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HYDROGEN PRODUCTION FROM AN INTEGRATED COKER GASIFIER SYSTEM

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ABSTRACT OF THE DISCLOSURE

High Conradson carbon feeds are coked to lay down extensive carbon deposit on a gasification catalyst. The coked catalyst is then steam gasified to produce hydrogen. Part of the coked catalyst may be partially burned to produce heat for the coking step.

RELATED APPLICATIONS

This is a continuation-in-part of application Ser. No. 802,800 filed Feb. 27, 1969 and now abandoned.

BACKGROUND OF THE INVENTION

The economic utilization of high Conradson carbon by-products obtained in petroleum processes such as catalytic cracking, vacuum distillation, etc., has long been a problem in the petroleum industry. E. W. Riblett (U.S. Pat. 2,600,430) proposed first coking at high temperatures, and then utilizing the coke produced either in an oil cracking reactor or in a noncatalytic gasification reactor. The cracked product from the oil cracking reactor or the synthesis gas produced from the gasification was recovered for use as fuel or for use in further refining processes. The primary obstacle in such processes is the extremely high temperature that must be maintained. In order to maintain the temperature, heat had to be added into the reactors. Such a requirement is very costly and makes such processes noneconomical.

Another problem in the petroleum industry has been the need to obtain hydrogen for use in the refining processes. Therefore, a process which could economically utilize high Conradson carbon by-products to produce hydrogen would be a significant advance in the petroleum industry.

SUMMARY OF THE INVENTION

It has now been found that high Conradson carbon feeds can be economically employed in low temperature, integrated coking/catalytic gasification process to produce hydrogen. More specifically, it has been found that by depositing metal supported gasification catalyst in a coking reactor to be contacted with the coke produced in the coking reactor, and then transferring the coke gasification catalyst to a steam gasification reactor, hydrogen may be economically produced. Most specifically, it has been found that nickel-uranium or thorium deposited on a bauxite gasification catalyst deposited in a fluid coking reactor to be contacted with the coke produced in the fluid coking reactor, and transferring the coked nickel-uranium or thorium deposited on a bauxite gasification catalyst to a burner reactor to provide heat for the coking reactor and to raise the temperature of the coked gasification catalyst to the desired temperature, and then transferring the heated coked gasification catalyst to the gasification reactor can economically produce hydrogen.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The drawing is a schematic representation of the preferred embodiment of the invention.

Referring now to the drawing, a high Conradson carbon and preferably high metal content feedstock is introduced into the upper portion of coking zone 1 by line 2 onto a fluidized bed 3 maintained at a temperature of 850–1050° F., and a pressure ranging from 5 to 150 p.s.i.g. The fluid bed preferably consists of particulate catalyst particles which may be any type of gasification catalyst known in the art, but which is preferably a Group VIII metal oxide, such as nickel or cobalt oxide, deposited on a suitable support. The support may contain from 0.5 to 5 percent of the active catalyst. The catalytic support may be either gamma alumina, bauxite, or activated clay. Other suitable catalysts include metal oxides of Group VII–B such as manganese oxide, Group V–B such as vanadium oxide, rare earths, thorium oxide and U₃O₈ combined or not with the above metal oxides on such basis.

The feed is preferably a low value, high-boiling residuum of about –10 to +20° API gravity, about 5–50 wt. percent or higher Conradson carbon, containing from 50 to 1000 p.p.m. of metal, such as nickel, vanadium and the like and boiling above about 900–1200° F. However, any stock having a Conradson carbon above 5 may be used. The particules of catalyst are maintained as a fluid bed by the upward passage of a fluidizing gas such as steam which enters the lower portion of coking zone 1 through line 4. The contact of the heavy feed and the catalyst results in the feed being converted to lower boiling vaporous hydrocarbons and to coke which is deposited on the gasification catalyst along with the metal in the feed. The vaporous hydrocarbons and steam are removed through line 5 while the fluidized catalyst particles descend in bed 3 and are withdrawn from the lower portion of coking zone 1 through line 8 and are introduced into coke burner 9 wherein part of the coke from the gasification catalyst is oxidized to produce carbon oxide by means of an oxygen-containing gas such as air introduced through line 10 with a resultant rise in temperature of the catalyst-coke mixture to at least 1250° F. and under preferred operating conditions of 1350–1500° F. The temperature at which the reaction in the oxidation zone is effected may be controlled by regulating the quantity of oxygen-containing gas, by regulating the temperature of the oxygen-containing gas, and by regulating the amount of coke present in the coke burner. It is also controlled by the amount of metal deposited on the catalyst which in turn is determined by the metal content of the feed. The more common of the metallic contaminants are nickel and vanadium, often existing in concentration in excess of 50 p.p.m., although other metals including iron, copper, etc., may be present. These metals may exist within the feed in a variety of compositions such as porphyrin structure. Additional catalytic metal components may be added with the feed as metal oxides or sulfides or as soluble salts. Usually, however, they are present in the form of high molecular weight organo-metallic compounds, including metal porphyrins and various derivatives thereof. The presence of these metals on the catalyst, particularly nickel, have an additional catalytic effect which in turn enables the gasification step to be carried out at lower temperatures. The amount of oxygen in the oxygen-containing gas may be regulated by blending inert gaseous material, such as steam, nitrogen or flue gas, with the air or oxygen used. If desired, the amount of coke burned may be controlled by the introduction of liquid or gaseous fuel to be burned instead of the coke.

A portion of the heated catalyst and coke in burner 9 may be returned to coking zone 1 by line 6 to control the temperature therein. Nitrogen, excess air, oxygen and other gases are removed from coke burner 9 through line 11. Care must be made to insure that all nitrogen is

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removed since it is highly desirable to prevent the introduction of any nitrogen into the gasifier 7. Therefore it should be removed prior to the introduction of the coked-metal contaminated catalyst to the gasifier. The presence of nitrogen will contaminate the hydrogen gas product, requiring an extra costly step for its removal.

It is also highly important that the production of methane in the gasification reactor be as low as possible. The production of methane results in less hydrogen being produced, because the hydrogen is being used to produce the methane. Preferably, there should be less than 2 mol percent on a dry basis of methane produced.

The remaining heated catalyst and coke particles are withdrawn from burner 9 through line 12 and supplied to the top of gasifier 7 with the particles dropped into fluidized bed 13 supplying heat thereto and maintaining the temperature therein between 1200 and 1450° F. However, whenever desired, coked catalyst may be with-

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ing operation. The coked catalyst would then be removed from the coking drum and transferred to a gasifier.

The following examples are presented as specific illustrations of the present invention. All quantities are expressed in the specification and claims on a weight basis unless stated otherwise.

EXAMPLE 1

A Bachaquero residuum having an API gravity of 13.5°, a Conradson carbon content of 11 wt. percent, metals content of 50 p.p.m. of Ni and 400 p.p.m. V and having an initial boiling point of 450° F. was contacted with various catalytic solids to deposit 8 to 22 wt. percent carbon. The catalytic support plus carbon was then steam gasified at temperatures of 1300 to 1400° F. Synthesis gas from 10 gram charges (catalyst plus carbon) was obtained which has the following mol. percent composition on a dry gas basis:

	Ni-U/ bauxite ¹	Ni-Th/ bauxite ²	Ni-U/ α -Al ₂ O ₃ ¹	Fe ₂ O ₃	Baux- ite ³	α -Al ₂ O ₃
Catalyst:						
Weight percent carbon.....	13.5	14.3	21.6	15.0	13.3	10.1
Gasification tempera- ture, ° F.....	1,350	1,355	1,360	1,350	1,350	1,345
Gas rate, s.c.v./15 minutes.....	0.09	0.099	0.047	0.066	0.047	0.034
Gas composition, molecular percent						
H ₂	61.5	59.4	57.1	65.8	63.5	62.1
CO.....	11.5	13.2	19.0	4.9	7.6	17.4
CO ₂	25.6	26.0	21.6	27.6	26.6	18.4
CH ₄	1.4	1.4	2.3	1.7	2.3	2.1

¹ Ni plus U concentration of 1.5 and 0.5 weight percent, respectively.

² Ni plus Th concentration of 1.5 and 0.5 weight percent, respectively.

³ No metal added to the base material.

⁴ Gas rate obtained for 60 minutes.

drawn through line 14 in order to prevent too high a buildup of metals in the system. The reactions in the gasifier may be effected at substantially atmospheric pressure or pressures up to 150 p.s.i.g., if desired, although it is preferable to operate at substantially atmospheric pressure in order to prevent the saturating effect of hydrogen on any volatile conversion products in the gasifier. Steam from fluidizing bed 13 and for gasifying the coke on the catalyst is introduced through lines 17 and 18.

Hydrogen-producing reactions are not simple and may require particular conditions to be maintained in the gasifier in order to produce the most desirable products. The various reactions between water and carbon produce principally hydrogen, carbon dioxide and carbon monoxide, with formation of minor amounts of methane and possibly heavier hydrocarbons. Each of the reactions operates independently with regard to the equilibrium established at each temperature. However, the reactions are interrelated in that variations of the equilibrium between products and reactants in one reaction will change the concentrations of reactants and products of the other reaction. The gas composition leaving vessel 7 through line 15 has the following typical composition by mol percent on a dry basis:

H ₂	57
CO	16
CO ₂	26
CH ₄	1.4

The solid catalyst particles which are coke depleted descend to the lower portion of gasifying zone 7 and are withdrawn through line 19 and returned to coking zone 1 through line 20.

From the above description it is evident that a process has been provided for economically coking a heavy residual or other oil have a Conradson carbon above 5 whereby coke is laid down on the gasification catalyst and used to produce hydrogen by reaction with steam.

While the above process has been described in connection with a fluid type process, it is obvious, of course, that other techniques may be used. For example, the coke may be laid down on the catalyst in a delayed cok-

The above data show that gasification rates are increased two-fold with metal promoters on bauxite as the base material at conditions evaluated. The bauxite base is four-fold better than the low surface area base such as α -alumina. Metals addition also increases the gasification rate when using the low surface area α alumina base. Lower methane formation is indicated for the metal-bauxite catalyst. It is desirable to produce minimum methane (<2%) since it becomes an impurity in the hydrogen stream after the CO shift reaction and eventual CO₂ removal operation.

EXAMPLE 2

Fluid coke deposition on a catalytic support, partial combustion to raise the temperature of the catalytic solids plus carbon above the desired steam gasification temperature and finally steam gasification of carbon from the catalytic support as described in the drawing were carried out to demonstrate the process for hydrogen manufacture. For the fluid process the particle size of the catalyst was adjusted to a 100-200 mesh. Bachaquero residuum feed used in Example 1 was contacted with catalytic fluid solids consisting of Ni-U/bauxite at 950° F. until a carbon level of 12.5 wt. percent was realized. The catalytic solids plus carbon was burned at 1500° F. with controlled quantity of air such that about 20% of the carbon was consumed. The catalytic support plus 10 wt. percent carbon was then contacted with steam at 1400° F. such that about 30% of the available carbon was gasified. Synthesis gas for the unburned and burned Ni-U/bauxite-carbon mixtures when gasifying at 1400° F. are shown below.

	Ni-U/Bauxite carbon mixture	
	Before the burner	After the burner
Gasification temperature, ° F.....	1,400	1,400
Gas rate, s.c.f./15 minutes.....	0.122	0.06
Gas composition, molecular percent:		
H ₂	37.9	68.1
CO.....	11.0	10.9
CO ₂	48.7	20.9
C ₁	2.4	0.1

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Although lower gasification rates were obtained with the preoxidized catalytic-carbon mixture, the hydrogen concentration is considerably better with one-half to one-third less methane impurity as that obtained for the freshly deposited carbon before the burner operation. After conventional water-gas shift of the CO and coupled with CO₂ removal, a >95% hydrogen stream is indicated for the integrated process.

EXAMPLE 3

Fluid operation was also carried out whereby carbon from Bachaquero residuum feed employed in Example 1 was deposited on MnO solids of 100–200 mesh at 950° F. such that a carbon level of 14.6 wt. percent was realized. The MnO-carbon mixture was then steam gasified at 1400° F. Gasification rate was equivalent to that obtained with the preoxidized Ni-U/bauxite-carbon mixture shown in Example 2. A yield of 0.055 s.c.f. 15 min. of synthesis gas from a 10 gram charge (catalyst plus 14.6 wt. percent carbon) was obtained which had the following composition, mol. percent on dry gas:

H ₂	65.9
CO	7.1
CO ₂	24.9
C ₁	2.1

EXAMPLE 4

A Bachaquero residuum having an API gravity of 13.5°, a Conradson carbon of 11% and having an initial boiling point of 450° F. was contacted with manganese oxide as catalyst under delayed coking type operations at a temperature of 950° F. such that 15 wt. percent coke was deposited on the catalyst. The catalyst was then steamed at 1300° F. for fifteen minutes with excess steam so that about 50% of the available carbon was gasified. A yield of 0.132 s.c.f. of synthesis gas from a ten gram charge (catalyst plus 15 wt. percent carbon) was obtained which had the following composition in mol. percent on dry gas:

H ₂	60.3
CO	12.3
CO ₂	25.8
CH ₄	1.6

The nature of the present invention having thus been fully described and illustrated and specific examples of the same given, what is claimed as new, useful, and unobvious and desired to be secured by Letters Patent is:

1. An integrated coking and steam gasification process for producing liquid hydrocarbon products and a low methane, hydrogen rich gaseous stream which comprises:

(a) treating a carbonaceous material having a Conradson carbon residue of at least 5 wt. percent and a supported Group V–B, VII–B or VIII metal oxide steam gasification catalyst in a coking zone operating at coking conditions in the absence of additional hydrogen to produce liquid hydrocarbon products and coke, a portion of which is deposited on said catalyst in an amount to provide between 8 and 22 wt. percent carbon thereon; and

(b) contacting the resultant coked catalyst with steam in a gasification zone operating at temperatures between 1250 and 1500° F. and a pressure between atmospheric and 150 p.s.i.g. to produce a low methane, hydrogen rich gaseous stream.

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2. The process of claim 1, wherein the catalyst support is selected from the group consisting of gamma alumina, bauxite and activated clay.

3. The process of claim 1, wherein said catalyst is nickel and uranium oxides deposited on bauxite.

4. A process according to claim 1 wherein said metal oxide is manganese oxide.

5. A process according to claim 1 wherein said metal oxide is nickel oxide.

6. A process according to claim 5 wherein uranium or thorium is also supported with said nickel oxide.

7. A process according to claim 5 wherein said catalyst is Ni-Th on a bauxite support.

8. A continuous integrated fluid coking steam gasification process for producing liquid hydrocarbon products and a low methane, hydrogen rich gaseous stream which comprises:

(a) treating a carbonaceous material having a Conradson carbon residue of at least 5 wt. percent and a supported Group V–B, VII–B or VIII metal oxide steam gasification catalyst in a coking zone operated at temperatures between 850 and 1050° F. and pressures between atmospheric and 150 p.s.i.g. in the absence of additional hydrogen to produce liquid hydrocarbon products and coke, a portion of which is deposited on said catalyst in an amount to provide between 8 and 22 wt. percent carbon thereon;

(b) contacting a portion of the resultant coked catalyst with steam in a gasification zone operating at a temperature between 1250 and 1500° F. and a pressure between atmospheric and 150 p.s.i.g. to produce a low methane, hydrogen rich gaseous stream; and

(c) recycling said steam treated catalyst to said coking zone.

9. A process according to claim 8 wherein a portion of said coked catalyst is heated to a temperature of at least 1250° F., and a first portion of said heated coked catalyst is recycled to said coking zone and a second portion of said heated coked catalyst is treated in said gasification zone.

10. A process according to claim 8 wherein said metal oxide is manganese oxide.

11. A process according to claim 8 wherein said metal oxide is nickel oxide.

12. A process according to claim 8 wherein said catalyst is Ni-Th on a bauxite support.

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HERBERT LEVINE, Primary Examiner

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