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Hamner

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[54] **STEAM GASIFICATION OF COKE**

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[21] Appl. No.: **264,056**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 45,096, June 9, 1970, abandoned.

[52] **U.S. Cl.** ..... **208/46,** 48/197 R, 208/127, 208/131

[51] **Int. Cl.** **C10g 9/32**

[58] **Field of Search** ..... 208/127, 131, 46; 48/197 R

[56] **References Cited**

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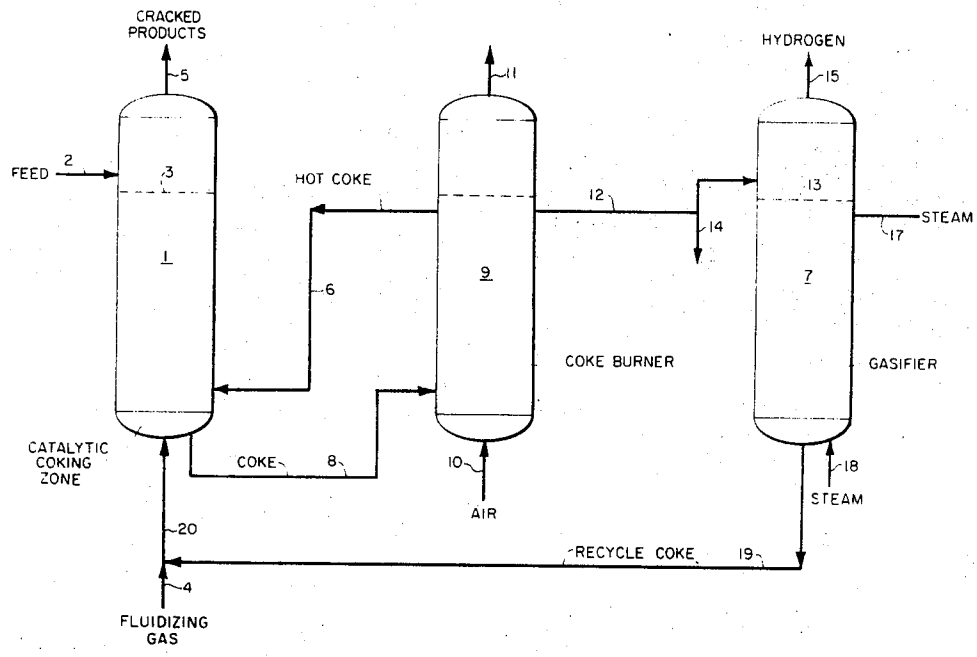
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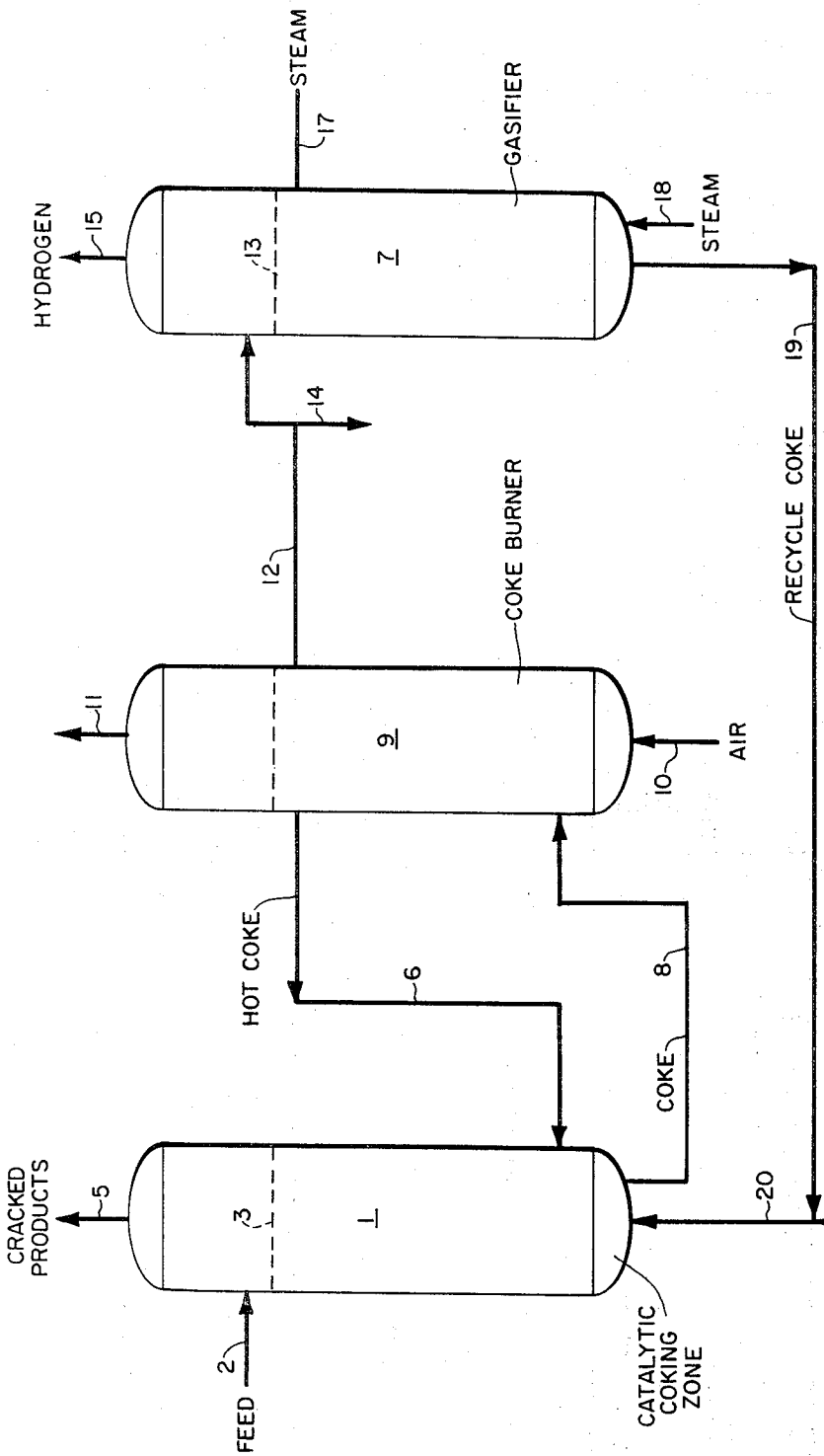
Primary Examiner—Herbert Levine

[57] **ABSTRACT**

A heavy carbonaceous material having a Conradson carbon residue of at least 5 wt. % is coked in the presence of an alkali metal compound to produce an active surface carbon containing the alkali metal compound. The coke is then partially gasified to produce a hydrogen-containing gas and the remaining coke is recycled to the coking zone as seed coke therein.

22 Claims, 1 Drawing Figure





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STEAM GASIFICATION OF COKE

RELATED APPLICATIONS

This application is a continuation-in-part of Ser. No. 45,096, filed June 9, 1970 by Glen P. Hamner now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to a combination coking and steam gasification process to produce a hydrogen-containing gas and a method of preparing an alkali metal promoted coke for use in the steam gasification process.

The use of alkali metal compounds in coking hydrocarbon oils to increase the hydrogen content of a coker gaseous product is known (see U.S. Pat. No. 3,179,584). Alkali metal compounds are also known to increase hydrogen production when solid carbonaceous material is steam gasified.

It has now been found that a hydrogen containing gas can be produced at high gasification rates at temperatures between 1,000° and 1,500° F. and that liquid coker products having a reduced heavy metal content can be obtained by a combination coking and gasification process wherein an alkali metal containing coke product produced in a coking zone is subsequently steam treated in a separate gasification zone and the resulting partially gasified alkali metal containing coke is recycled to the coking zone as seed coke on which additional coke is deposited.

It has also been found that a particularly effective method for incorporating the alkali metal compound in the coke is to coke a hydrocarbon feedstock in the presence of an alkali metal compound.

Further advantages of this invention will become apparent from the ensuing description of the invention.

SUMMARY OF THE INVENTION

In accordance with one embodiment of the invention, there is provided a method of preparing an alkali metal-containing coke for use in the steam gasification process which comprises (a) mixing a heavy carbonaceous material having a Conradson carbon residue of at least 5 wt. % with an alkali metal compound and coking the mixture in a coking zone maintained at a temperature between about 750° and 1,150° F. and at a pressure between about 5 and 150 psig to produce vaporous products and coke containing alkali metal compound; (b) passing at least a portion of said coke containing alkali metal compound to a separate gasification zone maintained at a temperature between about 1,000° and 1,500° F. to contact steam introduced into said gasification zone and thereby convert at least a portion of said coke to gaseous products and to obtain a partially gasified coke containing alkali metal compound; (c) passing said partially gasified coke containing alkali metal compound to the coking zone of step (a); and (d) coking an additional portion of said heavy carbonaceous material in said coking zone whereby a portion of said additional heavy carbonaceous material is converted to additional coke and said additional coke deposits on the partially gasified coke containing alkali metal compound.

In accordance with another embodiment of the invention, there is provided a process for steam gasifying coke which comprises (a) mixing a heavy carbonaceous material having a Conradson carbon residue of at least 5 wt. % with an alkali metal compound and coking the mixture in a coking zone maintained at a temperature between about 750° and 1,150° F. and at a pressure between about 5 and 150 psig to produce a vaporous product and coke containing alkali metal compound; (b) passing at least a portion of said coke containing alkali metal compound to a separate gasification zone maintained at a temperature between about 1,000° and 1,500° F. to contact steam introduced in said gasification zone and thereby convert at least a portion of said coke to a gaseous product and to obtain a partially gasified coke containing alkali metal compound; (c) passing said partially gasified coke containing alkali metal compound to the coking zone of step (a); (d) coking an additional portion of said heavy carbonaceous material in said coking zone whereby a portion of said additional heavy carbonaceous material is converted to additional vaporous product and to additional coke which deposits on the partially gasified coke containing alkali metal compound; and (e) recovering the additional vaporous product.

Furthermore, the coke coated partially gasified coke containing alkali metal compound resulting from step (d) may be passed to the steam gasification zone to gasify a portion of the coke and the resulting steam treated coke containing alkali metal compound may be returned to the coking zone to deposit additional coke on the coke containing alkali metal compound product for use in the steam gasification zone.

In accordance with a preferred embodiment of the invention, the gaseous product of the gasification zone is a high purity hydrogen-containing gas.

BRIEF DESCRIPTION OF THE DRAWING

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

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring to the drawing, a high Conradson carbon and preferably a high metal content feedstock to which has been added an alkali metal compound is introduced into the upper portion of catalytic coking zone **1** by line **2** onto a fluidized bed of coke particles **3** maintained at a temperature of 750°–1,150° F. and under a pressure ranging from about 5 to 150 psig. Suitable alkali metal compounds include any compounds soluble or dispersible in the feed such as the hydroxide, carbonate, sulfide or silicate or organic salts such as phthalate, oxalate, acetate, etc. of potassium, sodium, lithium, rubidium and cesium. The preferred catalysts are the alkali metal carbonates and silicates. The carbonate may be added as such to the feed or an alkali metal compound which is more soluble than the carbonate and convertible to the corresponding carbonate under the operating conditions and in the presence of the reaction products, such as CO_2 produced in the reaction zone can be initially mixed with the feed. If sulfur is present, some alkali metal sulfide may also be formed. Furthermore, any alkali metal silicate formed as a result of the corrosive effect of the alkali metal compound on the refractory lining of the reactor may also be present as effective catalyst. A preferred catalyst is therefore the alkali metal silicate since it will not react with the refractory lining of the reactor.

The feed is preferably a low value, high-boiling residuum of about −10 to +20° API gravity, about 5 to 50 wt. % or higher Conradson carbon and boiling above about 900° to 1,200° F. However, any stock having a Conradson carbon above 5 may be used. The particles of coke 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 coke results in the feed being converted to lower boiling vaporous hydrocarbons and to coke containing an alkali metal compound. The resulting coked alkali metal compound is deposited on the coke particles in the fluid bed along with the metals in the feed. The vaporous hydrocarbons and steam are removed through line **5** while the fluidized coked alkali metal compound containing coke particles descend in bed **3** and are withdrawn from the lower portion of coking zone **1** through line **8** and are introduced into the top of coke burner **9** wherein part of the coke is oxidized to produce carbon oxides by means of an oxygen-containing gas such as air introduced through line **10** with a resultant rise in temperature of the coke to at least 1,250° F. and under preferred operating conditions to 1,350° to 1,500° 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 burner. 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 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 removed since it is highly desirable to prevent the introduction of any nitrogen into the gasifier **7**.

The remaining heated coked alkali metal compound containing coke particles are withdrawn from burner **9** through line **12** and supplied to the top of gasifier **7** where the particles drop into fluidized bed **13** supplying heat thereto and maintaining the temperature therein between 1,000° and 1,500° F., preferably between 1,100° and 1,400° F. However, whenever desired, coke may be withdrawn through line **14**. The reactions in the gasifier may be effected at substantially atmospheric pressure and pressures up to 150 psig, 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 for fluidizing bed **13** and for gasifying the coke is introduced through lines **17** and **18**.

It is highly important that no nitrogen be present in the gasifier. Hence care must be maintained to remove it prior to the introduction of the coked alkali metal compound containing coke to the gasifier. The presence of nitrogen will contaminate the synthesis gas product, requiring an extra costly step for its removal.

The partially gasified coke particles containing the alkali metal compound descend to the lower portion of gasifying zone **7** and are withdrawn through line **19** and returned to coking zone **1** through line **20** as seed coke therein.

It is important to remember that the presence of the alkali metal compound in the gasifier enables the gasification to take place at a much lower temperature. When this partially gasified coke of increased surface area known as seed coke, is recycled, the resulting coke, though not increased in yield, gives increased gas yields on subsequent gasification. This gas contains over twice as much CO_2 which is easily removed, about half as much CO and less than half as much methane. It also results in a reduction in metals content of the liquid coker products which in turn improves any subsequent hydrotreating operation on these liquid products. Catalytic seed coke (increased in surface area) gives reduced gas make and increased distillate in the coking zone **1** operation.

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 with the alkali metal catalyst in a delayed coking operation. The coke containing alkali metal catalyst would then be removed from the coking drum, ground and transferred to a gasifier. To make the process continuous two coking drums are used. While coking is taking place in one, coke is being removed from the other. Delayed coking is carried out above 650° F. preferably between 850° and 1,000° F. and at a pressure between about 5 and 150 psig.

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

Bachaquero vacuum residuum with and without 5 wt. % of potassium hydroxide was coked in a laboratory 1-inch diameter vycor reactor at a temperature of 950° F., 10 psig for 2 hours to obtain 8–10 gram samples of coke. The temperature was then raised to 1,200° F. for 15 minutes to remove the last traces of the heavy oil fraction. The resulting coke containing the alkali metal component or not was ground to 65 mesh and 8 gram samples were gasified with steam at different temperatures. The following data were obtained.

STEAM GASIFICATION OF BACHAQUERO DELAYED COKE WITH POTASSIUM HYDROXIDE

(Excess steam with 8-gram sample)

Run number	1			2	3	4		5			6			7
Percent potassium on coke	5			None	1	None		None			1			1
Gasification conditions:														
Temperature, ° F	1,180			1,190	1,175	1,170		1,370			1,350			1,350
Time, hours	1st	2d	6th	1st	3d	1st	2d	4th	1st	2d	[1] 3d			
Gas rate, s.c.f./hr.	0.076	0.088	0.007	.118	.134	.010	.073	.046	.062	.624	0.44	.085		0.54
Gas composition, mol. percent:														
H_2	69.3	67.3	66.0	77.4	67.7	67.2	75.1	72.2	61.6	63.2	59.1	61.4	65.5	62.3
CO	2.6	2.4	2.5	5.0	2.3	1.9	4.7	6.1	9.4	9.4	20.6	14.9	5.0	16.2
CO_2	27.3	29.6	31.1	11.9	29.1	30.7	13.7	18.2	27.9	26.2	19.8	23.6	29.3	21.0
C_1	0.8	0.3	0.1	5.7	0.7	0.2	6.4	3.5	1.1	1.2	0.5	0.1	0.2	0.5

[1] All coke gasified.

The above data show that the base coke without a catalyst promoter gave low gasification rates. With potassium hydroxide promoted coke, the gasification rate at 1,180° F. was equivalent to that for the unpromoted coke at 1,370° F. At the higher temperature (1,350° F.) the gasification rate for the first hour with potassium-coke mixture increased tenfold. By the third hour all the promoted coke had been gasified. At the lower temperatures the carbon monoxide concentration was lower for the promoted than for the unpromoted coke.

EXAMPLE 2

The experiment of Example 1 was repeated except that potassium silicate was used as the alkali metal compound promoter. The following data were obtained:

STEAM GASIFICATION OF BACHAQUERO DELAYED COKE WITH POTASSIUM SILICATE

(Excess steam with 8 gram sample)

Run No.	8
% Potassium on Coke	1.2
Gasification Conditions	
Temperature, ° F.	1345
Time, Hours	15 min.
Gas Rate, SCF/Hr.	0.06
Gas Composition, Mol. %	
H_2	74.0
Co	6.8
CO_2	17.6
C_1	1.6

The above data show that potassium silicate is an effective promoter giving a high yield of hydrogen (74%).

EXAMPLE 3

The experiment of Example 1 was repeated except that residuum feed without additional alkali metal compound was coked in the presence of partially gasified coke containing alkali metal compound from a previous steam gasification run. The quantity of partially gasified recycle coke was 10 wt. % based on residuum feed. The coking results from this operation were compared with those obtained without the addition of the seed coke and with the results obtained when using partially gasified coke from an operation in which no alkali metal compound was used in the coking or coke gasification step. The results are set forth below.

COKING OF RESIDUA WITH 10% RECYCLE GASIFIED COKE

(Bachaquero Residua, 400° F. +)

Run	A	B	C
Coke Recycle	None	9.1	9.1
Recycle Coke Source		Catalytic Gasification(1)	Non-Catalytic Gasification(2)
Product Distribution from Coking, Wt. %			
Gas	8.0	7.2	8.3
Liquid Product	79.0	77.9	75.5
Coke	13.0	14.9	16.2
Liquid Product Inspections			
Gravity, °API	25.4	27.4	27.2
Sulfur, Wt. %	1.6	1.7	1.7
Ni and V, ppm	20–50	2 (approx.)	2 (approx.)

(1) Recycle coke from catalytic gasification, K_2CO_3 as promoter, surface area of 250 square meter per gram.
(2) Recycle coke from non-catalytic gasification, surface area of 230 square meters per gram.

STEAM GASIFICATION OF COKE FROM RUN B AND RUN C

(1250°F., 1 hour, 1 W/W/Steam to Carbon, Atmospheric Pressure)
(20 Gram Coke Charge)

Run No.	13	14
Coke Source	Run B (Catalytic Gasified Recycle Coke)	Run C Non-Catalytic Gasified Recycle Coke)
Dry Gas Yield, SCF	0.157	0.041
Dry Gas Composition, Mol. %		
H_2	69.2	77.5
CO	3.0	6.1
CO_2	25.5	10.7
C_1	1.9	4.9
C_2+	0.4	0.8

The above data show that the use of recycled seed coke in the coking step results in a drastic reduction of the metals content of the liquid products from coking. Catalytic seed coke (recycle operation) gave increased distillate yield with a corresponding reduction in gas make and coke production when compared to corresponding non-catalytic recycle systems. The gasification of the coke prepared with the use of alkali metal promoted partially gasified coke as seed coke gives a fourfold increase in steam gasification rate. The gaseous product contains half as much CO and less than half as much methane.

EXAMPLE 4

The liquid product obtained in the coking Run B of Example 3 was subjected to a hydrotreating step using a cobalt sulfide-molybdenum sulfide catalyst on silica stabilized alumina. The following results were obtained.

HYDROTREATING OF COKER DEMETALLIZED LIQUID PRODUCT

Run Number	D	
Coker Liquid Product Source	Coking Run B	
Hydrotreating Conditions (1)		
Temperature, °F.	650	
Pressure, psig	400	
V/V/Hr.	1	
Gas Rate, SCF H_2/bbl.	2000	
Hydrotreated Liquid Product Inspection		Feed-Coking Run B Liquid Product
Gravity, °API	29.0	27.4
Sulfur, Wt. %	0.2	1.7

(1) Co-Mo on silica stabilized alumina catalyst.

The results from the above run show that hydrodesulfurization of the liquid products obtained using seed coke during the coking step resulted in a drastic reduction in the sulfur content of these products. The removal of low molecular weight metal components from the coker distillate improves the catalytic activity maintenance of the hydrodesulfurization catalyst since such metals bring about deactivation of conventional alumina base catalysts normally employed for hydrodesulfurization.

What is claimed is:

1. A method of preparing a coke containing an alkali metal compound for use in a steam gasification process which comprises:

a. mixing a heavy mineral oil having a Conradson carbon residue of at least 5 wt. % with an alkali metal compound and coking the mixture in a coking zone maintained at a temperature between about 750° and 1,150° F. and at a pressure between about 5 and 150 psig to produce vaporous products and coke containing an alkali metal compound;

b. passing at least a portion of said coke containing the alkali metal compound to a separate gasification zone maintained at a temperature between about 1,000° and 1,500° F. to contact steam introduced into said gasification zone and thereby convert at least a portion of said coke to gaseous products and to obtain a partially gasified coke containing the alkali metal compound;

c. passing said partially gasified coke containing the alkali metal compound to the coking zone of step (a) as a separate stream from said mineral oil, and

d. coking an additional portion of said heavy mineral oil in said coking zone whereby a portion of said additonal heavy mineral oil is converted to additional coke and said additional coke deposits on the partially gasified coke containing the alkali metal compound.

2. The process of claim 1, wherein said gasification zone is maintained at a temperature between about 1,100° and 1,400° F.

3. The process of claim 1, wherein said gasification zone is maintained at a pressure between about 0 and 150 psig.

4. The process of claim 1, wherein the alkali metal compound mixed with said heavy mineral oil is potassium silicate.

5. The process of claim 1, wherein the alkali metal compound mixed with said heavy mineral oil is potassium carbonate.

6. The process of claim 1, wherein the alkali metal compound mixed with said heavy mineral oil is potassium hydroxide.

7. The process of claim 1, wherein the alkali metal compound mixed with said heavy mineral oil is potassium sulfide.

8. The process of claim 1, wherein the alkali metal compound mixed with said heavy mineral oil is cesium carbonate.

9. A catalytic process for steam gasifying coke, which comprises:

a. mixing a heavy mineral oil having a Conradson carbon residue of at least 5 wt. % with an alkali metal compound and coking the mixture in a coking zone maintained at a temperature between about 750° and 1,150° F. and at a pressure between about 5 and 150 psig to produce a vaporous product and coke containing an alkali metal compound;

b. passing at least a portion of said coke containing the alkali metal compound to a separate gasification zone maintained at a temperature between about 1,000° and 1,500° F. to contact steam introduced into said gasification zone and thereby convert at least a portion of said coke to a gaseous product and to obtain a partially gasified coke containing an alkali metal compound;

c. passing said partially gasified coke containing the alkali metal compound directly to the coking zone of step (a) as a separate stream from said mineral oil;

d. coking an additional portion of said heavy mineral oil in said coking zone whereby a portion of said additional heavy mineral oil is converted to additional vaporous product and to additional coke which deposits on the partially gasified coke containing the alkali metal compound, and

e. recovering the additional vaporous product.

10. The process of claim 9, wherein a portion of the coke containing alkali metal compound of step (d) is passed to the gasification zone of step (b) to convert a portion of the coke to additional gaseous product.

11. The process of claim 9, wherein said additional vaporous product comprises normally liquid hydrocarbon products having a reduced heavy metals content.

12. The process of claim 10, wherein said additional gaseous product is a hydrogen-containing gas.

13. The process of claim 9, wherein said gasification zone is maintained at a temperature between 1,100° and 1,400° F.

14. The process of claim 9, wherein said gasification zone is maintained at a pressure between 0 and 150 psig.

15. The process of claim 9, wherein a portion of the coke containing alkali metal compound is passed from the coking zone to a heating zone maintained at a temperature of at least about 1,250° F. and a portion of the heated coke containing alkali metal compound is recycled to the coking zone to provide a portion of the heat needed in the coking zone.

16. The process of claim 9, wherein the alkali metal compound mixed with said heavy mineral oil is potassium silicate.

17. The process of claim 9, wherein the alkali metal compound mixed with said heavy mineral oil is potassium hydroxide.

18. The process of claim 9, wherein the alkali metal compound mixed with said heavy mineral oil is potassium carbonate.

19. The process of claim 9, wherein the alkali metal compound mixed with said heavy mineral oil is potassium sulfide.

20. The process of claim 9, wherein the alkali metal compound mixed with said heavy mineral oil is cesium carbonate.

21. The process of claim 9, wherein said coking zone is a fluid coking zone.

22. The process of claim 9, wherein said coking zone is a delayed coking zone.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,803,023 Dated April 9, 1974

Inventor(s) Glen P. Hamner

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

On top page of the patent change "Filed: April 19, 1972" to read --Filed: June 19, 1972--.

Signed and sealed this 3rd day of September 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
* U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334.