

- [54] MANUFACTURE OF
METHANE-CONTAINING GASES USING AN
INTEGRATED FLUID COKING AND
GASIFICATION PROCESS**

3,684,689	8/1972	Patton et al.....	48/197 I
3,732,085	5/1973	Carr et al.....	48/197 I

- [75] Inventor: **John W. Herrmann**, Mountainside,
N.J.

FOREIGN PATENTS OR APPLICATIONS		
948,270	1964	United Kingdom

- [73] Assignee: **Exxon Research and Engineering Company, Linden, N.J.**

Primary Examiner—S. Leon Bashore
Assistant Examiner—Peter F. Kratz
Attorney, Agent, or Firm—M. L. Gibbons

- [22] Filed: Oct. 18, 1973

- [21] Appl. No.: 407,566

- [52] **U.S. Cl.**..... **48/214**; 48/197 R; 48/206;
208/127; 260/449 M
- [51] **Int. Cl.²**..... **C10K 3/06**
- [58] **Field of Search**..... 48/197 R, 202, 206, 211,
48/212, 213, 214, 215; 208/46, 50, 51, 53,
106, 108, 127; 201/17, 31; 260/449 M

- [56]
- References Cited**

UNITED STATES PATENTS

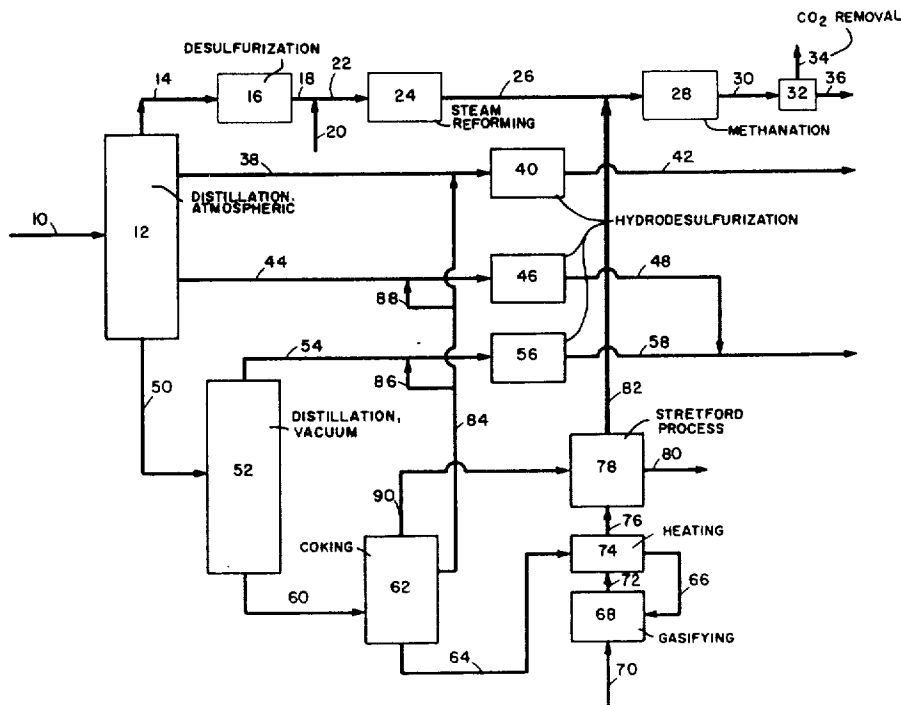
2,605,215	7/1952	Coghlan.....	201/31
-----------	--------	--------------	--------

- [57]

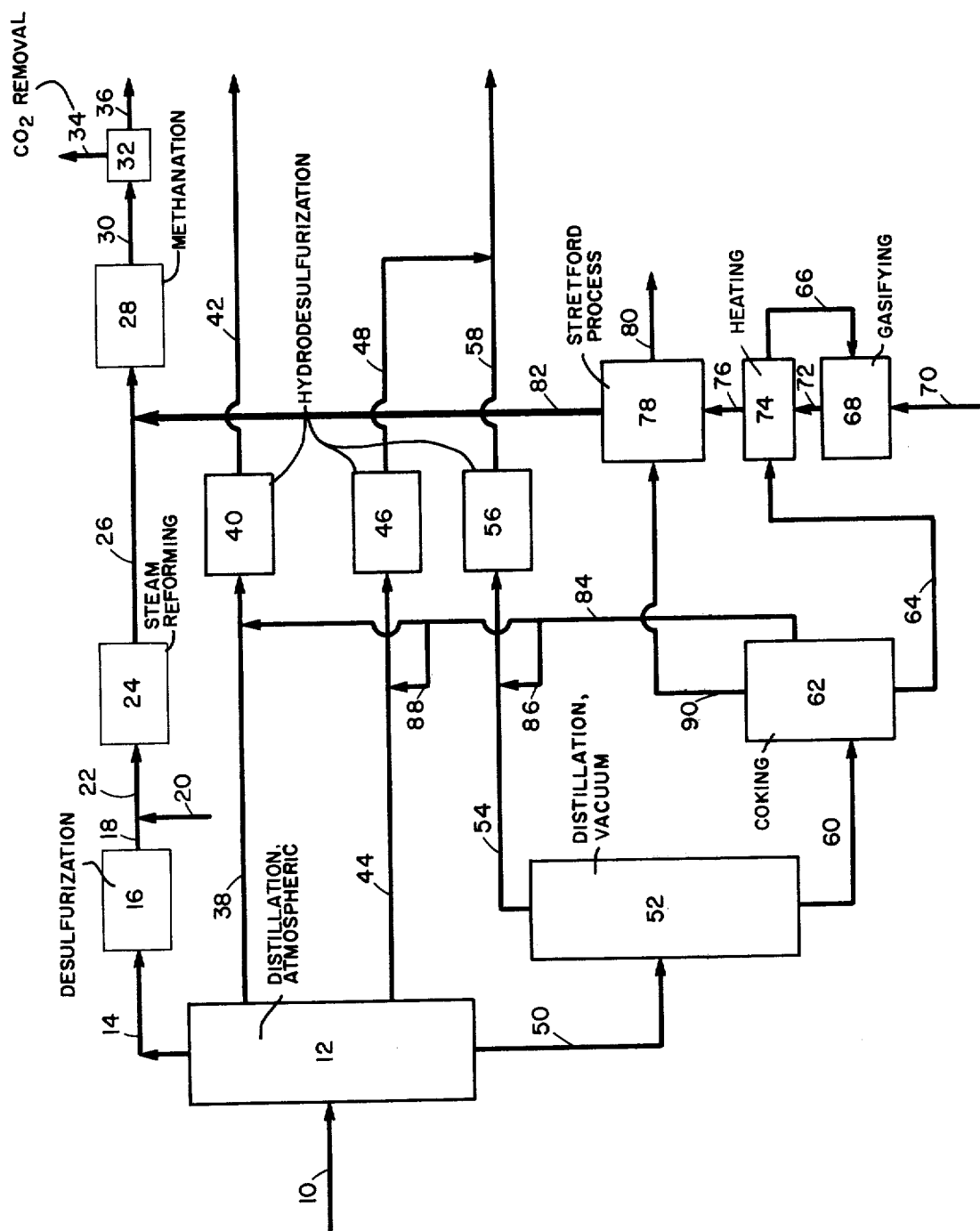
ABSTRACT

A petroleum refinery process for converting sulfur containing crude oil into a methane-containing gas and low sulfur oil, wherein the gaseous effluent of an integrated fluid coking and coke gasification process is desulfurized and utilized as incremental feed for the methanation stage of a naphtha gasification process.

- 5 Claims, 1 Drawing Figure**



Figure



MANUFACTURE OF METHANE-CONTAINING GASES USING AN INTEGRATED FLUID COKING AND GASIFICATION PROCESS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to a petroleum refining process for converting sulfur-containing crude petroleum oil into a methane-containing gas and a low-sulfur fuel oil.

2. Description of the Prior Art

It is known that methane-containing gases useful as fuel gases, town gas and substitute natural gas can be produced by catalytic steam reforming of hydrocarbon feedstocks, including naphtha, such as for example, the Catalytic Rich Gas (CRG) process developed by the British Gas Council, the GASINTHAN process developed by BASF/Lurgi; the Methane Rich Gas (MRG) process developed by Japan Gasoline Co. (see, for example, Hydrocarbon Processing, April 1973, pages 118-120). The Catalytic Rich Gas process and modifications thereof are shown in U.S. Pat. No. 3,415,634; U.S. Pat. No. 3,625,665 and U.S. Pat. No. 3,642,460, the disclosures of which are incorporated herein by reference.

Various refinery schemes have been developed to provide gases containing a high proportion of methane and low sulfur fuel oils. In the refinery schemes heretofore proposed, methane-containing gases, such as, substitute natural gas are obtained from naphtha and lighter fractions of the crude oil. The light distillate may be used as turbine fuel and the material boiling above about 500°F. is generally desulfurized and used as fuel. In most of the processes heretofore employed, however, the heavy hydrocarbons, e.g., the vacuum residuum is not economically capable of serving as a source of high methane-containing gas, such as, substituted natural gas or of substantial amounts of low sulfur-containing fuel oil.

SUMMARY OF THE INVENTION

According to the process of the present invention, a crude oil is distilled in an atmospheric pipestill to separate it into several fractions. The atmospheric bottoms are vacuum distilled and the distillate is hydrodesulfurized to produce additional low sulfur-containing fuel oil. The vacuum bottoms are subjected to an integrated fluid coking and coke gasification process which is more fully described in U.S. Pat. No. 3,661,543 and U.S. Pat. No. 3,702,516, which are incorporated herein by reference. The coker normally liquid products may be combined with the atmospheric gas oil stream and/or the vacuum distillate stream and subjected to hydrodesulfurization. The coke produced is heated to a higher temperature than the actual temperature maintained in the fluid coking zone. A portion of the heated coke is then gasified to a gaseous stream containing hydrogen and carbon oxides by treatment with steam and oxygen. Hydrogen sulfide will also be present in this gaseous stream, since most of the sulfur in the coke under gasification operating conditions will be converted to H₂S with a small amount of COS being formed. The gasification gaseous product stream and the coker gas are not suitable as such for treatment in the methanation step of a catalytic steam reforming process, such as, the CRG process, because they contain hydrogen sulfide which would deactivate conventional catalysts. In order to remove the hydrogen sul-

fide, these gases are cooled, if necessary, to a suitable temperature, such as, for example, to about 110°F. and subjected to a conventional scrubbing process, such as, the process shown in British Pat. No. 948,270 in which gases are contacted with an alkaline solution comprising an anthraquinone disulfonic acid and usually also a metal compound such as an alkali metal metavanadate to convert the hydrogen sulfide to a usable sulfur product. The desulfurized gas is then combined with the methane-containing gaseous effluent of the catalytic steam gasification process, as incremental feed for the methanation reaction, whereby the proportion of methane is further increased relative to the proportion of methane present in the gaseous effluent of the catalytic reforming stage. The gaseous product resulting from the methanation stage may be upgraded to town gas or synthetic natural gas by removal of undecomposed steam and carbon dioxide.

BRIEF DESCRIPTION OF THE DRAWING

The FIGURE is a diagrammatic flow plan of one embodiment of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The preferred embodiment will be described with reference to the accompanying figure.

Referring to the figure, a crude petroleum oil containing substantial amounts of sulfur is introduced by line 10 into an atmospheric pipestill 12 where it is subjected to atmospheric distillation and separated into several fractions. In the illustrated process, four fractions are obtained: (a) a naphtha fraction having a final boiling point of about 365°F.; (b) a light distillate (kerosene) boiling at a temperature of between about 365° and 460°F.; (c) an atmospheric gas oil boiling at a temperature of between about 460° and 650°F., and (d) an atmospheric residuum boiling at a temperature above about 650°F.

All boiling points to which reference is made in this description and in the claims are atmospheric pressure boiling points unless otherwise specified.

The naphtha stream comprising predominately paraffinic hydrocarbons is removed from the atmospheric pipestill 12 via line 14 and subjected to a desulfurization process indicated at 16 to purify the stream with respect to sulfur. For example, the desulfurization may be a hydrodesulfurization process in which a hydrogen-containing gas and naphtha are reacted in the presence of a nickel molybdenum catalyst at a temperature of about 660° to 750°F. and a pressure of at least 150 pounds per square inch gauge (psig) to convert the organic sulfur in the naphtha feed to hydrogen sulfide. The hydrogen sulfide is absorbed on zinc oxide in a sulfur adsorbent to reduce the sulfur level of the naphtha to less than about 0.2 wt. part per million to prevent deactivation of the catalyst used in subsequent process steps. The desulfurized naphtha is removed via line 18. Steam is introduced into line 18 via line 20. The mixture of steam and vaporized naphtha is passed via line 22 into a catalytic steam reforming stage indicated at 24. The desulfurized and vaporized naphtha feed is reformed in the illustrated embodiment in accordance with the Catalytic Rich Gas process to produce a gas containing a high proportion of methane. The Catalytic Rich Gas process comprises passing the desulfurized, preheated, hydrocarbon vapor and steam over a suit-

able reforming catalyst at about 930°F. at a pressure of at least 350 psig to produce a gas containing at least about 10 mole % methane. The catalyst may be any of the high activity catalysts suitable for steam reforming naphtha feeds, such as, for example, nickel and/or nickel oxide supported on a refractory oxide carrier, such as, alumina, chromia or titania. These catalysts may additionally contain other metallic promoters. A typical composition of the methane-containing gas resulting from the steam reforming state is 61.2 mole % methane, 17 mole % hydrogen, 1 mole % carbon monoxide, and 20.8 mole % carbon dioxide. The methane-containing gas resulting from the steam reforming step is cooled to about 570°F. and passed via line 26 to a methanation operation indicated at 28. The methanation operation may be carried out in one or more stages, that is, the cooled methane-containing gas is passed over a bed of a conventional methanation catalyst at a lower temperature than the steam reforming temperature, for example, at about 400°F. over a nickel catalyst, where the hydrogen content of the gas is reduced and the methane content of the gas is enhanced by reaction of hydrogen with carbon dioxide and carbon monoxide present in the gas. Active catalysts that are suitable for the low temperature steam reforming are also suitable for the methanation reaction. After cooling and rejection of part of the undecomposed steam remaining with the gas, the remaining gas may be subjected to a second stage of methanation to further enhance the methane content. After the methanation operation, the gaseous effluent of the methanation operation, from which undecomposed steam has been removed, is subjected to a conventional carbon dioxide removal step indicated at 32. Carbon dioxide is removed via line 34. The methane-containing gaseous stream recovered from the carbon dioxide removal step via line 36 has a high proportion of methane. Depending upon the particular operating conditions, the final product may be suitable as fuel gas, town gas or substitute natural gas, the latter being a gas that contains at least about 85% of methane by volume calculated on a dry and carbon dioxide free basis. The gas may also be enriched by inclusion of light petroleum gases, etc. depending upon the desired end use of the final product. Further details concerning the Catalytic Rich Gas process may be found in U.S. Pat. Nos. 3,415,634; 3,625,665; and 3,642,460, all of which are herein incorporated by reference. The various methods and improvements taught in these patents are usable in connection with the process of the present invention.

The light distillate (kerosene) fraction recovered via line 38 from the atmospheric pipestill 12 is subjected to a conventional hydrodesulfurization process indicated at 40 to make it usable as turbine fuel.

The atmospheric gas oil fraction recovered via line 44 is subjected to a conventional hydrodesulfurization process indicated at 46. The resulting partially desulfurized stream forms a portion of the product low sulfur-containing fuel oil. Desirably, the fuel oil product contains less than about 0.5 wt. %, preferably, less than about 0.3 wt. % of sulfur. Any suitable hydrodesulfurization process may be employed so long as it is capable of removing economically a sufficient amount of sulfur.

The atmospheric residuum is passed via line 50 to a vacuum pipestill 52 and subjected to vacuum distillation. There is thus obtained a vacuum distillate having

a boiling point below about 1050°F. and a vacuum residuum having a boiling point higher than about 1050°F. The vacuum distillate is passed via line 54 to a hydrodesulfurization process indicated at 56 to reduce the sulfur level to below about 1.00 wt. %. As with the hydrodesulfurization of the atmospheric gas oil, any suitable hydrodesulfurization process may be used for the vacuum distillate, so long as it has the capacity to remove economically a sufficient amount of sulfur.

The vacuum bottoms are subjected to an integrated fluid coking and gasification process, which is more fully described in U.S. Pat. No. 3,661,543, the disclosure of which is herein incorporated by reference. Briefly, this vacuum residuum, which has a boiling point of above about 1050°F., is passed via line 60 into a coker reactor 62 comprising a fluid bed of solid particles (preferably coke). The temperature in the reactor is maintained at between about 900° and 1200°F. In the coking reactor, there is produced coke, coker gas and various coker normally liquid products. Although the accompanying figure shows the coker normally liquid products as a single stream, it will be recognized that these products may be fractionated and recovered as multiple streams boiling, for example, in the naphtha range, in the gas oil range, etc. Pressure in this coking zone is maintained below 150 psig, for example, at about 20 psig.

A portion of the coke is withdrawn from the coking reactor via line 64 and passed to a heating zone 74 by means of a suitable fluidizing gas such as steam. In the heating zone, which comprises a fluidized bed of hot particles (coke), the coke from the reactor commonly called "cold coke" is heated to a temperature 100°F. to 300°F. greater than the temperature maintained in the coking reactor. A portion of the heated coke is then passed via line 66 into a gasifying zone 68 operated at a temperature between 1400°F. and 2800°F., preferably, between 1600°F. and 1900°F., where, in the presence of additional steam and oxygen introduced via line 70 there is produced a metallic rich ash and a gaseous stream containing hydrogen and carbon oxide gases. The gaseous stream, which may further contain entrained metal-rich ash, is passed via line 72 to heating zone 74 to provide at least a portion of the heat required therein by heat exchange. The gaseous stream produced in the gasifying zone is then recovered via line 76 as effluent from the heating zone 74. A typical composition of a gaseous effluent recovered from the heating zone via line 76 is as follows: 24.2 mole % hydrogen, 20.0 mole % steam, 34.2 mole % carbon dioxide, 0.1 mole % nitrogen, 1.7 mole % hydrogen sulfide. The composition will vary somewhat depending on the coker reactor feed and the reaction and stripping conditions. The gaseous effluent of heating zone 74 may be further cooled to a temperature suitable for subsequent processing.

Although this gaseous stream and coker gas contain only a minor amount of hydrogen sulfide, this amount is still too much to make these gases suitable as incremental feed for the methanation stage of a CRG process. Generally, the naphtha to a CRG process is desulfurized to contain not more than about 0.2 wt. ppm of sulfur in order to prevent deactivation of the reforming and methanation catalysts. However, by treatment according to the Stretford process, in which the hydrogen sulfide is adsorbed, the gaseous product of the integrated fluid coking and coke gasification process can

be sufficiently upgraded to provide an incremental feed for the CRG process.

The process used to remove hydrogen sulfide as sulfur from the coke gasification products is essentially an adsorptive method employing an alkaline solution comprising one or more anthraquinone disulfonic acid. The solution may further contain a metal vanadate or a salt of a divalent metal. Further details concerning the Stretford process may be found in Hydrocarbon Processing, Vol. 52, No. 4, April 1973, page 109.

Returning to the figure, the gaseous effluent of heater 74 is cooled to an appropriate temperature such as to about 110°F. and passed via line 76 to a Stretford process unit indicated at 78. Sulfur is removed via line 80. The gaseous stream 82 removed from the Stretford process unit 78 has a reduced content of hydrogen sulfide, that is, it is a substantially hydrogen sulfide free gaseous stream. This stream is passed via line 82 into line 26 to combine with the gaseous effluent of the naphtha steam reforming stage 24. The mixed stream is then introduced into methanation stage 28. Alternatively, the gaseous effluent of the Stretford process could be introduced directly into methanation stage 28. In either alternative, it is used as an incremental feed for the methanation stage of the naphtha steam reforming process.

The coker liquid products are removed from coker 62 via line 84. If desired, a portion of the coker liquid products may be combined with the vacuum distillate of line 54 via line 86 or with the atmospheric gas oil of line 44 via line 88 to be subjected subsequently to hydrodesulfurization simultaneously with these fractions and thus provide increased amounts of the desired low sulfur fuel oil products. Furthermore, if desired, a portion of the coker liquid products may be introduced via line 84 to combine it with the light distillate of line 38 to be hydrodesulfurized simultaneously with that fraction to form a portion of the turbine fuel product.

If desired, at least a portion of the coker gas may be

passed via line 90 to scrubbing zone 78 for removal of H₂S therefrom simultaneously with gaseous effluent 76. The resulting combined substantially H₂S free gaseous stream is then passed via line 82 for use as incremental feed of methanation stage 28.

I claim:

1. In a refinery process for manufacturing a gas containing methane wherein a naphtha gasification process comprising a steam reforming stage and a methanation stage is integrated with a fluid coking and coke gasification process, and wherein the gaseous product of said coke gasification process comprises hydrogen, carbon oxides and a minor amount of hydrogen sulfide, the improvement which comprises desulfurizing said gaseous product and utilizing the resulting desulfurized gaseous product, without intervening conversion, as incremental feed for the methanation stage of the naphtha gasification process.

2. The process of claim 1, wherein said fluid coking is conducted at a temperature between about 900° and 1,200°F and at a pressure below 150 psig to produce fluid coke and wherein said coke gasification gaseous product is obtained by contacting said fluid coke with steam and oxygen under gasification conditions including a temperature between 1,600°F and 1,900°F.

3. The process of claim 1, wherein said desulfurized gaseous product is substantially hydrogen-sulfidefree gas.

4. The process of claim 1, wherein said coke gasification gaseous product is desulfurized by contacting said product with an alkaline solution comprising an anthraquinone disulfonic acid in a scrubbing zone wherein at least a portion of the hydrogen sulfide is removed from the gaseous coke gasification product.

5. The process of claim 4, wherein said coke gasification gaseous product is cooled to a temperature of about 110°F. prior to its being passed to said scrubbing zone.

* * * * *

40

45

50

55

60

65