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PROCESS FOR CONVERSION OF COAL

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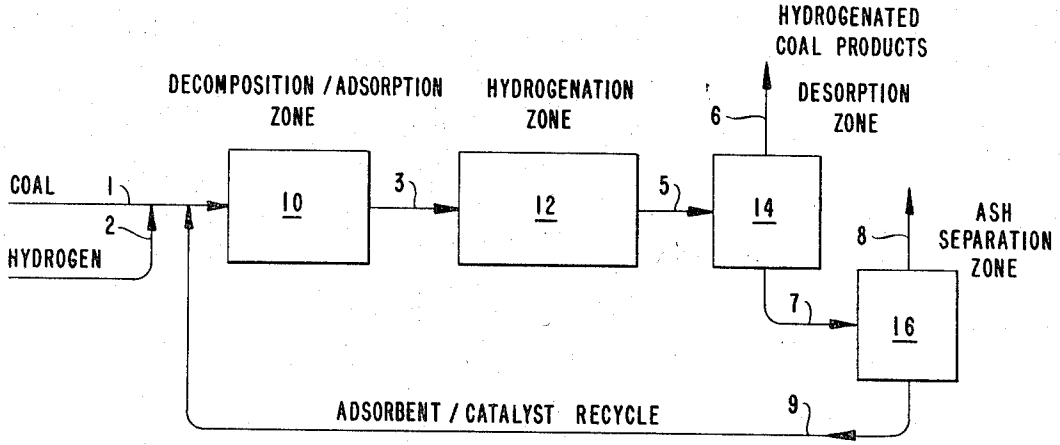


FIG. 1

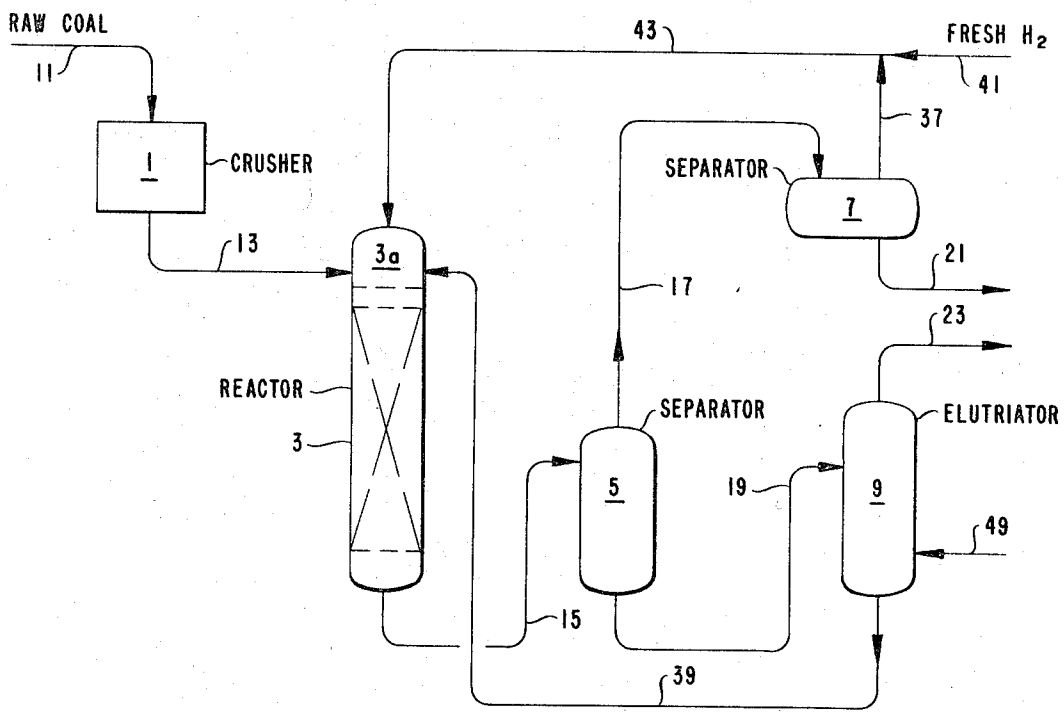


FIG. 2

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PROCESS FOR CONVERSION OF COAL

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ABSTRACT OF THE DISCLOSURE

A process for liquefication/hydrogenation of raw coal in which reactive decomposition intermediates are immediately adsorbed on a solid adsorbent, hydrogenated and desorbed in a moving bed process. Also disclosed are embodiments relating to a complete process providing recycle of adsorbent, recycle of reaction products and separation of ash and char from the adsorbent and products.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to the hydroconversion of coal to liquid products. More particularly it relates to an improved process for efficient conversion of coal to liquid products employing a dual functioning solid catalytic adsorbent and a novel processing scheme.

Description of the prior art

The conversion of coal to liquid products by hydrogenation is an established phenomenon. The basic conversion reaction was demonstrated nearly 60 years ago and coal hydrogenation underwent extensive development in Germany prior to World War II. Despite early interest, however, no process was developed which could compete with petroleum as a source of hydrocarbon fuel and liquid products. However, in recent years there has been a renewed interest in coal as a basic raw material source for petroleum products. Renewed interest has been stimulated by diminishing resources of crude oil (relative to demand) and the development of more complex and sophisticated petroleum refining techniques. Early coal hydrogenation processes required exceedingly high hydrogen pressures in the range of 5000–10,000 p.s.i. Technology now available allows substantially reduced pressures to the more manageable range of 2000–4000 p.s.i.

While the nature of coal itself and the mechanism of its decomposition and hydrogenation have been extensively explored, the constant improvement in analytical techniques and technological sophistication make the continued study of coal progressively more productive.

Proposed processes presently considered to have commercial potential are limited. A concise summary of four current contenders for commercial development is found in Chemical and Engineering News, June 12, 1967. In three of these processes, means other than hydrogenation are used for liquefication and only those liquid products obtained either by extraction or by pyrolysis are hydrogenated. None deal with the problem of reactive intermediate coal products. Thus, fairly large amounts of residue and/or char must be disposed of by coking or similar means to produce additional products and/or fuel. In the fourth proposal direct hydrogenation of raw coal is effected in a process utilizing an ebullating bed of catalyst. In this process the coal and catalyst are intimately mixed and the decomposition and hydrogenation take place in the presence of a continuous liquid phase of products. Significant amounts of very heavy liquid products are produced which must be recycled to the hydrogenation zone or disposed of, as for example, by coking. Ash is removed from the reaction zone with the liquid products.

A common characteristic of all these proposed processes is the relatively large amount of residue and char which is produced, either as refractory residual liquids, extract residue or pyrolysis coke. Economically to account for the large residue fraction, numerous proposals have been made, including gasification to produce hydrogen for the process and coking to produce fuel to supply some of the required heat in the process. Nevertheless, a common drawback of the proposed schemes is a high production of relatively low value residue.

It has long been recognized that a chief contributor to excessive refractory residue production during the decomposition/liquefication of coal is the polymerization and consolidation of the highly reactive initial decomposition products. This phenomenon arises from the very nature of the coal itself. Coal consists of a combination of carbon and hydrogen along with smaller amounts of other elements, such as oxygen, nitrogen and sulfur. The carbon is primarily combined in condensed ring structures of high molecular weight which are frequently bound directly together in large clusters by carbon, oxygen and carbon/oxygen linkages. When heated to about 400° C. the solid structure begins to disintegrate, the chemical rearrangements continuing up to a temperature of 1000° C. and higher. As the disintegration products are evolved they, together with the remaining solid matter, consolidate and/or polymerize into coke or char which is extremely refractory to hydrogenation. To overcome this undesirable effect at least partially, it has been proposed to heat the coal as rapidly as possible in the presence of hydrogen to temperatures above which the products remain predominantly aromatic. Such a process is proposed by Schroeder, U.S. 3,030,297 issued April 1962 and Schroeder, U.S. 3,152,063 issued October 1964. In the process of the patent, reaction at temperatures below 800° C. is limited to very short times in the order of about two minutes. In another proposed process, coal is destructively distilled in a flowing stream of hydrogen and the vapor products, including vaporized condensables, are hydrogenated with a solid catalyst. By maintaining these intermediates in the vapor phase, polymerization and consolidation is retarded until the intermediates are stabiilzed by contact with a hydrogenation catalyst. Char, nonvaporized residue and ash, presumably, are not passed over the catalyst. Huntington, U.S. 3,244,615 issued April 1966. While these methods have merit in reducing the inherent difficulties with coal decomposition, they are not wholly satisfactory due, inter alia, to engineering problems of implementation.

I have now found that selectivity of coal hydrogenation/liquefication is markedly improved in favor of gasoline and gas oil by immediately adsorbing the reactive intermediate disintegration products on a solid adsorbent as they are evolved. The polymerization being thus arrested, the absorbed materials can then be hydrogenated and cracked to stable liquid products with minimum production of refractory heavy products. Moreover, my process has the significant advantage of simple and efficient removal of ash and char from the catalytic system without the necessity of deashing the coal prior to direct hydrogenation.

SUMMARY OF THE INVENTION

In broad aspect, the process of the invention involves the following steps:

(1) Decomposition of coal at elevated temperatures in the presence of hydrogen and a solid adsorbent, which immediately adsorbs the decomposition intermediates, is carried out in the absence of a continuous liquid phase, and thus prevents secondary reactions.

(2) Hydrogenation and hydrogenative cracking of the intermediates adsorbed on the solid adsorbent to products which desorb from the solid adsorbent and

(3) Separation of the desorbed products from the solid adsorbent. This sequence encompasses the broad concept of the invention which includes within its scope additional steps which further characterize especially advantageous embodiments. These additional steps include:

(4) Separation of ash and char from the adsorbent/catalyst, a separation made especially easy because of the efficiency of conversion of the invention and

(5) Recycle of the adsorbent/catalyst together with adsorbed material to Step 1 in a continuous circulating catalyst process.

The chemical reaction mechanism leading to the improved results of the process of the invention involves several successive steps: initial decomposition of the coal to intermediate products; adsorption of the intermediates on the solid; hydrogenation and cracking of the adsorbed intermediates which desorb as stable, useful products and finally recovery of the desired products.

The foundation upon which the present invention rests is the discovery that the highly reactive intermediates evolved from the decomposition of coal can be prevented from consolidation and polymerization by immediate adsorption on a solid adsorbent. By immediately adsorbing the intermediates as they are evolved from the decomposing coal, their reactivity with each other is effectively arrested, allowing further reaction to be controlled as desirable. The desired reactions are hydrogenation and cracking to useful, stable hydrocarbon oils. Having arrested the reactivity of these species, they can be hydrogenated under proper conditions in the absence of the rapid competitive side reactions leadings to refractory polymerization products. Thus the adsorbent with the adsorbed intermediates may be transferred to a subsequent hydrogenation zone. Hydrogenation is, of course, far more effectively promoted with the aid of a catalyst. For example, the adsorbent, having the reaction intermediates adsorbed thereon may be impregnated with a hydrogenation catalyst—as by vapor phase deposition of a hydrogenation metal—and the hydrogenation effectively catalyzed. It is more convenient and appropriate, however, to have the hydrogenation catalytic component on the adsorbent initially, thus eliminating the need for subsequent impregnation. Thus, it has been found advantageous to use an adsorbent which has composited therewith a suitable hydrogenation catalytic metal component.

Rapid adsorption of the initial decomposition products is an essential key to the success of the process. To accomplish this objective the adsorbent/catalyst must initially be intimately mixed with the coal and the solid must be capable of adsorbing the decomposition products as they are formed. In order to insure rapid mass transfer of initial decomposition products to the solid, it is especially important that the decomposition/adsorption take place in the absence of a separate continuous liquid phase. The decomposition step in the absence of a separate continuous liquid phase—contrary to the customary practice in prior processes where the coal is fed in a paste with a heavy liquid and hydrogenation carried out in a single multiphase reaction zone—is one of the chief distinguishing features of the present invention.

By the absence of a separate continuous liquid phase is meant that during the decomposition adsorption step there is not sufficient liquid present to bridge the coal and catalyst particles and thus form a barrier to the immediate adsorption of intermediates. While there may be liquid present, as by addition of some liquid carbonaceous materials to the coal feed and/or recycle of heavy products in the process as well as instantaneously formed liquid decomposition products, the amount of such liquid and the conditions, i.e. temperature, hydrogen content, catalyst/coal ratio, must be maintained so that a continuous phase

of liquid is not formed. That such a condition as described can be easily achieved is well known in the petroleum refining art. For example, in catalytic cracking of heavy petroleum fraction in a fluidized riser reactor at least partially liquid feed is contacted with catalyst with the catalyst feed mixture remaining in a "dry" fluidized state. While liquid is present, no separate continuous phase of liquid exists under the conditions applied.

When the entire adsorption-hydrogenation-desorption sequence is carried out in a single well mixed reaction zone (as is the case in other prior art processes) the presence of liquid retards and/or prevents rapid adsorption of the reactive intermediates and allows consolidation and polymerization reactions which produce refractory residues.

Implementation of this mechanism in a continuous flow process requires the cocurrent flow of the coal, solid adsorbent/catalyst, and coal decomposition and hydrogenated products through the successive steps in the process of the invention. Several special aspects should be noted which serve to distinguish the process over the prior art and leads to the surprisingly superior results obtained. For this purpose and for more complete understanding of the invention, reference is made to the drawing wherein:

FIG. 1 is a diagrammatic representation of the reaction sequence of the process according to the invention.

FIG. 2 is a schematic representation of a preferred embodiment of the invention which will be subsequently described.

Referring to FIG. 1, raw coal is introduced via line **1** together with an adsorbent/catalyst solid (line **9**) to a decomposition/adsorption zone **10** where, at elevated temperature and pressure, the coal is thermally decomposed to intermediate products which are immediately adsorbed on the solid. Hydrogen enters the reaction scheme via line **2**. From zone **10** adsorbent, with intermediate products adsorbed thereon, together with any desorbed products and unadsorbed ash and char pass via line **3** to hydrogenation zone **12**. In this zone **12** the adsorbed intermediates are cracked and stabilized by hydrogenation. The hydrogenated intermediate products, adsorbent/catalyst, ash and char pass via line **5** to separation zone **14** where the hydrogenated coal products are desorbed to an equilibrium level and removed via line **6** for further processing. By equilibrium level is meant an amount which at a given set of conditions does not change substantially on continued recycle of adsorbent. The solid adsorbent/catalyst recycle, ash and char pass to separation zone **16** via line **7** where the ash is removed by suitable means such as elutriation or screening. Ash is removed via line **8** and the adsorbent/catalyst solid, now relieved of non-equilibrium adsorbed products is recirculated via line **9** to the beginning of the process where it again contacts a fresh charge of coal. It will be understood that the above description is diagrammatic only and the simultaneous reaction and mass transfer steps which actually occur in a practical flowing process cannot be so neatly segregated. However, this representation is useful in illustrating the complex sequential steps which make up the present novel process.

While the individual steps in the present process may be carried out in separate well mixed zones, backmixing from one stage to the prior stage is undesirable, i.e. decomposition in the presence of a separate continuous liquid phase of hydrogenated liquid products.

In the hydrogenation zone, the presence of a substantial liquid phase would lead to similar difficulties, e.g. retarding the transfer of hydrogen to the adsorbed intermediates and retardation of desorption of the hydrogenated products.

In the separation zone similar considerations apply. The presence of a liquid phase retards desorption and separation. It is a striking feature of the present process that the hydrogenation is so complete that when the separation stage is reached, the solid (adsorbent/catalyst plus ash and

char) appears completely dry. Whatever refractory material is produced remains with the solid adsorbent at an equilibrium level and is recycled with the solid through the system. The circulating solid (if chosen to have sufficient hydrogen catalytic activity) obtains an equilibrium level of adsorbed material which does not increase with repeated circulation. Because the solid adsorbent/catalyst is not admixed with a separate liquid phase, separation of ash is greatly facilitated. When properly sized, the solid adsorbent/catalyst is easily separated from ash and char by screening or elutriation.

Another important aspect of the present invention is the discovery that the kinetics of the decomposition/hydrogenation/desorption reactions of the present scheme allows the process in one embodiment to be carried out in a unitary reaction zone. Since the decomposition and adsorption—in the absence of a liquid carrier—is extremely rapid compared to the hydrogenation reaction, it is possible to carry out this step at the entrance portion of a unitary reactor, the adsorbent/catalyst with adsorbed intermediates moving to a longer residence time zone where hydrogenation takes place without interference from decomposition and adsorption reaction. In other words, in a moving bed unitary reaction zone coal and catalyst are initially mixed, the coal decomposed and intermediates adsorbed. As the adsorbent catalyst moves through the bed the decomposition adsorption is completed and hydrogenation, cracking and desorption become the dominant reactions in the middle section of the bed. After sufficient time the major portion of the adsorbed intermediates are hydrogenated and desorbed leaving at the exit of the reaction zone a physical mixture of adsorbent having some material thereon, desorbed stabilized products, and ash and char which were associated with the raw coal. This mixture is substantially "dry," the desorbed products being predominantly vaporous at the conditions applied. Thus, the separation into desired products, adsorbent and the ash and char fractions is greatly facilitated.

The process of the invention may be carried out for the conversion of any type of coal, as for example, bituminous, sub-bituminous or lignite coal. The coal is preferably ground or pulverized to facilitate transport and decomposition. However, the process may suitably be used to convert coal fines and coal or fines which have been agglomerated or pelleted by various means known to the art.

The decomposition/adsorption step can be carried out over a wide range of conditions of temperature and pressure. Temperatures in the range of 200 to 600° C. and pressures in the range of 500 to 3000 p.s.i.g. can be used. Generally, temperatures in the range of 350–450° C. and pressures in the range of 1000–2000 p.s.i.g. are suitable. These relatively mild conditions, in themselves, point up a significant advantage of the present process over those previously proposed. While both higher temperatures and pressures may be used, the practical problems of rapidly achieving higher temperatures and the economic detriment of higher pressures limit these variables to the ranges given.

The solid adsorbent/catalyst material suitable for the process has certain essential properties. This material must be solid at the reaction conditions and be capable of rapidly adsorbing the intermediate products of the decomposed coal.

Numerous materials are known to possess the adsorptive capabilities required to accomplish the purpose of the present invention. For example, naturally occurring or synthetic adsorbent inorganic metal oxides such as montmorillonite clays, kieselguhr, silica, alumina, magnesia boria, titania, zirconia, beryllia and mixtures thereof. Particularly desirable are the high surface area porous oxide such as cogels or coprecipitates of amorphous silica or alumina and crystalline alumino-silicate zeolites, etc.

While many of the adsorbent solids will have some inherent hydrogenative activity, in general such activity is not sufficient to accomplish the desired degree of hydrogenation necessary in the process of the invention. Therefore, catalytic hydrogenation activity is supplied by compositing with the adsorbent a hydrogenation component, preferably a metal hydrogenation component. Suitable for this purpose are the various hydrogenation metals, and metal compounds—such as the oxides and sulfides—known to the art for their hydrogenation ability. Of course, it is highly desirable that the adsorbent have a porous structure and high surface area and that the hydrogenation component be distributed in a finely divided or molecular state substantially over the effective adsorptive surface of the solid. Especially preferred hydrogenation components for the adsorbent/catalyst solid of the invention are metals and metal compounds—oxides and sulfides—of metals selected from Groups VB, VIB, VIIB, and VIII of the Periodic Table of Elements and mixtures thereof. The Periodic Table referred to herein may be found in the Handbook of Chemistry and Physics, 39th edition, Chemical Rubber Publishing Company (1957–1958).

While it is not essential that the adsorbent have catalytic cracking activity, such activity is a definite advantage. In order to obtain the desired hydrogenation and cracking of the adsorbed coal decomposition intermediates only catalytic hydrogenation activity is essential, it being possible to thermally crack the hydrogenated products under the proper conditions. However, catalytic cracking ability is desirable. As will be recognized, many of the adsorbent materials enumerated above possess cracking activity. Cracking activity can also be added and/or enhanced by various means such as acid treating and incorporation of halogen components.

Methods of manufacturing the refractory oxide adsorbent material and of incorporating hydrogenative metal and acidic promoters on these adsorbent materials are also well known in the art. The catalytic components may, for example, be deposited by impregnation or by ion exchange from a solution followed by treatment with other reagents to cause precipitation or modification by drying and heating or oxidation or other chemical treatments.

Specific examples of suitable materials which have been found to have especial utility for the purposes of the invention are Group VIII and/or Group VIB metal oxides and sulfides incorporated on alumina or silica-alumina and Group VIII metals on faujasite-type zeolites, such as palladium on Y-zeolite.

Zeolites having had at least a part of the alkali metal content exchanged for hydrogen ions or divalent metal ions have high intrinsic cracking activity and unusually good adsorptive properties and are thus very suitable for the present invention. Crystalline alumino-silicate zeolites are now well known in the art.

The adsorbent/catalyst may be in any of various physical forms, as for example, spheres, pills, extrudates, granules, etc. This size of these particles while not critical within the scope of the invention is an important variable in the effective utilization of specific embodiments. For example, relatively small particles are preferred to achieve effective adsorption, to facilitate fluidation and transfer in a moving bed process. The size and density of the solid adsorbent/catalyst should desirably be chosen to facilitate easy separation from dry ash and char by elutriation or screening. The choice of the proper form and size of the material to meet the exigencies of each particular process configuration is a matter within the skill of those practiced in the art.

In order to facilitate a clearer understanding of the reaction mechanism upon which this invention rests and practice of the invention, the following experiments will be described before discussion of a specific preferred embodiment. These experiments, while illustrative and not intended to be a limitation on the invention, are useful in

understanding the criticality of the sequential steps which characterize the invention.

The following experiments demonstrate the initial decomposition and adsorption of the decomposition products and serve to illustrate the importance and practicality of this step in the process of the invention.

Dried Illinois No. 6 coal (through 200 mesh) was reacted in a fixed bed tubular reactor with a charge of adsorbent/catalyst comprising cobalt and molybdenum impregnated on alumina (42–100 mesh). Hydrogen was passed through the bed of coal and adsorbent/catalyst which was maintained at about 1500 p.s.i.g. pressure. The coal and catalyst were sized so that separation of residual char and ash from the solid could be effected by screening. Successive charges of fresh coal were used with the same adsorbent/catalyst. Each charge of coal (10 g. fed in four 2.5 g. portions) was contacted with 10.3 g. of solid, the solid being recovered and used with a succeeding charge.

The results of this experiment and the pertinent operating conditions are given in Table I.

TABLE I

Temperature: 400–450° C.[a]
H_2 Flow: 400 cc./min. at 1,500 p.s.i.

	Run period (min.) [b]	Products (percent w. m.a.f.)				Conversion (percent w. m.a.f.)
		CH_4 to C_3H_8	Liquid	Res.[c]	Char [d]	
Coal charge No.:						
1	4×15	4.1	36	12	31	69
2	4×15	5.0	53	1	24	76
3	4×15	5.3	58	3	15	85
4	4×15	5.6	59	4	11	89
5	4×15	5.2	60	−2	17	83
6	4×15	5.6	66	7	9	91
Combined 7–8		6.2	68	0	9	91

[a] 450° C. maximum, time counted when reactor reached 400° C.
[b] The 10.3 g. charge introduced in four portions and reacted for 15 minutes each.
[c] Residual material remaining on adsorbent.
[d] Removed with ash.

These results show that stable operation was approached after the catalyst had been used with six times its weight of coal. At this point a slight decrease in space velocity to about 0.75 to allow increased hydrogenation time stable equilibrium operation was achieved. After stable operation was achieved, the liquid yield was 68% at a coal conversion of 91%.

The foregoing results point up two important functions of the solid adsorbent/catalyst: First, it rapidly adsorbs the intermediates which are formed in the initial coal decomposition; second, it catalyzes the hydrogenation of the adsorbed intermediates. The first function is carried out with coal and catalyst mixtures in the absence of any added liquid solvent or vehicle. The importance of the second function is illustrated by experiments made using silica which has no hydrogenation or hydrocracking activity. In the absence of hydrocracking activity, the intermediates continued to build up on the adsorbent solid (SiO_2) in a form which was not readily removable. This experiment was the same as previously described and after the first 10 g. charge of coal only 13% w. liquid was produced, the adsorbent contained 29% adsorbed residual liquid. Total conversion was only 60% leaving 40% of the coal charged as refractory char.

To more closely approximate a continuous process and further illustrate the process of the invention, experiments were made simulating staged operation. The adsorbent/catalyst which had previously achieved stable operation in the above example and containing about 25% adsorbent material was divided into equal portions. To one portion was added a charge of fresh coal and the mixture put at the inlet end of a tubular reactor. The other portion was placed at the exit end of the reactor and separated from the first portion by glass wool. After the reaction period, the catalyst at the exit end was screened to remove residual char and ash and then mixed with fresh coal and placed at the inlet of the reactor. At the same time, the coal and catalyst at the inlet were moved to the exit end of the reactor for the next reaction period. This operation was repeated over and over with the results in Table II. In this configuration at 450° C. and a H_2 flow of 400 cc./min. at 1500 p.s.i., stable operation was achieved at a coal space velocity of slightly over ½. The results are improved over single-stage operation. The coal is essentially completely converted with a liquid yield of about 70%.

TABLE II

Temperature: 400–450° C.
H_2 Flow: 400 cc./min. at 1,500 p.s.i.

	Run period (min.)	Products (percent w. m.a.f.)				Conversion (percent w. m.a.f.)
		CH_4 to C_3H_8	Liquid	Res.[a]	Char [b]	
Coal charge No.:						
1	4×15	----------	53	22	0	100
2	4×20	----------	70	−3	0	100
3	3×20[c]	----------	67	1	0	100
Combined 4–5		9.7	72	1	0	100
Combined 6–7		9.4	69	1	0	100

[a] Residual material remaining on adsorbent.
[b] Removed with ash.
[c] 7.5 g. coal—total charge.

In one embodiment of the invention, heavy liquid products, or a portion thereof may be recycled and included in the fresh charge of coal. Because of the efficiency of the single-stage conversion, the amount of recycle should always be below an amount sufficient to form a separate continuous liquid phase which would interfere with adsorption of the thermal decomposition products. By recycling the heavier products, even greater conversion to light products, as for example, gasoline boiling range material, can be realized. This is demonstrated by three-stage experiments simulating a continuous process with recycle.

In three-stage process experiments the contents of a tubular reactor (as in the previously described operations) were divided into three sections by glass wool. Coal was mixed with one-third of the adsorbent/catalyst solid used in previous experiments and placed at the inlet end of the reactor. Of the remaining two-thirds of the catalyst, one-third was placed in each of the middle and exit sections

of the reactor. The glass wool maintained the integrity of the three separate sections. After the reaction was carried out at temperatures in the range of 400–450° C., the reactor was cooled and depressured and the sections removed. The exit section was screened to remove any residual char and ash which had been formed and then replaced in the reactor as the first or inlet section. The middle section was moved to the bottom of the reactor and the initial inlet section to the middle. This procedure was repeated over and over, thereby effectively simulating a moving bed of adsorbent/solid and coal in a cocurrent flow of hydrogen.

Results of this three-stage operation together with pertinent operating conditions with and without added recycle of heavy products are given in the following Table III. In the recycle runs, heavy product obtained from previous runs was added with the coal feed as recycle. It should be pointed out that, even in the absence of added recycle, there is an effective recycle in the form of the adsorbed material on the recycled adsorbent/catalyst solid. It is interesting to note that in the recycle run the best results were obtained with an adsorbent/solid which had been used with 26 times its weight of coal.

TABLE III

Run	Products (percent w. m.a.f.) CH_4 to C_3H_8	Liquid	Res.	Char	Conversion (percent w. m.a.f.)
A—Without recycle—Results after 11 charges of coal in this operation mode	(1)	69	5	0	100
B—With recycle—Results after 6 charges of coal in this mode of operation	9.8	72	0	2	98

[1] Not measured.

It is of particular significance that in the staged operation, heavy refractory products (975° F. plus boiling point) are substantially eliminated, a striking demonstration of the efficiency and critical importance of the process sequence and conditions. Product boiling range analysis for the one, two and three-stage operation experiments are shown in the following Table IV.

TABLE IV

	Products (percent w. m.a.f.) C_1–C_3	IBP 400° F.	400–680° F.	680–975° F.	975+ F.	Total liquid yield
One-stage (Runs 4–8)	6	18	25	21	4	68
Two-stage (Runs 4–7)	10	22	27	18	4	71
Three-stage with recycle (Run B)	10	30	33	9	0	72

In view of the favorable results obtained with recycle it is obvious that some heavy liquid materials can be included with the coal charge so long as the amount is below that which would result in a separate liquid phase. Thus heavy petroleum fractions such as petroleum residues, pitches, asphaltene fractions, coal extract or heavy liquid products from coal pyrolysis or extraction could be included with the coal charge in place of or in addition to product recycle.

The amount of liquid which can be included depends upon the nature of the liquid, the specific adsorbent used, operating conditions—particularly catalyst/feed ratio—as well as other factors. The maximum amount of liquid includable can be determined by those skilled in the art without experimentation upon consideration of the above factors but in general will be less than about 25% basis solid coal feed.

In another embodiment of the invention, the coal charge may be impregnated with a hydrogenation catalyst prior to introduction to the conversion zone. In this case the catalyst impregnated coal is decomposed more rapidly without adverse affect on the adsorption and subsequent hydrogenation of the coal products. Various catalysts and methods of impregnation may be used in the embodiment, such as for example, hydrogenative metal salts and sulfides as are disclosed in my copending application, Ser. No. 746,820, filed July 23, 1968.

This embodiment and the effects of several different adsorption/catalyst materials is demonstrated by the following experiments.

Powdered Illinois No. 6 coal was impregnated with molybdenum chloride by slurrying the coal with an ether solution of the salt to obtain about 0.1 to 0.2% w. $MoCl_5$ on the impregnated coal.

Several absorbent/catalysts were mixed with impregnated coal and tested under the following conditions: 425° C., 1500 p.s.i., H_2 flow of 200 cc./min. for 5 hours (reaction was essentially complete in 2 hours), and 10 g. each of coal and adsorbent/catalyst. The results are summarized in the following Table V. The level of coal conversion was observed to be almost independent of the adsorbent/catalyst, indicating that it is the impregnated catalyst and the reaction conditions which largely determine the depth of conversion. On the other hand, the product distribution was markedly affected by the choice of adsorbent/catalyst. Zeolite-based adsorbent/catalysts produced more gasoline-range products than amorphous silica-alumina adsorbent/catalysts. The increased gasoline range material was accompanied by increased light gas make. With the zeolite catalysts, the importance of a hydrogenation function (i.e., Pd) and the proper level of acidity was also demonstrated. The differences between the various amorphous catalysts were not marked, although the increased acidity of the silica-alumina supported materials compared to $Co/Mo/Al_2O_3$ resulted in slightly more gasoline range material.

TABLE V

Catalyst	Products (percent w. m.a.f.) C_4–200° C.	200–400° C.	Conversion (percent w. m.a.f.)
SiO_2	22	37	78
H–Y (Hydrogen form of Y—zeolite)	30	11	75
Pd/Y (Linde SK–100)	57	4	85
$Co/Mo/Al_2O_3$	34	33	85
$Ni/W/F/SiO_2$–Al_2O_3	36	18	81
$Ni/Mo/F/SiO_2$–Al_2O_3	32	29	87

While the impregnated catalyst improves the rate of and lowers the temperature required for initial conversion, it should be emphasized that this feature is not essential to the novel process of the invention since the decomposition temperature and/or reaction time may be adjusted to achieve substantially complete decomposition without catalyst impregnated on the coal.

DESCRIPTION OF A PREFERRED EMBODIMENT

Having demonstrated the chemical efficiency and feasibility of the process of the invention, a preferred embodiment of the complete process which makes use of and implements the demonstrated mechanism of the process will now be described.

FIG. 2 of the attached drawing is a schematic representation of an embodiment of the process of the invention. This scheme illustrates an effective means of utilizing the invention and further illustrates the process but is not to be taken as a limitation thereon.

Raw coal is introduced via line **11** to crusher **1** where it is pulverized to facilitate further processing. The crushed coal passes via line **13** to the reaction zone **3**. Coal, recycle catalyst from line **39** and hydrogen from line **43** are mixed in the mixing zone **3***a* and enter the reaction zone as an intimate mixture where there they pass cocurrently at relatively low velocity through the reactor. Low velocity is desired to prevent gross backmixing of liquid products to the decomposition zone which could produce a separate continuous liquid phase and restrict the required rapid adsorption necessary to achieve the advantages of the invention. The reaction zone is maintained at a tempera-

ture of about 450° C., a pressure of about 1500 p.s.i.g. and a coal space velocity of about 0.5 (weight of coal per weight of catalyst per hour). Hydrogen is introduced via line **43** at a rate equal to about 100 s.c.f. H_2 per lb. of coal. In the reaction zone the coal is decomposed and the intermediate products immediately adsorbed on the adsorbent/catalyst. The adsorbed products are then more slowly hydrogenated and cracked to stable hydrocarbon products in the middle zone and desorbed from the adsorbent/catalyst leaving residual material on the adsorbent. The reactor effluent is a physical mixture of hydrogenated products, product gas, excess hydrogen, char and ash, adsorbent/catalyst having adsorbed thereon heavy liquid products. This effluent passes via line **15** to separator **5** where the stabilized hydrocarbon products are separated and pass via line **17** to separator **7**. Hydrogen is removed from separator **7** via line **37** and recycled to the reaction zone together with fresh make-up hydrogen from line **41**. Stabilized hydrogenated products are removed via line **21** for further separation and/or refining. From separator **5** the adsorbent/catalyst, char and ash pass via line **19** to elutriator **9** where ash and char are separated from the adsorbent. Elutriation gas enters elutriator **9** via line **49**. Elutriation gas may be any suitable or convenient gas stream including synthesis gas, hydrogen, nitrogen or mixtures which contains little or no oxygen. Oxygen-containing gas such as air are to be avoided since they lead to combustion of the adsorbed materials. The ash and char are removed via line **23**. The adsorbent/catalyst, now separated from the ash and char, but containing equilibrium adsorbed heavy liquid is recycled to the reactor zone where it is mixed with incoming hydrogen and fresh coal.

Make-up hydrogen is introduced into the hydrogen recycle via line **41**. Pure hydrogen is not required since any suitable hydrogen-containing gas which is predominantly hydrogen can be used. For example, hydrogen-rich gas containing on the order of 70% volume or more hydrogen is adequate and is often available in a petroleum refinery, as for instance, as off-gas from a catalytic reforming process or other hydroprocessing operations. Of course, synthesis hydrogen gas as from steam-hydrocarbon or steam-coal reforming is suitable.

The total amount of hydrogen charged to the process should be such that there is an excess of hydrogen over that consumed in the conversion. A relatively large excess is usually employed to provide a longer catalyst life and to absorb heat liberated by the exdothermic reaction. The amount of hydrogen to be employed is within the skill of those practicing the art. In general, the total amount of hydrogen charge will range up to about 100 s.c.f./lb. of coal or more.

Various modifications, depending on the coal charge, the desired products, depth of conversion and other individual requirements will be immediately obvious to those in the art and are included within the intended scope of the present invention.

I claim as my invention:

1. The process for hydrogenation/liquefaction of coal which comprises:

(a) decomposition of coal at a temperature of 200–600° C. and under a hydrogen pressure of 500–3000 p.s.i. in contact with a solid adsorbent/catalyst consisting essentially of an adsorptive porous refractory inorganic oxide having a metal or metal compound with activity as a hydrogenation catalyst deposited thereon, the conditions of contact being selected such that the process is carried out in the absence of a continuous liquid phase,

(b) desorbing hydrogenated products from the adsorbent/catalyst leaving an equilibrium amount of adsorbed material on the catalyst,

(c) recovery hydrogenated products,

(d) returning catalyst with adsorbed material thereon into contact with coal.

2. The process of claim **1** wherein the adsorbent/catalyst is separated from ash and char.

3. The process of claim **1** wherein the adsorbent/catalyst comprises an adsorptive refractory oxide having incorporated therewith a hydrogenation component selected from a group consisting of metals and oxides and sulfides from Groups VB, BIB, VIIB, and VIII of the Periodic Table of Elements and mixtures thereof.

4. The process of claim **1** wherein the adsorptive/catalyst comprises an adsorptive refractory oxide having incorporated thereon a hydrogenative catalyst component selected from a group consisting of metal and metal oxides and sulfides of metals from Groups VB, VIB, VIIB, and VIII of the Periodic Table of Elements and mixtures thereof and the process is carried out at a temperature in the range of 200–600° C. and pressures in the range of 500–3000 p.s.i.g.

5. The process of claim **4** wherein heavy product is recycled to the process in an amount below that which would result in a continuous liquid phase at processing conditions.

6. The process of claim **4** wherein a liquid hydrocarbon fraction is included with the feed coal to the process in an amount below that which would result in a continuous liquid phase at processing conditions.

7. The process of claim **4** wherein the solid adsorbent/catalyst is recycled through the process and contacts at least six times its weight in fresh coal feed.

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