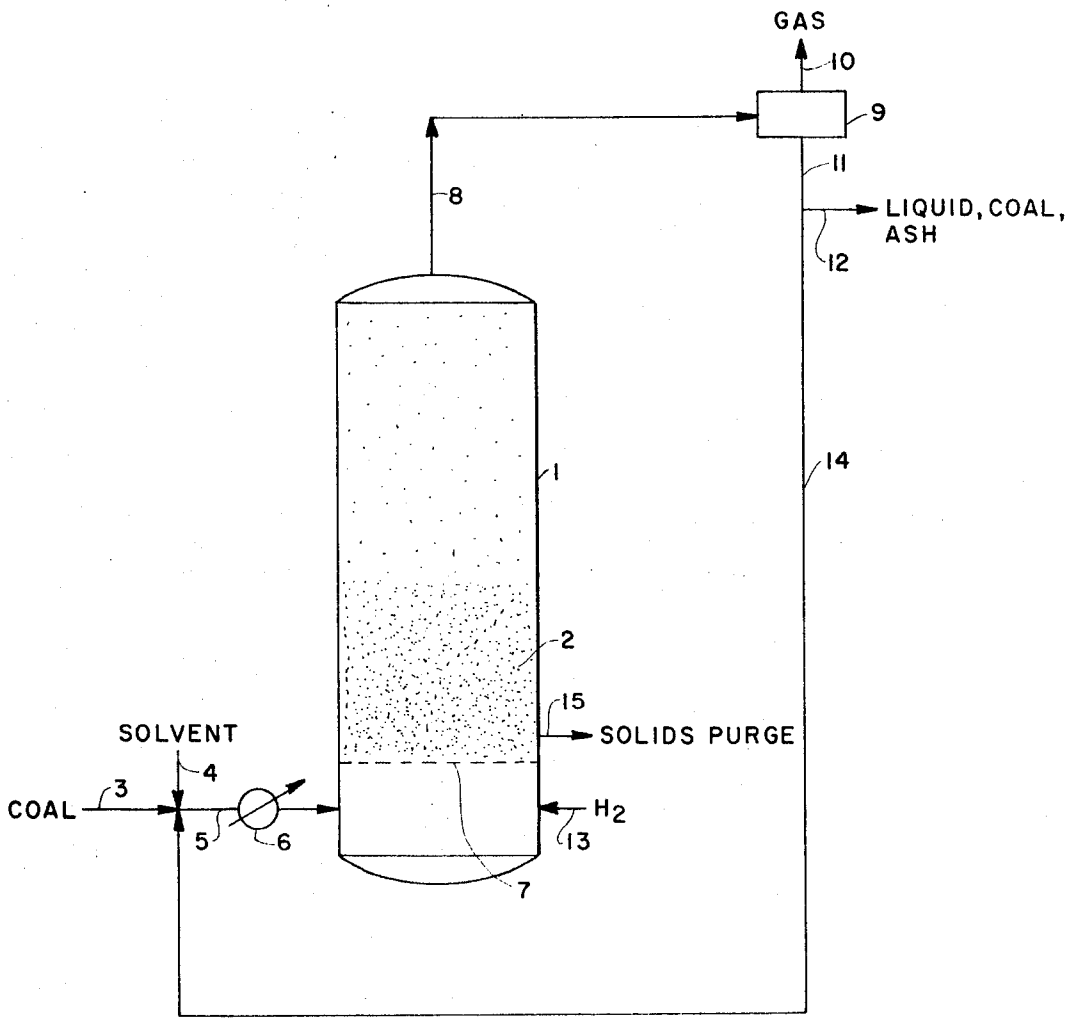
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COAL PROCESSING

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INVENTOR
ROBERT W. RIEVE
HAROLD SHALIT

Roderick W. MacDonald
ATTORNEY

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COAL PROCESSING

Robert W. Rieve, Springfield, and Harold Shalit, Drexel Hill, Pa., assignors to Atlantic Richfield Company, New York, N.Y.

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ABSTRACT OF THE DISCLOSURE

A method for hydrogenating coal to at least partially liquify same wherein the hydrogenation is carried out in at least one zone containing an ebullated bed of substantially inert, solid contact particles.

BACKGROUND OF THE INVENTION

Heretofore it has been taught that subdivided, solid coal can be gasified and liquified by hydrogenation in an ebullated bed of externally supplied hydrogenation catalyst such as a cobalt molybdate catalyst. Such a process is fully and completely disclosed in U.S. Pat. Re. 25,770, the disclosure of which is incorporated herein by reference.

In conducting these catalytic processes the temperature of the reaction was generally kept in the range of 825 to 900° F. to avoid undue pyrolysis of the coal, or coal products as evidenced by substantially increased gas production from the reaction zone.

SUMMARY OF THE INVENTION

It has now been found that the hydrogenation of coal to substantially gasify and liquify same can be carried out in the absence of an externally supplied hydrogenation catalyst when using an ebullated bed of substantially solid contact particles composed of a material which is substantially inert and non-catalytic as to the hydrogenation reaction.

It has additionally been discovered that by utilizing these inert and non-catalytic contact particles in lieu of catalytic particles, temperatures in excess of 900° F. and up to 1000° F. can be employed without undue pyrolysis as evidenced by increased gas production.

It has additionally been discovered that when employing a reaction temperature of from about 850 to about 1000° F. and a coal feed rate of from about 15 to about 200 pounds of coal per hour per cubic foot of reactor, substantially the same product distribution can be achieved as if the reaction was carried out at a lower temperature with the use of catalytic particles and with less hydrogen consumption than the catalytic reaction.

Thus, this invention is useful in converting normally solid coal or similar carbonaceous materials to liquid hydrocarbonaceous products which are useful in producing gasoline, fuel oil, and the like.

Accordingly, it is an object of this invention to provide a new and improved method for carrying out a coal hydrogenation process. It is another object to provide a new and improved process whereby a non-catalytic reaction can be substituted for a catalytic reaction without sacrifice in the product distribution of the reaction. It is another object to provide a new and improved method for employing a non-catalytic coal hydrogenation process wherein the hydrogen consumption is decreased without sacrifice in the product distribution normally achieved by the catalytic process. It is another object to provide a new and improved process for the hydrogenation of coal wherein the reaction temperature of the process can vary over a wider range than that of the catalytic process without experiencing undue pyrolysis of the coal.

Other aspects, objects, and advantages of this invention will be apparent to those skilled in the art from this disclosure and the appended claims.

DETAILED DESCRIPTION OF THE INVENTION

The drawing shows a diagrammatic representation of an apparatus useful in practicing this invention.

More specifically, the drawing shows a conventional ebullated bed reactor **1** which contains no hydrogenation catalyst but rather contains only a bed of particular material **2** which is substantially inert and non-catalytic as to the hydrogenation reaction. Thus, no subdivided catalytic material is supplied to reactor **1**.

What is supplied to reactor **1** is comminuted coal by way of pipe **3** and hydrocarbonaceous slurry medium (solvent) by way of pipe **4** to form a coal slurry which is passed by way of pipe **5** after being heated by heater **6** into a lower portion of reactor **1**. The mixture passes upwardly through perforate screen **7** and bed **2** to effluent pipe **8**. Hydrogen and/or hydrogen-donating liquid and/or hydrogen-donating gas is supplied by way of pipe **13**.

The overhead effluent from reactor **1** is passed by way of pipe **8** to a conventional separation system **9** which can include fractionators, cyclones, strippers, and the like and which separates a gaseous hydrocarbonaceous product by way of pipe **10** and a substantially liquid hydrocarbonaceous product by way of pipe **11**. The hydrocarbonaceous liquid product also contains certain solid residual matter such as unconverted coal, char, coke, and ash. This product can be taken by way of pipe **12** for further treatment whereby the unconverted coal, etc. are separated from the liquid and the liquid fractionated into various grades of products such as resid, kerosine, and the like.

Part or all of the product in pipe **11** can be returned by way of pipe **14** to pipe **5** whereby it re-enters reactor **1** for retreatment.

In the operation of reactor **1** in accordance with this invention, reactor **1** can be initially started up with the contact particles already therein. These contact particles can be subdivided refractory and/or inert materials such as sand, alpha-alumina, quartz, pumice, glass beads, silicon carbide, mullite, and the like.

Pipe **15** is employed above screen **7** so that solids can be removed from the bed as desired. Also, if desired, solids can be added to reactor **1** by way of pipe **15**.

If desired, more than one reactor **1** can be employed in parallel and/or series and still be within this invention. The operation of one reactor is fully and completely disclosed here only for sake of brevity.

Reactor **1** is, therefore, operated so that amounts of coal slurry, hydrogen, and the like added to bed **2** and the velocities of these materials is adjusted in a manner known in the art so as to provide and maintain an ebullated bed **2**, the distinction here being that the ebullated bed is composed of a plurality of contact particles that are substantially non-catalytic as regards the hydrogenation reaction taking place in reactor **1**.

The inert contact particles are subdivided and are preferably in the size range of from about plus 200 mesh (Tyler) to about ¼ inch in largest cross-sectional dimension. The amount of inert, non-catalytic particles empolyed in bed 2 can vary widely but generally will be from about 5 to about 70 percent by weight.

If desired, there can be added to reactor **1** water in the amount from about 0.1 to about 50 weight percent based on the total weight of the coal being added to reactor **1**. If water is added it can be injected into any one or more of reactor **1**, pipes **3**, **4**, **5**, **14**, and the like, and/or by accompanying the coal which is being fed into pipe **3**. The water can be added in the form of cool, ambient, or heated liquid water and/or steam. If part of the water

supplied is that which accompanies the raw coal feed to pipe 3, this water can be that which accompanies the coal from the mine or can be added during comminuation of the coal, and the like.

It should be noted a distinct advantage for this invention is that wet coal can be charged to the hydrogenation reactor without fear of disrupting the hydrogenation reaction. This is not always so when a hydrogenation catalyst is employed. For example, water is a deactivating poison to some catalysts, such as platinum or alumina, and the use of wet coal would be avoided when such catalysts are present. Accordingly, in the practice of this invention coal drying is eliminated since wet coal can be used with impunity.

Substantially any coal can be employed in this invention. For example, semi-anthracite, bituminous, semibituminous, sub-bituminous, lignite, peat, and the like can be used.

The slurrying medium in pipe 4 can be a liquid hydrocarbonaceous material produced by reactor 1 and/or a hydrogen-donor liquid such as tetralin or partially hydrogenated 3 or 4 ring aromatics such as anthracene, naphthalene, phenanthrene, and the like. Other hydrogen-donor mediums may be obtained by hydrogenation of the hydrocarbonaceous liquid products of reactor 1. Such a medium would boil within the range of from about 400 to about 950° F. The hydrogen-donor liquids are optional from a hydrogenation standpoint because adequate hydrogenation can be obtained with molecular hydrogen from pipe 13 alone.

The coal should be comminuted and can have a maximum particle size of about minus 8 mesh (Tyler). The comminuted coal is mixed with the slurry medium to form the coal slurry charged to reactor 1. The coal slurry preferably has a solvent/coal weight ratio as added to reactor 1 of from about 0.1 to about 4. The solvent part of the coal slurry can be formed completely or partially from externally added solvent from pipe 3 or hydrocarbonaceous liquid products from pipe 14 or combinations of the two as desired.

Molecular hydrogen and/or hydrogen containing gas can be charged by way of pipe 13 in an amount such that the hydrogen partial pressure in reactor 1 is maintained at from about 400 to about 3000 p.s.i.a.

Reactor 1 should be operated at a temperature of at least about 850° F. and a total pressure of from about 400 to about 5000 p.s.i.g. The total liquid and gas passing into reactor 1 should be in an amount and at a velocity sufficient to cause the solid particles present in bed 2 to become an ebullated bed, i.e., so that the solids are in an expanded state and occupy at least 10 percent greater volume than the settled volume of the particle mass of bed 2 and additionally are in random motion in the gas-liquid system. In an ebullated bed there is a sharp and finite level of the solid particles of the solid inert, non-catalytic particles, below which the solid particles exist at a concentration in excess of 5 pounds per cubic foot of reactor space and above which the solid particles exist at a concentration less than 0.1 pound per cubic foot of reactor space.

It is preferable in order to practice a preferred embodiment of this invention and to obtain a product distribution in pipe 18 approximating that of a catalytic reaction to operate reactor 1 in a temperature range of from about 850 to about 1000° F. using a coal addition rate of from about 15 to about 200 pounds of coal per hour per cubic foot of reactor. By keeping within these ranges with an inert particle ebullated bed, not only is catalyst cost saved but there is no sacrifice in product distribution and this is accomplished with a decrease in hydrogen consumption. Further, the reaction can be operated at a temperature up to 1000° F. without encountering undue pyrolysis as evidenced by increased gas production.

Being able to operate at a higher temperature without undue pyrolysis has the advantage of allowing a higher throughput of material for reactor 1 thereby, for a given set of reaction conditions, increasing the product output of reactor 1. Alternatively, one can keep the same throughput for a given set of reaction conditions but use a smaller volume reactor.

EXAMPLE I

A Pittsburgh No. 8 coal comminuted to 100 percent through a No. 40 U.S. Sieve particle size range was mixed with a solvent composed of coal derived oil having a 350 to 850° F. boiling range in a solvent/coal addition weight ratio of 4/1 and subjected to hydrogenation with molecular hydrogen using a coal addition rate of 31.2 pounds of coal per hour per cubic foot of reactor and a reaction time of 0.38 hour. One run was carried out at 825° F. using cobalt molybdate catalyst as the solid particles in the ebullated bed, the catalyst particles being in the 1/16 inch cylindrical extrudate size. One run was carried out at 850° F. using tabular alumina as the solid particles in the ebullated bed, the inert particles passing through a No. 8 and being retained on a No. 12 U.S. Sieve.

The results of the runs were as follows:

	Catalytic bed	Inert bed
CO and CO_2*	0.3	0.5
Methane through propane*	4.5	4.4
Butane and heavier benzene soluble liquid	67.5	66.6
Benzene insoluble liquid product	11.5	12.3
H_2 consumption	4.8	1.0
Unconverted coal	6.2	5.9

* Weight percent based on MAF coal.

It can be seen from the above data that the product distribution was substantially maintained between the catalytic bed run and the inert bed run but that the hydrogen consumption for the inert bed run was substantially reduced. Had the inert bed run been carried out at 825° F. less methane through propane gas would have been produced and at least one of unconverted coal and the benzene insolubles would have increased. Therefore, to maintain the product distribution of the catalytic run, the inert bed run needed to be carried out at 850° F.

EXAMPLE II

A Pittsburgh No. 8 coal comminuted to 100 percent pass through a No. 40 U.S. Sieve was mixed with a solvent composed of a coal derived oil having a 350 to 850° F. boiling range in a solvent/coal addition weight ratio of 4/1 and subjected to hydrogenation with molecular hydrogen using a coal addition rate of 93.7 pounds of coal per hour per cubic foot of reactor and a reaction time of 0.12 hour. Two runs were carried out at 850° F. and 893° F. using cobalt molybdate catalyst, in the 1/16 inch cylindrical extrudate size, as the solid particles in the ebullated bed. Two additional runs were carried out at 850° F. and 893° F. using tabular alumina, having a particle size passing through a No. 8 and retained on a No. 12 U.S. Sieve, as the solid particles in the ebullated bed.

The results of the runs were as follows:

	Catalytic bed		Inert bed	
	850° F.	893° F.	850° F.	893° F.
CO and CO_2*	0.4	0.6	0.4	0.5
Methane through propane*	3.7	7.4	2.4	4.2
Butane and heavier benzene soluble liquid product*	71.0	70.3	58.4	68.7
Benzene insoluble liquid product*	14.5	9.9	27.5	14.7
Unconverted coal*	9.3	6.4	8.3	6.6
Hydrogen Consumption*	5.6	5.2	0.8	0.7
Bbls. of oil/ton of MAF coal	4.4	4.2	4.1	4.0

*Weight percent based on MAF coal.

It can be seen from the above data that the inert bed run at 893° F. had essentially the same product distribution as the catalytic bed run at 850° F. but that the hydrogen consumption was substantially reduced.

Reasonable variations and modifications are possible within the scope of this disclosure without departing from the spirit and scope of this invention.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. In the hydrogenation of coal wherein a mixture of subdivided coal and a hydrocarbonaceous solvent is subjected to hydrogenation conditions of from about 850 to about 1000° F. and from about 400 to about 5000 p.s.i.g. in at least one hydrogenation zone, the improvement comprising said zone containing an ebullated bed of substantially solid contact particles, operating said at least one hydrogenation zone in the absence of externally supplied hydrogenation catalyst, and employing as said contact particles a material which is not derived from coal and which is substantially inert and non-catalytic as to the hydrogenation reaction.

2. A process according to claim 1 wherein said particles are composed of sand, alumina, quartz, pumice, glass beads, silicon carbide, and mullite.

3. A process according to claim 1 wherein said particles are in the size range of from about plus 200 mesh to about ¼ inch.

4. A process according to claim 1 wherein said hydrogenation conditions include a solvent/coal addition weight ratio of from about 0.1 to about 4 and a hydrogen addition rate sufficient to maintain a hydrogen partial pressure of from about 400 to about 3000 p.s.i.a.

5. A process according to claim 1 wherein said particles are present in said bed in the range of from about 5 to about 70 percent by weight.

6. A process according to claim 1 wherein said solvent boils in the range of from about 400 to about 950° F. and is at least one of a hydrogen-donor hydrocarbonaceous liquid and a hydrocarbonaceous oil derived from a coal and/or oil hydrogenation process.

7. A process according to claim 1 wherein said hydrogenation is carried out in the coal addition range of from about 15 to about 200 pounds of coal per hour per cubic foot of reactor.

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DELBERT E. GANTZ, Primary Examiner

V. O'KEEFE, Assistant Examiner