

2,860,101

BALANCED HYDROGENATION OF COAL

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No Drawing. Application April 20, 1953
Serial No. 349,988

5 Claims. (Cl. 208—10)

(Granted under Title 35, U. S. Code (1952), sec. 266)

The invention herein described and claimed may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of royalties thereon or therefor.

This invention relates to a process for the hydrogenation of a carbonaceous material to convert it into a useful product with a higher hydrogen to carbon ratio, basically a synthetic liquid or gaseous fuel. The invention further relates to an improved process for the hydrogenation of coal to form oil and gaseous hydrocarbons. In one of its more specific aspects the invention relates to an improved process for the hydrogenation of coal wherein a carbonaceous material can be converted in one step to a desirable product containing a higher hydrogen to carbon ratio.

An object of this invention is to provide an improved process for the hydrogenation of solid carbonaceous fuels to produce liquid fuels.

A further object of the present invention is to simplify conversion of coal into liquid or gaseous products and thereby reduce the cost of coal liquefaction.

Still another object of this invention is to provide a process for the hydrogenation of solid carbonaceous materials, particularly coal, under high pressure and high temperature in the presence of a catalyst to produce synthetic liquid fuels.

A further object of the invention is to provide a process for the hydrogenation of a solid carbonaceous material, particularly coal, under elevated temperature and pressure to form specification liquid fuels in one step.

A still further object is to provide a process for the almost complete conversion of coal to a non-asphaltic oil and gaseous hydrocarbons by a balanced one-pass hydrogenation, eliminating additional steps required in conventional coal hydrogenation processes, and utilizing the CH_4 as a source of the H_2 gas required for the process.

In conventional practice, carbonaceous raw materials such as coal are commonly hydrogenated in the liquid phase under high pressure and in the presence of catalysts. To prepare the feed, first, pulverized coal is mixed with a catalyst; and with pasting oil obtained from the process itself to form a mud-like paste; its composition is approximately 50% coal particles, 1% catalysts, the remainder being the pasting oil. Catalysts usually employed have been compounds of iron and tin. The coal paste admixed with hydrogen is preheated to reaction temperatures usually 450° to 480° C. and injected into a reactor at a pressure of 300 to 700 atmospheres. The residence time is usually about one hour.

The products of the reaction are separated. A separation system normally consists of a hot separator or hot catch pot at reaction pressure wherein a heavy oil and solid residue mixture are drawn off at the bottom while the overhead vapors consisting of a mixture of oil vapors, hydrocarbon gases and hydrogen are passed to a cold separator wherein the oil vapors are condensed. The bottom product of the hot catch pot is discharged from the high pressure system and contains 25–30% solids and

is called "heavy oil letdown" (H. O. L. D.). This must be processed to recover the heavy oil and this processing requires considerable equipment and labor, and represents a formidable expense which must be charged to the cost of the final synthetic liquid product. The materials condensed in the cold catch pot are discharged to atmospheric pressure and distilled to produce an overhead fraction with an endpoint of 325° C. All material boiling above this temperature is recycled as pasting oil together with heavy oil recovered from the heavy oil letdown (H. O. L. D.). The fraction with an end point of 325° C. is a liquid product which is not suitable for sale as gasoline but must be further hydrogenated over a solid catalyst to produce a stable specification gasoline. In many hydrogenation plants two hydrogenation steps utilizing solid catalysts are required before a satisfactory gasoline is produced. This brief summary of the present state of the industrial usage of the coal hydrogenation process can be amplified by reference to such contemporary reports as "Ministry of Fuel and Power, Report on the Petroleum and Synthetic Oil Industry of Germany, B. I. O. S., Overall Report" No. 1, London, England (1947).

In addition to the industrial art considerable prior art exists as a result of research conducted both in this country and abroad. This prior art has indicated, among other information, certain critical data of importance to the applicant's invention. These are as follows:

(1) Coal can be hydrogenated to produce some liquid products at a variety of conditions ranging in temperature from 300° to 600° C. and in pressure from 20 to 2000 atmospheres.

(2) Various metals, compounds of metals, alloys of metals and combinations of metals and their compounds have a beneficial catalytic effect on the reaction of coal with hydrogen to produce liquid materials. These catalytic substances may be added as powders, solutions or slurries.

(3) The coal may be introduced into the reactor as a dry powder, in suspension using either distillable or non-distillable fluids, or solvated in suitable solvents.

(4) Various types of reactors may be used including cylindrical vessels, inclined or spiral tubes of small diameter, vessels containing various types of baffles, and mechanically stirred or agitated vessels.

However, in all this prior industrial and experimental art summarized above, several limitations are apparent: namely, that more than one hydrogenation step is required to produce a stable motor or aviation gasoline; that in the first or liquid stage process a considerable percentage of the coal is converted to a refractory material known to those versed in the art as asphalt or asphaltene, and while the quantity of this material may be reduced, sufficient is always produced to require removal from the process in some manner; the removal and separation of a mixture of heavy oil and solids adds considerable expense and complexity to the process.

The applicant on the other hand has by a suitable and critical combination of several variables invented a process which in one hydrogenation step produces a premium grade, stable gasoline from coal or other carbonaceous material. The process is as follows:

(1) Powdered coal, impregnated with an active catalyst, is mixed with a distillable oil obtained from the process. Suitable active catalysts which have been utilized are nickelous chloride, stannous chloride, and ammonium molybdate.

(2) The resultant paste is introduced into a vessel together with gaseous hydrogen under a pressure of more than 475 atmospheres and a temperature of more than 500° C. While a cylindrical vessel may be used, excel-

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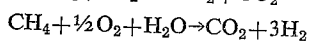
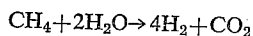
lent results have been obtained with a tubular converter consisting of a helical tube of large length to diameter ratio. The residence time of the reactants is kept at from about 15 seconds to 15 minutes. The favorable results shown in Example 2 at 15 seconds strongly suggest that satisfactory conversions might be obtained at even shorter times, say 5 seconds.

(3) The products from the reaction, solid and gaseous, are cooled and reduced in pressure. The resulting liquids are distilled to separate a distillate product oil with an end point of less than 200° C. The liquid remaining after the distillation is a distillable oil which may be easily removed from the small amount of unreacted coal by simple distillation, decantation or filtration. This oil is recycled to produce paste for introducing additional coal. The product oil is gasoline with an end point of 200° C. The gasoline meets all specifications for premium grade motor fuel, being highly aromatic in character and showing excellent stability.

The applicant's process thus shows a radical and greatly improved departure from the prior art. No objectionable heavy oil or asphalt is produced. The distillable oil utilized to make a paste with coal is easily separable from the coal, ash, catalyst and other solid matter. The product oil can be directly sold as a premium grade specification gasoline without further hydrogenation or other expensive treatment. Further, the conversion of the coal is almost complete, being over 94% and over 50% of the coal is converted to liquid product. Several examples of the process are listed illustrating the type of product obtained, the necessary combinations of conditions and the yields possible. Both continuous and batch experiments are illustrated.

EXAMPLE 1

100 grams of Rock Springs, Wyoming, coal neutralized with sulfuric acid and impregnated with ammonium molybdate equivalent to 1 wt. percent molybdenum based on coal was mixed with 115 grams of a distillable oil obtained by a previous hydrogenation of coal. The mixture was hydrogenated in a batch autoclave at 500° C., 7000 p. s. i. g. (475 atmospheres) for 15 minutes. The products were distilled and a yield of 42.5 grams of light oil obtained with an end point of less than 300, the remainder consisted of 115 grams of distillable oil suitable for introducing a second batch of coal, 8.7 grams of solid matter which easily separated from the distillable oil, and 42.5 grams of hydrocarbon gas. This hydrocarbon gas was sufficient to provide a feed material for the production of all hydrogen needed in the reaction. This is done by reforming the hydrocarbon gas with steam with or without oxygen, according to this type of reaction:



An excess of 17.5 grams of hydrocarbon gas is available for sale. The light oil boiling in the gasoline range contained over 50 percent aromatics, 38 percent naphthenes and less than 12 percent paraffins, indicating a high octane rating. The presence of nitrogen was less than 0.15% and no sulfur was found, indicating excellent stability.

EXAMPLE 2

A mixture of (1) 40% coal impregnated with ammonium molybdate equivalent to 1 wt. percent molybdenum based on coal and (2) 60% distillable oil obtained by the hydrogenation of coal, was continuously pumped, together with hydrogen gas, into a 40 ft. tube maintained at 525° C. and 600 atmospheres pressure at a rate so that the residence time of the coal-oil-hydrogen mixture was about 15 seconds. The product obtained in this manner was cooled, reduced in pressure and distilled. A gasoline production of 56.4% by wt. of coal was obtained. Sufficient distillable oil was produced to prepare a paste

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with additional coal. Sufficient hydrocarbon gas was produced to supply all hydrogen requirements of the process. Continuous operation was maintained for more than 8 hours.

A light oil prepared under conditions described in Example 2 was subjected to detailed analysis. The following important chemicals and their quantities were discovered.

	Wt. percent
Benzene	18.6
Toluene	31.7
Xylenes and ethyl benzenes	24.5
C ₉ aromatics	6.9
Naphthenes	17.1
Paraffins	1.2
	100.0

The large quantity of aromatics present indicate the possibility of using this process to prepare these valuable compounds for which a tremendous demand exists.

The following data presents significant data for this run.

Hydrogenation of Wyoming coal

	Wt. in gm.	Hydrogen	Carbon	Nitrogen	Sulfur	Oxygen
In:						
Coal	37.75					
Oil	62.25	8.35	82.91	1.28	0.81	6.65
	100.00					
Out:						
Benzene insolubles	2.2	0.05	1.64	0.05	.29	0.17
Oil	83.43	8.16	75.07	.15	0.01	.04
CH ₄	8.27	2.07	6.20			
H ₂ S	0.54	0.03			.51	
NH ₃	1.31	.23		1.08		
H ₂ O	4.99	.55				
		11.09	82.91	1.28	0.81	4.44
H ₂ consumed		2.74				

Gasoline production: 83.43-62.25=21.18 oil=56.1 wt. percent on coal and 25.5 percent on total oil.

Hydrogen balance: $\text{CH}_4 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} = \text{CO}_2 + 3\text{H}_2$
8.27 3.10

The process described and illustrated by examples represents a novel method for the production of premium motor fuel and/or aromatic chemicals from coal in one hydrogenation step. This is accomplished by a combination of certain critical variables consisting of a high temperature (not less than 500° C.), an elevated pressure (not less than 450 atmospheres), an active catalytic material such as compounds of nickel, tin or molybdenum, and short residence time in the reaction zone (less than 15 minutes). To point out the importance of the particular and critical nature of this combination a consideration of the chemistry of the coal hydrogenation reaction is helpful. The hydrogenation of coal may be considered as two competing reactions, one an undesirable thermal reaction, and the other a desirable reaction between coal and hydrogen. At the normal reaction time of one hour an increase in temperature above 480° C. results in an undesirable formation of coke to the detriment of the product. However, when the applicant utilized the combination of active catalytic materials, higher pressure, and a large decrease in reaction time, the undesirable effects of high temperature were avoided and in addition the characteristics of the product oils were radically altered. Instead of an oil containing a sizeable fraction of high boiling pitch and asphalt a product oil low in nitrogen compounds and free of sulfur was produced. As illustrated above, large quantities of valuable chemicals were present in this oil.

It is instructive to consider also the ultimate analysis

of coal, our starting material. Rock Springs coal has the following ultimate analysis:

Ash	Moisture	Hydrogen	Carbon	Nitrogen	Sulfur	Oxygen
5.62	3.32	4.59	69.43	1.60	1.76	13.68

If we could remove all the ash, moisture, nitrogen, sulfur, and oxygen we would have a material containing 6.20% hydrogen, 93.80% carbon and representing about 74% of the original coal. To convert this material to an aromatic oil in the gasoline boiling range the hydrogen content would have to be increased to approximately 11 wt. percent. If, on the other hand, we remove sufficient carbon from the material above, we would obtain approximately 56% of the original coal as gasoline, and this would require a removal of approximately 20% of the carbon content of the original coal. One might depict this process as one which removes carbon in the form of hydrocarbon gas, leaving a product oil free of undesirable nitrogen, sulfur and oxygen. The hydrocarbon gas production can be balanced against the requirements of the process for hydrogen since the production of hydrogen from hydrocarbon gases by reforming with steam is well known. We thus have a balance between (1) the production of sufficient distillable oil to convey additional coal into the plant and (2) the production of hydrocarbon gas as a source of hydrogen. Hence one could call the process a balanced hydrogenation, self-sufficient in itself, and not dependent on an external source of hydrogen.

I claim:

1. A process for the production of motor fuel of high aromatic content substantially free of asphaltic fraction by the direct hydrogenation of coal in a single stage which comprises the steps of pulverizing the coal, impregnating the pulverized coal with a hydrogenation catalyst selected from the group consisting of ammonium molybdate, nickelous chloride, and stannous chloride, mixing the impregnated coal with an asphalt-free distillate fraction of oil from the hydrogenation of coal, to form a coal-oil paste, subjecting said paste to conversion in the presence of hydrogen for a period of time of about 15 seconds to 15 minutes at a temperature of not less than 500° C. and under a pressure of not less than 475 atmospheres, passing the effluent from said conversion through a cooling zone to separate out a non-asphaltic liquid fraction admixed with solid residues and an overhead fraction com-

prising non-condensable hydrocarbon gases, introducing said non-condensable hydrocarbon gases into a reforming zone, reacting the said gases with steam and oxygen to produce hydrogen, conducting the hydrogen to the conversion step of the process, distilling from said liquid fraction an aromatic gasoline boiling below 200° C., separating from the residual oil the solid residues and recycling the major portion of said residual oil for admixture with fresh impregnated coal supplied to the process.

2. Process of claim 1 wherein the reforming is conducted under operational pressure.

3. A process for the direct production of liquid hydrocarbons boiling essentially in the gasoline range by the destructive hydrogenation of coal in a single stage without concomitant production of asphaltic material which comprises reacting said pulverized coal with hydrogen at a temperature of at least 500° C. and under a pressure of at least 450 atmospheres, for not in excess of fifteen minutes, treating the resulting products by distillation and condensation, recovering therefrom a substantially dry ash-containing residue, a first liquid fraction composed essentially of non-asphaltic oils boiling above 200° C., a second liquid fraction composed essentially of aromatic hydrocarbons boiling in the gasoline range, and a gaseous fraction comprising hydrocarbon gases and hydrogen, converting at least a major portion of the gaseous fraction to hydrogen by reaction with oxygen and steam, to produce all the hydrogen required for the hydrogenation step and recycling the resulting hydrogen to said hydrogenation step.

4. A process according to claim 3 wherein the hydrogenation is conducted continuously.

5. A process according to claim 3 in which the conversion of the gaseous fraction is conducted under a pressure substantially equal to that of the hydrogenation step.

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