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[54] **LOW-PRESSURE HYDROGENATION OF COAL**
4 Claims, 1 Drawing Fig.

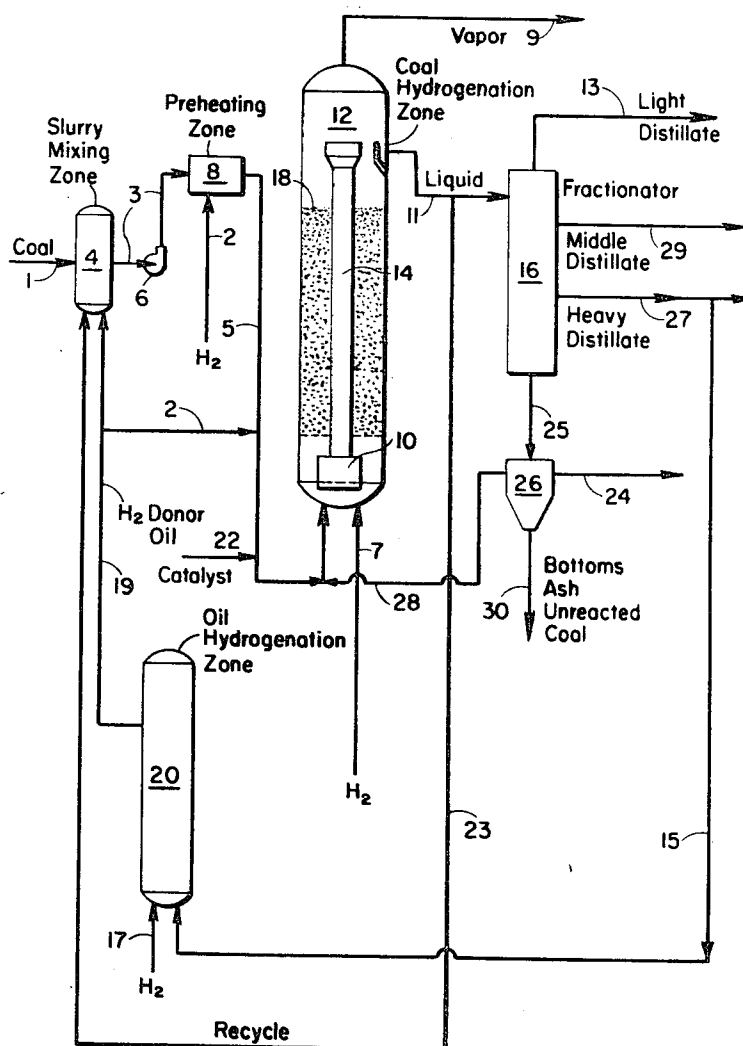
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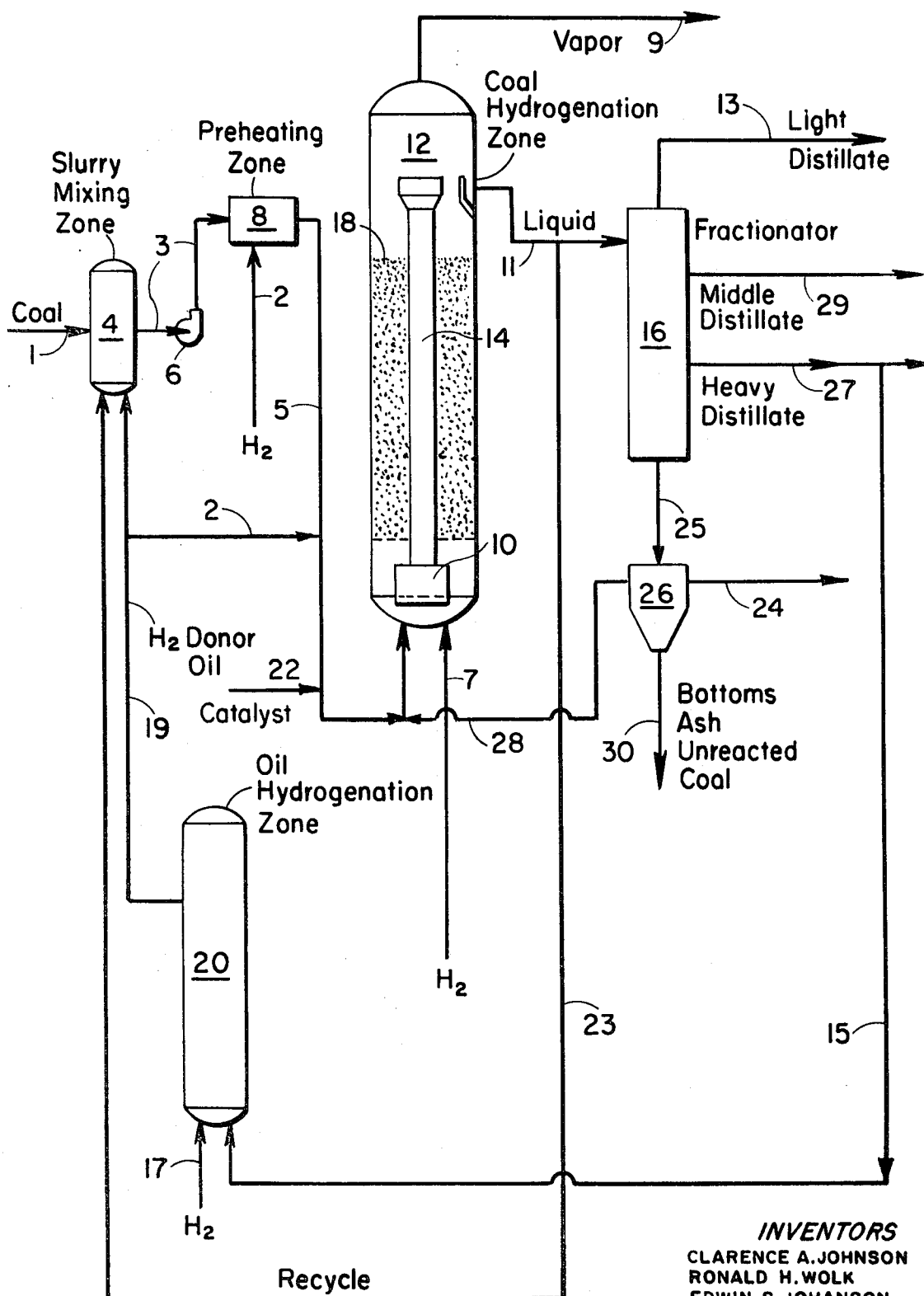
[56] **References Cited**

UNITED STATES PATENTS

2,885,337 5/1959 Keith et al. 208/8

ABSTRACT: The hydroconversion of coal to benzene-soluble hydrocarbon products is accomplished at conversion pressures with a hydrogen partial pressure of less than about 1,000 p.s.i. in the presence of a hydrogen donor oil and a particulate contact material. Under these operating conditions, the particulate contact material is maintained in random motion. Hydrogen partial pressures as low as 350 p.s.i. are practical and economical. From the resulting liquid effluent, a distillate fraction is recovered and it is further hydrogenated to produce an effective hydrogen donor oil.





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LOW-PRESSURE HYDROGENATION OF COAL

BACKGROUND OF THE INVENTION

The conversion of carbonaceous solids, such as bituminous, semibituminous and subbituminous grades of coal and lignites, for the production of more valuable products including solid, liquid and gaseous fuels and chemical byproducts is known. Some of these products can, by hydrocracking and other means, be converted into gasoline and valuable hydrocarbon end products.

Processes have used high pressures and low pressures, single and multiple stages, catalysts, and hydrogen donor oils as solvents for the coal. These various methods have been well documented in the existing art. U.S. Pat. No. 2,464,271 discloses one process for coal liquefaction by hydrogenation. South African Pat. No. 683,312 (U.S. Counterpart Pat. No. 3,488,279) discloses a two-stage, two-pressure system. U.S. Re. Pat. No. 25,770 describes another method. None of these prior processes has proved itself economical as a suitable commercial coal hydrogenation process.

The problem of reacting hydrogen with coal solids, in spite of the prior art disclosures, remains however a very difficult one. It is found that the consumption of hydrogen per pound of coal is a function of increasing pressure. Theoretically, at a hydrogen partial pressure of 2,250 p.s.i. and 90 percent hydrogen, a consumption of 8.1 percent can be accomplished. Obviously such pressures require very high capital costs for the equipment as well as high utilities cost for the compression of the hydrogen. Alternatively, the consumption of hydrogen that was found for prior-disclosed operations at a hydrogen partial pressure of 500 p.s.i. is nearer to 2 percent. Under such a system of low pressure there is a lower coal conversion with a poorer quality of liquid effluent produced, which again is not economical.

By the present invention, it is now found that by using a selected boiling range fraction of the liquid effluent, and hydrogenating it under substantial pressure, one can obtain a hydrogen donor oil of superior characteristics. This in turn permits an effective coal hydrogenation to be carried out at materially reduced pressures, thereby making it feasible to provide hydrogen more economically to the system.

SUMMARY OF THE INVENTION

It has been discovered in this invention that the hydrogenation of coal can take place efficiently at low pressures with the use of the ebullated bed technique. The description of the ebullated bed concept and technique is set forth in U.S. Pat. No. Re. 25,770. A specific characteristic of the ebullated bed is the random motion which is imparted to the solid particles in the reaction zone.

In this invention, coal particles having a size range so that it all passes through at least 20 mesh (U.S. standard) are fed in admixture with a hydrogen donor oil to a liquid phase reaction zone containing particulate contact material. The coal-oil mixture passes upwardly through the reaction zone with gaseous hydrogen at a combined rate between about 0.05 and about 0.5 feet per second, but preferably between about 0.1 and about 0.4 feet per second. At this rate, the contact particles in the reaction zone are expanded by between about 10 and about 100 percent of the static bed height and are thus kept in random motion in the liquid by the upflowing streams. The extent of the random motion of the particles is controlled by the recycle of a portion of the liquid from the upper portion of the reaction zone to the lower portion of the reaction zone. Suitable contact particles are cobalt-molybdate on alumina, tabular alumina, nickel-molybdate on alumina and the like, in a close size range between about 100 mesh granular up to about 1/8-inch-diameter cylindrical pellets.

The reaction zone is maintained at a hydrogen partial pressure between about 350 and about 1,000 p.s.i., preferably

between about 500 and about 700 p.s.i., but most preferably between about 500 and about 600 p.s.i. The temperature in the reaction zone is maintained between about 800° and about 900° F., but most preferably between about 825° and about 875° F.

The residence time within the reaction zone is between about 10 and about 60 minutes; but it is preferred to operate between about 20 and about 40 minutes.

The throughput rate for the coal particles is between about 10 and about 100 pounds per hour per cubic foot of reaction zone; but it is found that the optimum rate is best maintained at between about 15 and about 50 pounds of coal per hour per cubic foot of reactor.

A liquid effluent is removed as overhead from the reaction zone. This effluent is fractionated to obtain an oil distillate boiling between about 500° and about 1000° F., but preferably between about 650° and about 900° F. The distillate is catalytically hydrogenated at a hydrogen partial pressure between about 750 and about 3,000 p.s.i., a temperature between about 600° and about 800° F. and with a hydrogen flow rate between about 1,000 and about 5,000 s.c.f./b.b.l. A preferred hydrogenation of distillate takes place with a hydrogen partial pressure of about 1,000 to 2,000 p.s.i., a temperature of about 700° to 800° F., and a hydrogen flow rate of about 1,500 s.c.f./b.b.l. The distillate oil takes up an amount of hydrogen equivalent to between 0.5 and 4.0 percent of the weight of the oil. It is preferred to have the oil take up 0.5 to 2.0 percent of hydrogen, based on the weight of the oil. The oil is fed to the hydrogenation zone at a rate between about 1 and about 10 liquid volumes per hour per volume of reactor with a preferred rate of about 2 to 4 volumes of oil per hour per volume of reactor.

The hydrogenated distillate, being a hydrogen donor oil, is preferably used as the slurry oil for the coal but may be added directly to the coal hydroconversion reaction zone. The use of a hydrogen donor oil is critical to the effective operation of the low-pressure ebullated bed hydrogenation of coal. As can be seen from table I, the use of a hydrogen donor oil improves the overall conversion of the coal when compared to another type of oil with a low hydrogen content. Table I also shows the use of a hydrogen donor oil in this low-pressure coal conversion system giving coal conversion about equivalent to that of the high-pressure system. In the experiments in this table, an external source was used for the slurry oil. In the high-pressure coal conversion system, a suitable hydrogen donor oil is available as a fraction of the liquid effluent from the conversion zone which is directly recycled to the coal-slurry zone. It was discovered that in a low-pressure coal conversion system such a suitable hydrogen donor oil fraction did not exist. In was further found in this invention that if a suitable fraction of the liquid effluent from the low-pressure conversion zone was hydrogenated under the proper conditions, then a suitable hydrogen donor oil was available for use in the conversion zone:

TABLE I

Type of coal	Illinois No. 6		Pittsburgh Seam	
	1	2	3	4
Experiment				
Size Range (%)				
100/325 mesh	28	28	32	32
325/pan	72	72	67	67
Coal Conversion				
Condition				
Temperature (° F.)	850	850	850	850
Pressure (p.s.i.)	2,700	2,700	2,250	500
Coal Feed Rate				
gms./hr./cc. reactor	0.25	0.25	0.50	0.50
Hydrogen feed,				
mols/gm. coal	0.14	0.15	0.22	0.15

Slurry Oil Type	A*	B*	B*	B*
Boiling range, ° F.	500–912	500–912	372–810	372–810
Hydrogen content, W %	5.9	8.2	7.5	7.5
Oil/Coal gms./gms.	12.0	12.5	4.0	4.0
Coal Conversion to Benzene Soluble Liquids	24	79	90	84

A* Anthracene Oil

B* Prepared from anthracene oil by hydrogenation at 2250 p.s.i.g. and 750° F.

Oils suitable for use as hydrogen donor oils are preferably fractions of the liquid product itself and are modified, by hydrogenation, to enhance their capability for delivery of hydrogen. The fractions are to be selected principally with three characteristics in mind.

a. The relative ease of recovery of the fraction from the converted coal product slurry for recycle as the hydrogen donor oil.

b. The ease of hydrogenation of the fraction with minimum cost, i.e., minimum catalyst deactivation at moderate pressure hydrogenation.

c. Volatility characteristics such that the greater part of the donor oil is retained as liquid in the slurry phase in the reactor at the conversion conditions.

The optimum materials are the product fraction in the 500°–1,000° F. boiling range, preferably 650°–900° F., which includes substituted naphthalene and phenanthrene structures and the like. Such fractions would not foul conventional hydrogenation contact particles excessively. The oil fraction can then be recovered simply from the product slurry by atmospheric and vacuum flashing.

The degree of coal conversion resulting from the use of a hydrogen donor oil with the upflow coal conversion was unexpected because the added catalytic benefit discovered in operating at 500 p.s.i.g. pressure was not anticipated, (a) in promoting the reaction of heavy coal liquids to light liquids and, (b) in promoting such a significant consumption of gaseous hydrogen concurrently with the coal conversion. This second factor permits the use of lower proportions of donor oil to coal, in itself advantageous, while also permitting the conversion of the coal to a higher percentage of coal-derived primary products providing for a considerable enhancement of the secondary reaction of heavy coal liquids to light liquids.

The bottoms obtained from the fractionation of the liquid effluent is effective as the recycle to the reaction zone as it increases the overall conversion of the coal to lower boiling liquid fraction while providing the required recycle for ebullated bed control. On the second pass through the reaction zone, the bottoms fraction is further hydrogenated to the lower boiling, more valuable light liquid fractions. This improves the overall conversion of coal to the more valuable light liquid fractions which greatly enhances the commercial economics of the process.

DESCRIPTION OF THE DRAWING

The drawing is a schematic view of the principal elements of a process for the low-pressure hydrogenation of coal to liquid, gaseous and solid products.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Coal which has been ground so that it all passes through at least 20 mesh (U.S. standard) is fed from line 1 to slurry-mixing zone 4. The coal and suitable oil from the system, hereinafter described are mixed to form a slurry of 1 part coal per 1 to 10 parts oil. The mixing zone 4 is usually maintained at atmospheric or low pressure.

The slurry mixture in line 3 is pumped via pump 6 through preheating zone 8 wherein the temperature of the slurry is raised to between about 400° and about 700° F. Hydrogen in

line 2 can be fed to the preheater as it exerts an inhibiting effect on coke formation. The heated slurry then enters reaction zone 12 via line 5 and preferably has an upward velocity of between about 0.05 and about 0.15 feet per second in the reaction zone. At the same time, gaseous hydrogen enters reaction zone 12 via line 7 at an upward velocity of between about 0.05 and about 0.3 feet per second. It is preferred that the combined upward flows of coal slurry and hydrogen be between about 0.2 and about 0.4 feet per second. It is not necessary that the slurry temperature be the same as that of reaction zone 12 inasmuch as the hydroconversion reaction is exothermic. When the process according to this invention is being carried out, the contact particles can enter the system at 22 and are in constant random motion in the reaction zone 12 with respect to each other and the gross mass expands so that its upper boundary or upper level of ebullation is at 18. There is substantially no carryover of contact particles while the finer coal solids are carried out of reaction zone 12 in the liquid effluent.

A recycle of liquid from above the dense phase catalyst zone permits the recycle of essentially solids-free liquid to below the solids-containing bed to assist in keeping the particles in random motion. As shown, this is accomplished by an internal draft tube 14 and pump 10 but as described in the Johanson Re. U.S. Pat. No. 25,770, this can also be accomplished externally. The recycle rate is dependent upon slurry feed rate, hydrogen feed rate, reactor size, contact particle size and other system variables affecting ebullation.

In reaction zone 12 there is a simultaneous consumption of gaseous hydrogen and transfer of hydrogen from the slurry oil to the coal. The coal conversion consumes an amount of hydrogen equivalent to 2 to 4 percent of the weight of the coal present. The gaseous hydrogen passing through the reaction zone accounts for about 25 to 75 percent of the hydrogen consumed and the balance of the reacted hydrogen is provided by the hydrogen donor oil.

A vapor effluent leaves reaction zone 12 through line 9. This effluent is suitable for use in hydrogen recovery, hydrogen manufacture and petroleum refining as it contains excess hydrogen, normal gaseous hydrocarbons and naphtha range and middle distillate range hydrocarbons.

The liquid effluent leaving reaction zone 12 through line 11 is fractionated at 16 into light and middle distillates, heavy gas oil distillates, residuum boiling range oils, unconverted coal and ash.

The bottoms in line 25 from fractionator 16 pass through separation zone 26 and a portion of the essentially solids-free liquid bottoms pass by line 28 to reaction zone 12 to provide additional recycle as well as undergoing further hydrogenation to lower boiling liquids. Separation zone 26 is preferably a cyclone separator. The remainder of the materials entering separation zone 26 through line 25 leaves in lines 24 and 30 and is suitable for coking, fuel or as a raw material for hydrogen manufacture. In addition, the effluent in line 24 can be subjected to further hydroconversion to low-boiling liquids. Part of the effluent in line 11 may be drawn off before fractionating through line 23 for use in mixing zone 4. The advantage to be found in using either of the recycle streams 23 and 28 is that the recycle helps to maintain the level of residuum boiling range liquids in the reactor which in turn helps to achieve the greatest conversion of coal to low-boiling liquids. It is preferably to recycle the portion of the bottoms in line 28 to reaction zone 12 for the above-mentioned maintenance of residuum level in the reactor.

The effluent in line 11 enters fractionation zone 16 wherein a light distillate fraction is removed through line 13, a middle distillate fraction is removed through line 29, a heavy distillate is removed through line 27 and a bottoms fraction is removed through line 25. The required quantity of distillate having a boiling range between about 500° and about 1,000° F., is recycle via line 15 for hydrogenation for use as the hydrogen donor oil and the net production of this distillate is removed through line 27.

The distillate in line 15 enters oil hydrogenation zone 20 for supplemental hydrogenation. Hydrogen enters zone 20 through line 17. Zone 20 is operated at a hydrogen partial pressure between about 750 and about 3,000 p.s.i., at a temperature between about 600° and about 800° F., with a hydrogen rate of between about 1,000 and about 5,000 standard cubic feet (s.c.f.) of hydrogen per barrel but preferably at 1,000 to 2,000 p.s.i., 700° to 800° F., and with 1,500 s.c.f. of hydrogen per barrel. A catalyst suitable for reaction zone 20 is nickel molybdate or cobalt molybdate on alumina and the like.

The hydrogen donor oil passes via line 19 to mixing zone 4 to form the slurry with the coal or by line 2 to the reactor 12. The following examples shown in table II are illustrative of the invention:

TABLE II

Contact Particles	Cobalt-Molybdate on Alumina				Alumina
Coal Feed 0/hr./ft. ³ of Reactor	94	31	31	31	31
Pressure, p.s.i.	2,250	2,250	500	500	2,250
Slurry Oil					
Oil/Oil	4	4	4	4	4
Temperature °F.	850	850	850	850	850
Yield % of Coal					
gaseous hydrocarbons	3.4	8.1	5.4	6.6	4.5
C ₄ -400° F. liquid	4	12	12	12	4
400-975° F. liquid	40	29	25	14	27
975° F. oil soluble in C ₆ H ₆	23	32	29	31	36
975° F. oil insoluble in C ₆ H ₆	12	3	10	17	12
Unconverted coal	9	6	6	7	6
Ash, H ₂ O, H ₂ S, NH ₃ , CO ₂	14	16	15	14	12

Table II shows for comparative purposes the results of hydrogenating coal under different conditions of temperature, pressure and contact material. It will thus be observed that using a hydrogen donor oil and operating the coal conversion at 500 p.s.i. results in conversions that are substantially equivalent to prior operations at 2,250 p.s.i. Operation at the low pressure materially reduces the costs involved in the reactor construction and the cost of compressing the hydrogen. The slurry oil used in the experiments of table II was anthracene oil of a 500° to 900° F. boiling range which had been hydrogenated so as to increase its hydrogen content from 5.9 to 7.5 weight percent.

Having thus described the invention with reference to specific examples thereof, it is to be understood that other

modifications, alterations and applications will become apparent to those skilled in the art without departing from the scope of the present invention. The present invention is limited as defined in the claims appended hereto. This invention will, of course, have application to a wide range of known hydrocarbon processes and therefore this description should not be construed as unduly limiting the scope thereof.

We claim:

1. A process for the hydroconversion of a carbonaceous solid selected from the group consisting of coal and lignite to benzene soluble products which comprises:

- preparing a slurry of said carbonaceous solid and a hydrogen donor oil as hereinafter defined;
- preheating said slurry to a temperature approximately that of the reaction zone;
- passing said preheated slurry with a coal throughput rate between 10 and about 100 pounds per hour per cubic foot of reactor and a hydrogen rich gas upwardly through a reaction zone in the presence of solid contact particles under conditions of temperature and a hydrogen partial pressure of between 350 and 1,000 p.s.i. to accomplish the hydroconversion of the carbonaceous solid;
- maintaining the upward velocity of said slurry and gas so as to place said solid contact particles in random motion in the liquid without substantial carryover of said solid contact particles;
- removing a liquid effluent from the upper part of the reaction zone;
- separating a fraction having a boiling range of between 500° and 1,000° F.;
- hydrogenating said fraction at a hydrogen partial pressure in excess of 750 p.s.i. to produce a hydrogen donor oil containing at least 7 to 11 weight percent hydrogen and using said hydrogenated fraction as the hydrogen donor oil in step (a).

2. The process of claim 1 wherein the carbonaceous solids take up an amount of hydrogen equivalent to 2 to 4 percent of the weight of said carbonaceous solids present with at least 25 percent up to 75 percent of said hydrogen taken up coming from the hydrogen donor oil.

3. The process of claim 1 wherein a bottoms fraction from the separation of the liquid effluent is passed to said reaction zone so as to maintain a residuum concentration therein so as to promote further hydroconversion of said bottoms to lower boiling distillates.

4. The process of claim 1 wherein the hydroconversion of carbonaceous solids is carried out under a hydrogen partial pressure of about 500 p.s.i. with a coal throughput rate between about 15 and about 50 lbs. of coal per hour per cubic foot of reactor while hydrogenating the fraction boiling between 500° and 1,000° F. at a hydrogen partial pressure between about 1,000 and about 2,000 p.s.i. at 700° to 800° F. to produce a hydrogen donor oil containing between about 7 and about 11 percent hydrogen.