted coal, catalysts, and the like, are separated. Overhead vapors from the hot catchpot are cooled and passed to a second separating vessel, a cold catchpot. The overhead product from the cold catchpot is recycle gas. In conventional coal hydrogenation systems about five stalls are normally employed, and the coal hydrogenation procedure is termed liquid phase operation. In accordance with the present invention the conditions maintained in the liquid phase hydrogenation zone are such that the coal fed to the zone is converted into normally liquid products boiling above gasoline which consist principally of heavy oils and contain a minor portion of middle oil, as described more fully below.

The principles involved in the present invention are set forth in detail below in connection with the description of the drawings in which various aspects and/or preferred embodiments of the present invention are shown. It is to be understood that these aspects and/or embodiments are to be regarded as illustrating the present invention rather than restricting its scope.

In the drawings:

Fig. 1 is a general schematic flow sheet of an entire plant employing the present invention.

The liquid phase hydrogenation procedure may be employed as one phase of the overall plant or system shown in Figure 1. As shown therein, a portion 98 of the total
raw coal 81 needed for the entire plant is dried and ground 82, solid catalyst 83, such as iron salts, for example, iron sulfate, iron ore, tin or molybdenum salts and other catalysts known to the art, being added during the grinding in order to obtain uniform admixture through the coal as shown in Figure 1. To the dry ground coal and catalyst 84 is added pasting oil 85 (heavy oil recycled from the process) and the coal, oil, coal and catalyst mixed 86, such as by mulling, grinding and equivalent operations, to form a paste 87. The paste then is hydrodramed in liquid phase 88 in the manner herebefore described.

In accordance with the present invention the conditions maintained in the liquid phase hydrocarbonation zone are such that the coal fed to the zone is converted into normally liquid products boiling above gasoline which consist principally of heavy oil and contain a minor portion of middle oil, as described more fully below. The slurry 89 from the hot catchpot, which consists of heavy oil, catalyst, unconverted coal, and substantially non-volatile conversion products of coal, such as asphalt, is directed to a thermal decomposition zone 91, operated as described more fully below, together with portion of the intermediate catchpot liquid product 92.

The thermal decomposition zone is preferably a coking zone, such as a moving bed of coke particles on or into which the slurry is sprayed, the coke particles being hot enough to effect vaporization and partial thermal decomposition of the relatively high boiling hydrocarbons from the coal (a typical thermal coking system of this type is described in an article on "Continuous Contact Coking" by W. H. Schutte and W. C. Offutt, which was published in the July 14, 1949 issue of the "Oil and Gas Journal"

Other types of coking known to the art, such as delayed coking or coking on fixed or moving beds of particles of inert refractory heat carriers such as fused inorganic oxides, for example, quartz or alumina, may be employed.

In the conversion zone, e.g. coking zone 91, the heavy oil and any asphalt present are thermally decomposed and/or vaporized, under conditions described more fully below, into vaporous products and solid carbonaceous residue 90. The vaporous products consist principally of middle oil and gasoline 93 formed by either thermal cracking or coking of the heavy oil fed to the coking zone but also include some gas and a substantial minor amount of heavy oil produced by vaporization and/or cracking of any asphalt or other substantially non-volatile products of hydrocarbonation present. Thereby, if desired, the conditions of the thermal cracking can be controlled in such a way as to obtain the products which contain a certain quantity of olefins for further use. The solid carbonaceous residue consists principally of the coke used as heat carrier and the coke resulting from the conversion of heavy oil into middle oil and gasoline together with the solid catalyst, the ash (metallurgical constituents) of the coal, and particles of unconverted coal.

The vaporous products from the coking zone 91 are condensed and the liquid portion 93 thereof directed, together with the liquid hydrocarbonation products 94 from the catchpot, to a distillation operation or zone 95. By distillation there is obtained (a) a heavy oil fraction 96 which fraction has an initial boiling point of about 625° F., such as from 600° to 650° F., and contains all higher boiling volatile oil from the coal, at least a portion of which is recycled 85 to the pasting operation as pasting oil, or sold or stored 97 for sale or other uses, (b) a fraction containing middle oil 98 which fraction has an end boiling point or dew point at atmospheric pressure of about 625° F., and which is forwarded 98 to the vapor phase hydrocarbonation operation or zone 99 and (c) a phenol-containing fraction 101, boiling between about 320° to 450° F. which is forwarded to a phenol recovery operation or zone 102 in which phenols are separated from hydrocarbons, such as by extraction, reaction with caustic or other known methods. The hydrocarbons 103 so separated are added to the charge to the vapor phase hydrocarbonation 99 while the phenols 104 are sent to storage for sale. The gasoline and middle oil formed in the liquid phase hydrocarbonation operation and in the coking zone are converted in the vapor phase hydrocarbonation zone into gasoline, together with some gas, using catalysts and conditions known to the art.

By a series of catchpots or condensers similar to those described the vapor phase hydrocarbonation products are separated in rich gas 105, rich gas 106 and normally liquid products 107. The rich gas 105, together with like material from the liquid phase hydrocarbonation 108 and from coking 100, is treated to remove sulfur-containing compounds, principally hydrogen sulfide, and fractionated, yielding a low pressure gas, fraction 109, containing substantially completely of propane and butane, commonly referred to as L. P. G., which can be sold as such, low boiling olefins, such as propane and butene 110 and a lower boiling fraction 111 containing methane, ethane, ethylene and some hydrogen and impurities. The lean gas 106, together with similar material 112 from the liquid phase hydrocarbonation is subjected to separation 113, by low temperature or in a Hyproscrubber system or the like with the production of (a) a fraction 114 containing carbon dioxide, hydrogen sulfide, nitrogen and ammonia, which may be disposed of or further processed, (b) a hydrogen sulfide concentrate 115 containing from about 95 to 98 per cent of hydrogen and (c) a hydrocarbon fraction 116 containing carbon monoxide, methane and ethane.

The hydrocarbon fraction 116, together with similar material remaining after polymerization 117 of olefin in the olefinic fraction 110 of the lean gas, is subjected to stream splitting 118 (i.e., catalytic conversion by known methods of low boiling hydrocarbons to hydrogen and carbon oxides). The product gas 119, from the steam splitting 118 together with water gas 121 produced in a standard water gas machine 122 from all or a portion of the coke 90 from the coking zone 91, is fed to an operation or zone 123 in which the carbon monoxide, together with steam, is converted, as by known catalytic methods, into hydrogen and carbon dioxide, the latter being scrubbed out of the gas to yield a substantially pure (95 to 98 percent) hydrogen 124. This hydrogen is then used in the catalytic cracking zones in the conversion zone (such as to 20 in zone 125 then 700 atmospheres in zone 126) and employed as make-up hydrogen 127 charged 128 to the liquid phase hydrocarbonation 88 and charged 129 to the vapor phase hydrocarbonation 99.

The products 107 from the vapor phase hydrocarbonation 99 are forwarded to a distillation operation or zone 130 wherein they are separated into gas, gasoline 131 and higher boiling products 132, which are recycled in the vapor phase hydrocarbonation step. The gasoline 131 from vapor phase hydrocarbonation may be combined with polymerized gas 133 produced by polymerization of low boiling olefins produced in the system.

A portion, generally one-third or less, of the total coal needed for operation of the entire plant or system is used 134 to operate the necessary utilities 135 providing steam at high and low pressures and electricity. The required fuel gas is manufactured 136 from a portion of the coke from the coking zone 91, from the high nitrogen gases 139 produced in the standard water gas machine 122 and the remainder from coal generally about one-tenth to one-sixth of the total coal 140. The fuel gas 137 so manufactured is used for firing boilers, preheaters and the like. A portion of the coal needed for fuel gas manufacture is saved by substituting a portion of the coal produced in the coking operation or by augmenting the fuel gas with gas 139 produced in the water gas operation 122.

In accordance with the present invention, the operating conditions or variables in the liquid phase hydrocarbonation are selected from conversion conditions or variables of amount and type of catalyst, contact time (or the related variable, specific coal throughput), temperature and press-
pounds per square inch gauge being particularly useful with moving bedokers. The oil slurry fed to a moving bed coker should be hot but below the conventional temperature, generally about 850° F. The hot particles of coke in a moving bed should be at a temperature sufficiently above that of the oil slurry so that the coke will furnish the heat to raise the oil to the coking temperature and to crack and/or vaporize the oil, coke to oil weight ratios of greater than unity, such as a ratio in the range of about 2 to 5, being effective.

In a specific aspect of the invention, the conditions in the coking zone are selected so that the vaporess products of coking contain an amount of heavy oil just sufficient to keep the amount of petting oil constant, so that the overall process produces, as normally liquid products, only gasoline and chemicals, such as phenols, the middle oil being recycled in the vapor phase hydrogenation operation. However, because of its flexibility, the process may be operated so as to produce an excess of middle oil and/or heavy oil, which can be sold, such as for diesel fuel or fuel oil.

Also the heavy oil can be employed as a source of ash-free coke by directing the liquid bottom (1) from the intermediate cattph to a second coking zone or system (not shown in Fig. 1) independent of the zone used for the thermal decomposition of the heavy oil slurry from the hot cattph. Alternatively, when high ash coal is used, part of the ash-free heavy oil can be blended with the ash-containing heavy oil to produce coke of desirably low ash content, such as less than 50 weight percent. Since the liquid bottoms from the intermediate cattph are produced by decondensation of vapor, these bottoms contain substantially no solids and the coke produced therefrom is substantially ash-free and hence a premium product. Indeed, conditions can be adjusted so that the liquid bottoms from the intermediate cattph can be employed as the source of most or all of the heavy oil needed for use as petting oil in the liquid phase hydrogenation zone since these bottoms are ash-free. In the event that the liquid bottoms from the intermediate cattph furnish all of the petting oil, the conditions in the coking zone are adjusted to produce from the ash-containing heavy oil, predominantly or even solely middle oil and gasoline as the normally liquid products.

As indicated hereinafter, middle oil and gasoline produced by both the liquid phase hydrogenation and by the thermal decomposition are fed to a vapor phase hydrogenation zone wherein the middle oil is converted into gasoline, and the quality of the pre-existing gasoline is improved. As indicated, conventional vapor phase operating conditions are employed in accordance with this invention. Such vapor phase conditions are well-known in the chemical literature relating to coal hydrogenation and, of course, vary considerably depending upon the catalysts employed in the vapor phase stage. Normally, however, conditions for vapor phase operation include a pressure of from 300 to 700 atmospheres, a temperature in the range of from 750° F. to 910° F., preferably about 800° F., and a throughput of from 35 to 75 pounds of moisture and ash-free coal (MAC) per cubic foot of reaction volume per hour.

All of the above described variations in the overall processing scheme are operated, however, in accordance with one feature characteristic and distinctive of the present invention. This is the ratio of the sum of the middle oil and gasoline produced by liquid phase hydrogenation to that produced by coking (the latter including such material produced in a second coking zone when two separate zones are employed). This ratio lies between about 2 to 1 and 1 to 2, a ratio of about 1 to 1 being particularly effective. As a consequence, the feed to the vapor phase hydrogenation contains from about 30 to 70 percent of middle oil and gasoline produced by thermal.
decomposition. Approximately the same ratio can be employed should only middle oil be charged to the vapor phase hydrogenation, the gasoline being processed by other means known to the art such as "Platforming" or "Houdriflashing.

In an exemplary system, projected to a commercial size plant producing over 12,000 barrels per calendar day (B/CD) of gasoline, a total charge of 368 tons of coal per hour consumed by the plant 81 is proportioned by feeding 206 tons per hour 90 to the drying and grinding zone 82, 110 tons per hour to the power house 135 and 52 tons per hour to fuel gas manufacture 136.

To the coal directed to the drying and grinding zone 82 is added solid catalyst, such as iron sulfate 83, at the rate of one ton per hour. The dried and ground coal, which now amounts to 186 tons per hour of coal (containing 1.6 percent moisture and 6 percent ash) together with the catalyst is directed 84 to the paste preparation zone 86 together with 187 tons per hour of pasting oil 85. The coal paste 87 amounting to 374 tons per hour, is mixed with 19,100 thousand standard cubic feet per hour (MSCF/H) of hydrogen, which contains about 3,000 MSCF/H of make-up hydrogen 127, the remainder being recycle hydrogen. This mixture is directed to the liquid phase hydrogenation zone 88 which consists of two stalls each having four converters totalling 3900 cubic feet converter volume. As described above, the hydrogenation products pass to a hot catchpot. The liquid slurry from the hot catchpot, together with a portion of the liquid products from the intermediate catchpot 92, is directed to the coking zone 91 at the rate of 136 tons per hour 89. Vaporous products 93 from the coking zone, amounting to 70 tons per hour, together with 111.5 tons per hour of liquid bottoms from the cold catchpot 94, are directed to a distillation zone 95. Heavy oil from the distillation zone 85, at the rate of 97 tons per hour, together with 90 tons per hour of the intermediate catchpot product 100, are recycled to the paste preparation zone 86 as pasting oil.

The fraction boiling between 320° to 450° F, is removed from the distillation zone 95 at the rate of 24.4 tons per hour 101 and directed to the phenol recovery zone 102 wherein 6 tons per hour of phenol 104 are separated from 18.4 tons per hour of hydrocarbons boiling in the stated range 163. The hydrocarbon fraction, together with 59.1 tons per hour of middle oil and gasoline from the distillation zone 95 and 57 tons per hour of recycle middle oil 132, are directed to the vapor phase hydrogenation zone 99 together with 11,000 MSCF/H of hydrogen, which contains 1,560 MSCF/H of make-up hydrogen 129, the remainder being recycle hydrogen.

From the vapor phase hydrogenation zone 99, consisting of two stalls a converter volume of 3600 cubic feet, 126 tons per hour of normally liquid hydrocarbons are removed and directed to the vapor phase distillation zone 129 wherein is produced 67.5 tons per hour of gasoline, which together with 2 tons of polymer gasoline 132, constitutes the gasoline output of the system (12,330 bbls per calendar day).

The rich gas 106 from the liquid phase hydrogenation zone 99, together with the gas from the coking zone 91, are processed as previously described to yield 109 15.6 tons per hour or 4,000 bbls, per calendar day of C1-C3 low pressure gas fraction, called L. P. G.

The coke from the coking zone, which contains 22.5 percent ash, is divided, 43.0 tons per hour being directed to the standard water gas machine 122, and 11.3 tons per hour being directed to fuel gas manufacturing zone 136. Nitrogen rich gas from the standard water gas machine 122, amounting to 45 million B. t. u. per hour (mm. B. t. u./H.) together with 940 lb. of B. t. u./H. from the fuel gas manufacturing zone 136 supplies the fuel gas requirements of the system 137. The water gas (the low nitrogen fraction) made in the standard water gas machine 122, amounting to 1,550 MSCF/H and containing about 50 percent Hz, 40 percent CO and 10 percent CO2 is directed 121 to the CO conversion zone 123, together with 3,000 MSCF/H of gas containing 17.5 percent CO and 5.5 percent CO2, from steam splitting zone 118. The hydrogen produced in zone 123, amounting to 4,080 MSCF/H of 98 percent hydrogen is directed to first compression zone 125 where it is compressed in several stages to 20 atmospheres and then to the second compression zone 126 where it is compressed in several stages to about 700 atmospheres.

The operation of the above described exemplary plant according to the present invention is summarized in Table I under the column marked Plant B. In order to contrast its operation with the standard type of operation known to the prior art, data on such a plant is presented in the column marked Plant A.

The analysis of the coal referred to in Table I is as follows:

<table>
<thead>
<tr>
<th>Moisture and ash-free basis:</th>
<th>Weight percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>79.5</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>5.5</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.7</td>
</tr>
<tr>
<td>Oxygen</td>
<td>12.2</td>
</tr>
<tr>
<td>Sulfur</td>
<td>1.1</td>
</tr>
<tr>
<td>Moisture</td>
<td>10.7</td>
</tr>
<tr>
<td>Ash</td>
<td>5.3</td>
</tr>
</tbody>
</table>

The many advantages, including the lower capital investment and lower cost of operation, of plants embodying the present invention over those employing prior art processes become manifest when the two types of systems are compared.

A system or process operated according to the present invention (called the present process) may use a high ash bituminous coal, such as a coal containing more than about 8 to 10 percent ash, as feed stock, whereas the standard process cannot utilize such feed stock without such difficulty as to render the process impractical or impossible. The standard process is unable to use such a high ash coal due to the minimum concentration of ash that can be handled in the H. O. L. D. recovery (three parts of heavy oil per part of ash); high ash coals therefore require so much heavy oil to render the H. O. L. D. amenable to processing that the heavy oil loss, which is roughly proportional to the amount of solids present, increases to an impractical and uneconomical amount.

The amounts of gas formed in both the liquid phase and vapor phase hydrogenation operations are substantially lower in the present system than in the standard with the result that the hydrogen consumption is significantly smaller with attendant savings in both capital investment and operating costs. This is because a proportionately greater amount of hydrogen is consumed in forming gas than in forming gasoline. Additional saving of hydrogen results from the formation of gasoline in the coking zone which consumes no outside hydrogen.

Additionally, because of the lower severity of conversion required in the liquid phase hydrogenation zone of the present process, a lower partial pressure of hydrogen can be employed. It is therefore not necessary to use, as does the standard process, a system for oil scrubbing the recycled hydrogen (the function of such scrubbing system is to remove methane, ethane, nitrogen, carbon monoxide and similar gases). The omission of the oil scrubbing system in the present process lowers capital investment and operating costs and in addition permits a fuller use of hydrogen by saving the hydrogen that would otherwise be lost when scrubbed by the oil under high pressure.

The liquid phase hydrogenation in the present process can be operated more smoothly than in the standard process because of the considerably lower solids content.
of the material passing through the converter arising from the greater production of heavy oil which is liquid under the conditions of operation. A lower solids content results in more uniform processing conditions, such as temperatures, with less risk of losing control and less risk of drying out of the converters with the attendant possibility of forced shut down and repair of the converters. Also the present process employs a considerably smaller converter volume than the standard process for the same capacity, because of the much higher throughput (See Table I, line 4 of sect. II). Because the converters are large capacity high pressure equipment, they are quite expensive and a reduction in total converter volume effects considerable savings in their cost. In the example discussed above (Table I), the overall capital expenditures required for the standard process is about one fourth greater than for the present process. In addition, the pasting oil derived from the coking zone of the present process contains little or no asphalt whereas there is considerable asphalt in the recovered oil in the standard process, resulting in decreased coal throughput and causing difficulties in operation. Further, the rate of heat transfer is decreased and the tendency to foul equipment increased when the oil contains substantial quantities of asphalt, thus resulting in operational difficulties in the heat exchangers as well as in the converters.

As pointed out above, the bottoms fraction from the intermediate coker is free of solids and asphalt and is high in hydrogen content so that such a fraction forms an excellent coker stock and assures smooth coker operation, as well as producing, if a separate coking zone is employed for the bottoms fraction, a coke that is especially free of ash. In addition, the coking operation as a whole produces considerable amounts of olefins which are useful, when polymerized, in upgrading the gasoline.

An additional feature in the present process is the recycle of the heavy oil produced from the coking zone through the liquid phase hydrogenation zone (instead of being recycled to the coking zone as commonly practiced in coking operations in the petroleum industry). Because of its passage through the liquid phase hydrogenation zone, the heavy oil tends to be less aromatic (i.e., has a higher hydrogen content) with the result that it is considerably less refractory and more amenable to coking when again passed through the coking zone. Additionally, a substantial portion of the coker feed stock is freshly formed from the coal so that it is virgin material and hence more readily thermally decomposed to coke. Also, relatively large amounts of gasoline, generally about 20 to 40 percent of the total gasoline and middle oil, are formed in the coking zone, as is true of the liquid phase of hydrogenation operation, so that less reaction volume is needed in the vapor phase hydrogenation than is used in the standard process, to produce the same amount of gasoline.

It will be noted from Table I, that although more coal is fed in the present process to the liquid phase hydrogenation zone than in the standard process (for the same amount of gasoline produced), the total amount of coal required for the entire plant is considerably lower for.
the present process because of the production and internal utilization of lower hydrogen consumption which, in the example referred to above, is about one-seventh lower than in the standard process. The lower hydrogen consumption results in less conversion of coal to carbon dioxide, a waste product. The savings in the amount of basic raw material for the process, which in the example set forth in Table 1 amounted to about 13 percent, together with the savings in capital expenditure for the overall process, which amount to about 15 to 20 percent, are sufficient to so alter the economics of the process that gasoline produced by the present process is competitive, when credit is taken for by-products, in price with gasoline produced at the present prices, while the gasoline produced by the standard process is not. Additionally, more by-products, such as phenols, sulfur, ammonia, ammonium sulfate and the like per barrel of produced gasoline are realized from the present process because of the higher throughput of coal through the liquid phase hydrogenation zone. In addition, the gasoline produced by the present process has a higher aromatic content than that produced in the standard process due to aromatics formed in the coking zone and hence is more suitable for use as aviation gasoline or as a source for aromatics which are cheaper in short supply and which at any time have a high economic value when separated from the other hydrocarbon constituents of gasoline.

Obviously many modifications and variations of the invention as herebefore set forth may be made without departing from the spirit and scope thereof and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim as our invention:
1. A process for converting coal into synthetic fuels and chemicals by liquid phase and subsequent vapor phase hydrogenation which comprises: subjecting a coal-oil feed mixture to destructive hydrogenation under liquid phase conditions including a temperature of from 825° to 925° F., a pressure of from 200 to 1000 atmospheres and a high throughput of 40 to 110 pounds of moisture and ash-free coal per cubic foot of reaction volume per hour, said conditions resulting in the conversion of the coal feed into normally liquid products boiling above the boiling range of gasoline and comprising predominantly a heavy oil boiling above 625° F., and a minor portion of a middle oil boiling in the range of about 350° to 625° F.; thermally converting said heavy oil at a temperature of from 900° to 1150° F., and a pressure of from atmospheric to 100 pounds per square inch to convert the heavy oil into vaporous products comprising heavy oil, gasoline, asphalt and unconverted coal in said products, and at least part of each of said fractions is separately thermally decomposed; and recycling at least a portion of the heavy oil produced in the coking zone to the liquid phase dehydrating hydrogenation, and destrucitively hydrogeanting middle oil and gasoline produced in both the coking zone and in the liquid phase destructive hydrogenation under the vapor phase destructive hydrogenation conditions to produce gasoline.

2. The method according to claim 2, which comprises separating the products of the liquid phase destructive hydrogenation into heavy oil and gasoline, and separating at least a portion of the heavy oil produced in the coking zone to the liquid phase dehydrating hydrogenation, and destructively hydrogeanting middle oil produced in the coking zone to the liquid phase destructive hydrogenation, and destructively hydrogeanting middle oil produced in both the coking zone and in the liquid phase destructive hydrogenation under the vapor phase destructive hydrogenation conditions to produce gasoline.

3. The method according to claim 2, which comprises separating the products of the liquid phase destructive hydrogenation into a heavy oil fraction and a lower boiling fraction comprising middle oil and asphalt, recycling at least a portion of the heavy oil produced in the coking zone to the liquid phase dehydrating hydrogenation, and destrucitively hydrogeanting middle oil produced in both the coking zone and in the liquid phase destructive hydrogenation under the vapor phase destructive hydrogenation conditions to produce gasoline.

4. The method according to claim 2, which comprises separating the products of the liquid phase destructive hydrogenation into a heavy oil fraction and a lower boiling fraction comprising middle oil, recycling at least a portion of the heavy oil produced in the coking zone to the liquid phase dehydrating hydrogenation, and destructively hydrogeanting middle oil produced in the coking zone to the liquid phase destructive hydrogenation, and destrucitively hydrogeanting middle oil produced in both the coking zone and in the liquid phase destructive hydrogenation under the vapor phase destructive hydrogenation conditions to produce gasoline.

5. The method according to claim 2, which comprises separating the products of the liquid phase destructive hydrogenation into vaporous products containing heavy oil and gasoline, and separating at least a portion of the heavy oil produced in the coking zone to the liquid phase dehydrating hydrogenation, and destructively hydrogeanting middle oil produced in both the coking zone and in the liquid phase destructive hydrogenation under the vapor phase destructive hydrogenation conditions to produce gasoline.

6. The method according to claim 5, which comprises thermally decomposing a mixture of said heavy oil and converting the mixture into a vaporous product comprising middle oil and a solid carbonaceous residue containing less than about 30 percent ash, destructively hydrogeanting middle oil from both the thermal decomposition and from the liquid phase destructive hydrogenation under the vapor phase destructive hydrogenation conditions to form gasoline and employing said carbonaceous residue as a source of fuel to generate energy utilized in the process.

7. The method according to claim 5, which comprises thermally decomposing a mixture of said heavy oil and converting the mixture into a vaporous product comprising middle oil and a solid carbonaceous residue containing less than about 30 percent ash, destructively hydrogeanting middle oil from both the thermal decomposition and from the liquid phase destructive hydrogenation under the vapor phase destructive hydrogenation conditions to form gasoline and employing said carbonaceous residue as a source of fuel to generate energy utilized in the process.

8. The method according to claim 1, in which the heavy oil is separated from the liquid phase destructive hydrogenation products as an ash-free fraction and a fraction containing substantially all of the ash, asphalt and unconverted coal in said products, and at least part of each of said fractions is separately thermally decom-
posed to form ash-free coke and ash-containing coke respectively.

9. The method according to claim 8, wherein the fraction of said heavy oil containing ash is thermally decomposed into a substantial amount of middle oil, gasoline, gas, and coke, wherein at least a portion of the ash-free heavy oil fraction is coked to the ash-free coke and vaporous products containing middle oil, gasoline, and gas, and wherein the middle oil and gasoline from the thermal decomposition, from the coking zone and from the liquid phase destructive hydrogenation are destructively hydrogenated under the vapor phase destructive hydrogenation conditions to produce gasoline.

10. The method according to claim 8, wherein at least a portion of the ash-free heavy oil fraction is coked to ash-free coke and vaporous products containing middle oil, and wherein middle oil derived from the coking and from the liquid phase destructive hydrogenation is destructively hydrogenated under the vapor phase destructive hydrogenation conditions to produce gasoline.

11. The method according to claim 8, wherein at least a portion of the ash-free heavy oil fraction is cracked at a temperature of from 900°F. to 1000°F. and a pressure of from atmospheric to 100 pounds per square inch to convert said ash-free heavy oil to ash-free coke and vaporous products comprising middle oil, and a normally gaseous hydrocarbon stream containing olefins, and wherein middle oil derived from the cracking and from the liquid phase destructive hydrogenation is destructively hydrogenated under the vapor phase destructive hydrogenation conditions to produce gasoline.

12. The method according to claim 8, which comprises thermally decomposing the fraction of said heavy oil containing ash into a substantial amount of middle oil, gasoline, gas and coke, using at least a portion of said ash-free heavy oil fraction as pasting oil for the coal fed to the liquid phase destructive hydrogenation zone, and destructively hydrogenating middle oil from both the thermal decomposition and from the liquid phase destructive hydrogenation under the vapor phase destructive hydrogenation conditions to produce gasoline.

13. The method according to claim 12, in which the ash-free heavy oil fraction is the sole source of pasting oil and in which the ash-containing fraction of heavy oil is converted solely into middle oil, gasoline, gas and coke in said thermal decomposition.

14. The method according to claim 13, in which the ratio of middle oil and gasoline produced by the liquid phase destructive hydrogenation to the middle oil and gasoline produced by the thermal decomposition is between 3 to 1 and 1 to 2.

References Cited in the file of this patent

UNITED STATES PATENTS

1,864,855 Pier et al. 6 June 28, 1932
1,917,324 Pier et al. 11 July 1933
1,958,528 Wilson 15 May 1934
1,972,944 Morrell 11 Sept. 1934
2,436,938 Scharrmann et al. 2 Mar. 1948

FOREIGN PATENTS

288,148 Great Britain 28 June 1929
431,795 Great Britain 16 July 1935