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(54) Process for hydrocarbon
reforming and apparatus therefor

(57) A gaseous mixture of
sulfur-containing hydrocarbon with a
reforming oxidizing agent such as
steam and optionally carbon dioxide, is
heated to at least 800°C while passing
through packing bed containing alkali
metal and/or alkaline earth metal, the
heated gaseous mixture is brought into
contact with a nickel-containing catalyst
at 800°C or higher to produce a mixed
gas containing hydrogen and carbon

monoxide.

The apparatus comprises a furnace
(10) having burners (11) in its side wall
to heat portions of a set of vertical
reaction tubes (1) wherein the catalyst
bed (3) is contained. A reformed gas
conduit (6) leads through bed (3) to and
through the alkaline packing bed (2) to
an exit (7). Heat transfer to incoming
hydrocarbon, is provided by coiling the
conduit (8) traversing bed (2) and an
external heat-transfer packing is located
around the tube (1) in a combustion gas
discharge duct (13).

FIG. 4

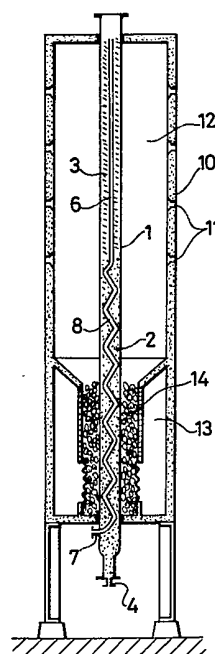


FIG. 1a FIG. 1b

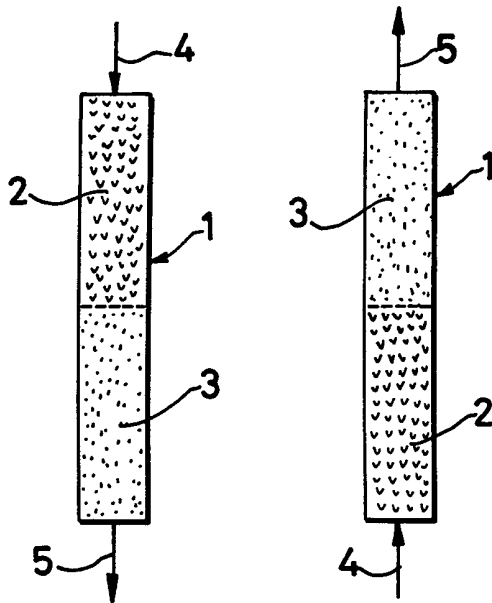


FIG. 2a FIG. 2b

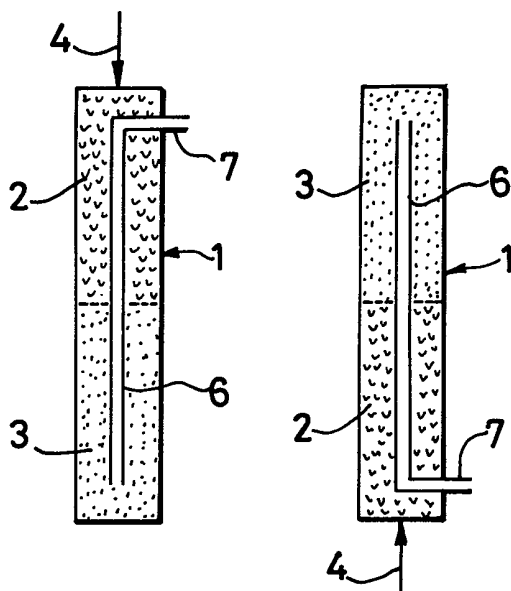
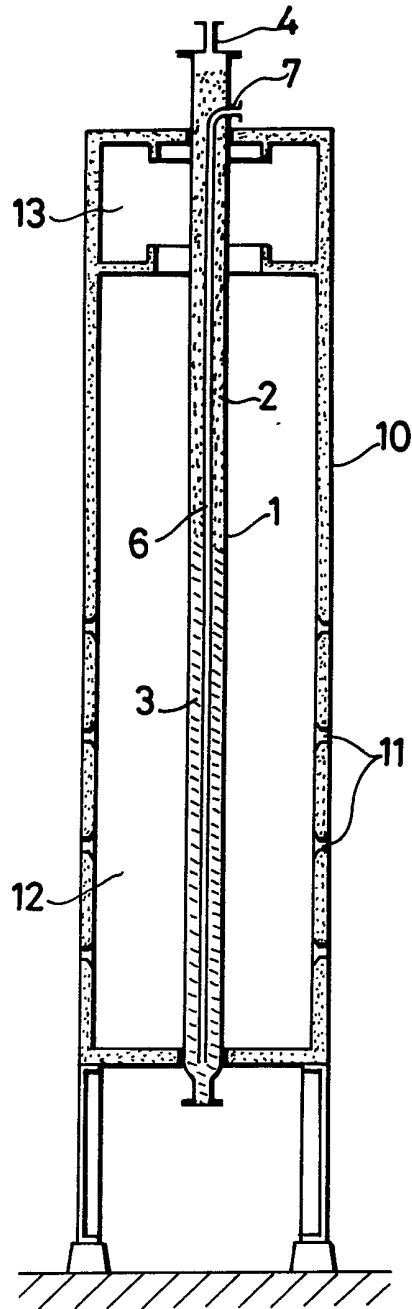


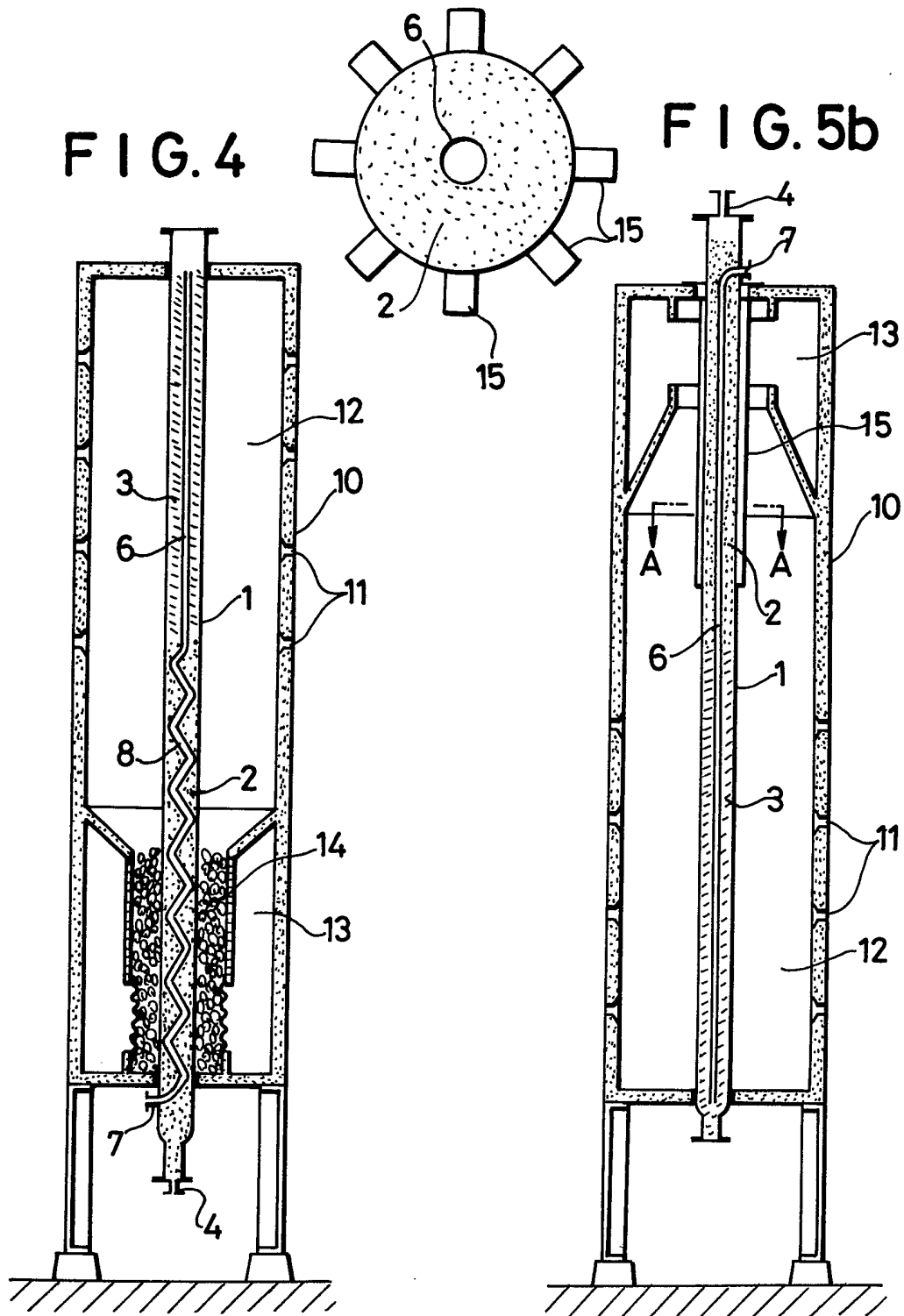
FIG. 3



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FIG. 5a



SPECIFICATION

Process for hydrocarbon reforming and apparatus therefor

This invention relates to a process for hydrocarbon reforming and apparatus therefor.

More particularly, the invention relates to a process and apparatus for producing a gaseous mixture containing hydrogen and carbon monoxide in which sulfur containing hydrocarbon is directly subjected to steam reforming without prior desulfurization.

Sulfur-containing hydrocarbons, particularly extracted oil such as kerosene, gas oil, and vacuum distillation gas oil, obtained by subjecting petroleum to atmospheric distillation and/or vacuum distillation, contain a considerable amount of sulfur. Typical sulfur contents are, for example, 40 to 100 ppm for commercially available deulsulfurized kerosene, 200 to 1,500 ppm for gas oil, and more for vacuum distillation gas oil. At such sulfur levels, these sulfur-containing hydrocarbons are unable to be subjected directly to steam reforming in the presence of the conventional nickel containing catalyst.

The technical problems to be solved in a process for steam reforming, in which light hydrocarbons such as butane and naphtha are subjected to steam reforming with an oxidizing agent for reforming such as steam at a high temperature of from 500 to 850°C in the presence of a nickel-containing catalyst, consist in maintaining the activity of the nickel-containing catalyst and preventing carbon deposition on the catalyst. Many conventional processes have been proposed so far and have been brought into industrial practice. However, all the conventional steam reforming processes have the drawback that light hydrocarbon raw materials must be subjected to a preliminary desulfurization so that sulfur may substantially be removed. Sulfur left in the raw material converts nickel in the catalyst to nickel sulfide, and the activity of the catalyst is lost and deposition of carbon is caused, which makes a long-term operation impossible. The higher the sulfur content in the raw material, the greater the troubles due thereto.

There is a description relevant to the foregoing at page 69 of an article entitled "Production of Hydrogen by Naphtha Steam Reforming" beginning at page 66, No. 10, Vol. 21, "Petroleum & Petrochemistry", which states as follows: "A complete steam reforming of light gas oil (LBP/FBP = 134°C/314°C) by the use of a laboratory apparatus under the same conditions as in the production of ammonia synthesis gas is attained. However, the insufficient desulfurization (20 ppm) of the raw material causes to poison the catalyst, and 2 to 3 hours later a part of the raw material is not subjected to reforming and leaves the catalyst bed as it is to be contained in outlet gas." That is, the above description shows that even 20 ppm of sulfur causes loss of catalytic activity within the short period of time of 2 to 3 hours. Accordingly, the raw material must be subjected to a desulfurization process such as hydrodesulfurization in advance so that the sulfur content in the raw material may be less than 1 ppm,

preferably less than 0.1 ppm before being subjected to steam reforming in order to make possible a long-term operation.

Most sulfur compounds contained in a light fraction such as naphtha are generally thiols and sulfides, and the sulfur moiety thereof can readily be removed by hydrodesulfurization. However, sulfur compounds contained in a heavy fraction such as kerosene are mainly thiophenes, which are extremely difficult to desulfurize by hydrodesulfurization from both technical and economical viewpoints.

Thus, conventional processes for high temperature steam reforming of hydrocarbons by use of a nickel containing catalyst have the drawback that sulfur in the raw material must be removed in advance, but desulfurization of heavy fractions is difficult technically as well as economically. Therefore raw materials containing such heavy fractions are unable to be subjected to steam reforming.

With respect to the raw material, an emphasis must be put on the saving of natural resources, and on the use of heavier and diversified raw materials to take the future shortage of petroleum resources into consideration. Accordingly, there is a demand for a process for hydrocarbon steam reforming and an apparatus therefor in which heavy fractions left after atmospheric and vacuum distillation of petroleum can be widely used as the raw materials, and in which sulfur-containing materials can be used without having to be desulfurized in advance.

An object of this invention is to provide an improved process and apparatus for steam reforming sulfur-containing hydrocarbons, including sulfur-containing heavy fractions, and which are able to utilise raw feedstocks without them necessarily being desulfurized in advance.

According to the present invention, there is provided a process for reforming hydrocarbons, in which a gaseous mixture of sulfur-containing hydrocarbon and a hydrocarbon reforming oxidizing agent is brought into contact with a catalyst to be reformed into a mixed gas containing hydrogen and carbon monoxide, and wherein the gaseous mixture is heated to a temperature of above 800°C during passage through an alkaline solid packing bed containing alkali metal and/or alkaline earth metal, and the heated gaseous mixture is then passed through a nickel-containing catalyst bed at a temperature above 800°C to reform the mixture into the said mixed gas.

The invention also provides an apparatus for reforming hydrocarbons, comprising a heating furnace having a radiation heat transfer zone in which there is a plurality of reaction tubes, each tube containing an alkaline solid packing bed and a nickel-containing catalyst bed built therein and the tubes being fitted vertically and in parallel in the said zone, the heating furnace being provided on at least one sidewall thereof with a plurality of burners for heating portions of the reaction tubes containing the catalyst bed.

The invention will now be described in more detail by way of example with reference to the accompanying drawings, in which:

Figure 1a, 1b are diagrammatic views of one embodiment of the present invention;

Figure 2a, 2b are diagrammatic views of another embodiment of the present invention;

5 Figure 3 is a vertical sectional view illustrating one embodiment of apparatus for use in practising the present invention;

Figure 4 is a vertical sectional view illustrating another embodiment of apparatus for use in practising the present invention;

10 Figure 5 is a vertical sectional view illustrating a further embodiment of apparatus for use in practising the present invention, and

Figure 5a is a view taken on the line A-A of Figure 15 5.

Conventional high temperature steam reforming by use of a nickel containing catalyst is effected at 500 to 850°C. In this temperature range, sulfur contained in the raw material converts nickel in the catalyst into nickel sulfide, with resultant loss of catalytic activity, causes deposition of carbon on the catalyst, and makes a long-term operation impossible. Depending on the amount of sulfur contained therein, that is, at a high temperature of 800°C or higher for a low sulfur content, or of 900°C or higher for a high sulfur content, nickel in the catalyst is mostly present in the form of nickel from its equilibrium, so that the activity of the catalyst can be maintained without deposition of carbon. Reforming at a temperature of 800°C or higher was effected taking the above fact into consideration to find out problems to be solved technically.

That is, the high temperature reforming involved heating up to a high temperature of 800°C sulfur-containing hydrocarbon alone or along with an oxidising agent for reforming, e.g. steam or steam and carbon dioxide, and it was found that in the case of hydrocarbon in the form of liquid at room temperature, deposition of carbon occurred in the course of heating up to 800°C. The carbon deposition in the course of heating up as mentioned above makes it impossible to effect the subsequent steam reforming by use of the nickel catalyst. However, many experiments have shown that heating up from a temperature range of 350 to 600°C to 800°C for decomposition, during passage through an alkaline solid packing bed free of nickel and containing alkali metal and/or alkaline earth metal, caused no deposition of carbon on the nickel catalyst.

50 The alkaline solid packing may be composed of an alkali metal or alkaline earth metal oxide and oxide of aluminium, and preferably is free of nickel. At a temperature range lower than 800°C loss of potassium is small so that it is desirable to incorporate 55 potassium as an ingredient which serves to prevent carbon deposition.

The gas containing lower hydrocarbons and other gases leaving the alkali or alkali earth bed is then introduced into a nickel-containing catalyst bed and is subjected to steam reforming therein at least at 800°C or higher, preferably 900 to 1,000°C, whereby the activity of the catalyst is maintained, and a long-term continuous operation is made possible without any carbon deposition. A nickel-containing catalyst 65 is employed at a temperature higher than 800°C, and

there is no need for a carbon deposition-preventing ingredient such as potassium which would escape at such high temperatures, because of the state of gaseous mixture introduced into the nickel catalyst bed and of the activity of the catalyst being maintained. The catalyst used is prepared by incorporating a given amount of nickel into one or more of oxides of the elements belonging to Group II of the periodic classification of the elements, such as beryllium, magnesium, calcium, strontium and barium, and the oxide of aluminium belonging to Group III.

Suitable alkaline solid packings may include, for example, those described in U.S. Patent No. 3,969,542, and further may include other alkaline solid packings known in the art. Suitable nickel catalysts may include, for example, those disclosed in U.S. Patent No. 4,101,449, and other nickel-containing catalysts known for hydrocarbon reforming.

85 There is no restriction on the pressure employed for the reaction, but the pressure is naturally limited by restrictions on the material of the reactor.

The temperature in the alkaline solid packed bed and the nickel-containing catalyst bed inter alia depends on the constitution of the hydrocarbon feedstock and its flow rate. The temperatures should not be such as would cause decomposition at the inlet of the alkaline solid packed bed. The temperature should be 800°C or higher, and preferably 900 to 1,000°C at the outlet thereof, while the reaction in the nickel containing catalyst bed is effected at 800°C or higher, preferably 900 to 1,000°C.

In Figure 1a, b, a reactor 1 is provided with a packed bed 2 of an alkaline solid packing and a packed bed 3 of a nickel-containing catalyst therein, and is externally supplied with heat necessary for steam reforming. Hydrocarbon as raw material is mixed with steam in the form of gas, and is introduced into the reactor 1 through a conduit 4 at 350 to 600°C. The hydrocarbon-steam mixture is heated up to 800°C or higher for decomposition in the alkaline solid packed bed, and then decomposed completely at 800°C or higher in the nickel-containing catalyst bed to form a mixture containing hydrogen and carbon monoxide, which is taken out of the reactor through a conduit 5. In Figure 1, (a) and (b) show the cases where the flow of hydrocarbon-steam mixture and the gaseous mixture so formed is in the opposite direction from each other.

115 The temperature of hydrocarbon-steam mixture introduced into the reactor 1 depends on the boiling point range of the hydrocarbon raw material, and is selected from temperatures in the range of from 350 to 600°C. In the case of liquid hydrocarbon, carbon deposition must not occur in the step of evaporation-preheating thereof. Gas oil and vacuum distillation gas oil were considered to cause carbon deposition even at 500°C, but the present inventors have found that the rate of carbon formation is so low that continuous operation is made possible without carbon deposition by shortening residence time in the step of evaporation-preheating. However, a temperature above 600°C should be avoided because the rate of carbon deposition becomes high enough at 600°C or higher to cause blocking of pipes, 130

for instance.

Example 1

In the inlet portion of a reaction tube having an inner diameter of 60 mm, the length of which is 2/3 the total length of the reaction tube, an alkaline solid packing containing $12 \text{ CaO} \cdot 7 \text{ Al}_2\text{O}_3$ as its major ingredient was packed, and over the remaining 1/3 the length of the reaction tube a catalyst prepared by supporting 15% by weight of Ni on a carrier containing $12 \text{ CaO} \cdot 7 \text{ Al}_2\text{O}_3$ as its major ingredient was

Amount of gas formed
Composition of gas formed

5 Nm³/hr

H ₂	59.3% by volume
CH ₄	14.6% " "
CO	11.6% " "
CO ₂	14.5% " "
H ₂ S + COS	180 ppm

During operation no carbon was recognized in the gas formed, and an examination of the reaction tube after completion of the operation found no carbon deposition.

Conventional hydrocarbon steam reforming was limited to application to a naphtha fraction, having a boiling point range of about 220°C or lower, technically and economically and was applicable only to a substantially desulfurized material. However, in accordance with the process of the present invention, steam reforming can be effected without carbon deposition over a wide range of materials from sulfur-containing methane to heavy petroleum fractions except for residual oil. Steam reforming of liquid hydrocarbon free of sulfur can apparently be effected without carbon deposition. This indicates that the present invention has a great effect especially in the case of a petroleum fraction, desulfurization of which is difficult technically as well as economically prior to subjecting to steam reforming, as well as in the case where the incorporation of sulfur in the gas formed by steam reforming is allowable.

The present invention also has an advantage in that sulfur compounds contained in the raw material and difficult to be desulfurized can be converted into H₂S or COS by subjecting them to steam reforming by the present invention. Substantially complete desulfurization by removal of the H₂S or COS can be readily attained by the conventional acid gas removal technique.

Another embodiment provides a preferred process for the practice of the present invention. The

Gas oil having a boiling temperature of from 210 to 353°C and containing 900 ppm of sulfur was used as stock oil. The stock oil was mixed in the gas phase with steam at a flow rate of 1.34 kg/hr to make the ratio of (steam moles)/(number of carbon atoms) 3.5, and the mixture was fed into the inlet of the alkaline solid packing bed under 20 kg/cm²G at 400°C, heated up to 900°C therein, and then subjected to reaction in the nickel containing catalyst bed at 950°C to obtain the following results:

first embodiment described above is performed at a temperature higher than the reaction temperature in conventional steam reforming, that is, 800°C or higher, so that an increase in utilization of thermal energy is more desirable than ever. Figure 2 a, b diagrammatically shows this embodiment. The process shown in this embodiment differs from that shown in Figure 1 in that there is provided a formed gas conduit 6 passing through an alkaline solid packing bed 2 and a nickel-containing catalyst bed 3 packed in a reaction tube 1. A high temperature gas formed by steam reforming in the nickel containing catalyst bed 3 is introduced into the formed gas conduit 6. As the gas so formed passes through the formed gas conduit 6, the sensible heat of the formed gas is fed to the gas passing through the nickel-containing catalyst bed and alkaline solid packing bed by indirect heat exchange. Then the formed gas is discharged out of the reactor through a formed gas discharge conduit 7. As will be appreciated, the formed gas flows in a direction counter to the direction in which the feedstock is admitted to the tube 1.

Example 2

Example 1 was repeated except that a formed gas conduit 6 having an inner diameter of 10 mm was fitted in the reaction tube 1 of Example 1, where the temperature of an outlet of the formed gas conduit 6 (that is conduit 7) was 590°C. Both the amount and composition of the formed gas were the same as those in Example 1. In Example 2, however, a saving in the amount of fuel consumed by 31%, as compared with Example 1, was achieved.

	Example 1	Example 2
Temperature of hydrocarbon-steam gaseous mixture (°C)	400	400
Formed gas outlet temperature (°C)	950	590
Combustion gas discharge temperature (°C)	980	980
Ratio of amounts of fuel consumed	1	0.69

A specific relationship or arrangement with a furnace and burners which supply heat with the reaction tube in the above two embodiments is described below. The apparatus has a plurality of

vertical reaction tubes each provided with an alkaline solid packing bed and nickel-containing catalyst bed are fitted in parallel to form a furnace, and the reaction tubes are heated by a plurality of side wall burners on the side wall of the furnace positioned mainly adjacent the nickel-containing catalyst bed.

The amount of heat and temperature level needed in the alkaline solid packing bed, where hydrocarbon-steam mixture is heated up from a temperature of 350 to 600°C to 800°C or higher for thermal decomposition, may be at a lower level than needed for the nickel-containing catalyst bed, which is maintained at 800°C or higher throughout. However, the application of a top firing system or a bottom firing system, which has been widely used, as main heating means cannot avoid local heating. Accordingly, in the practice of the invention, a side firing system is adopted as the main heating means, by which system the amount of combustion can be controlled over a wide range according to the amount of heat absorbed in the zone corresponding to the nickel-containing catalyst bed. Side firing makes prevention of localised heating of the reaction tubes and saving of fuel possible. Many experiments have shown that it is desirable from the standpoint of heat economy that the side wall burners are fitted on the side wall of the furnace facing the nickel-containing catalyst bed so as to supply the reforming zone at a high temperature level with heat, and then the alkaline solid packing bed is supplied with heat while the combustion gas leaves the radiation heat transfer zone.

Figure 3 is one embodiment of the present invention. In Figure 3, a radiation heat transfer portion of a heating furnace 10 is provided with a plurality of reaction tubes 1 in parallel, one only being visible as Figure 3 is drawn. The tubes 1 each have an alkaline solid packing bed 2 in the upper part thereof and a nickel-containing catalyst bed 3 in the lower part thereof. A formed gas conduit 6 passing through both beds has an opening at one end at the bottom of the reaction tube, and the other end of the formed gas conduit 6 leads out of an upper portion of the reaction tube. A plurality of side wall burners 11 are fitted on one or both furnace side walls in the region of the nickel-containing catalyst bed portion of the reaction tube 1. The combustion gas from the side wall burners 11 is discharged to a convection heat transfer portion (not shown in Figure) through a duct 13 fitted in an upper portion of the heating furnace. In Figure 3, a formed gas conduit 6 of the second embodiment (Fig. 2a) is fitted. A gaseous hydrocarbon-steam mixture at 350 to 600°C is fed to each reaction tube 1 through a conduit 4, is supplied with heat from the combustion gas passing outside the reaction tube and from the formed gas in the formed gas conduit 6 so as to be heated to a temperature of 800°C or higher for decomposition and then is supplied with heat from the combustion gas passing outside the reaction tube and the formed gas in

the formed gas conduit 6 for steam reforming at 800°C or higher in the nickel-containing catalyst bed. The high temperature formed gas flows into the formed gas conduit 6 and flows up therethrough to be discharged from a formed gas discharge conduit 7. If use is made of the first embodiment (Fig. 1), the formed gas conduit 6 is absent, so that the formed gas discharged from the reaction tube is subjected to a waste heat recovery step after discharge from the heating furnace. It should be understood that in the case where the flow of the hydrocarbon-steam gaseous mixture and the formed gas is in the opposite direction respectively, upwardly or downwardly, each element is fitted in the opposite direction, upwardly or downwardly to what is shown.

In the above description of Figure 3, the reaction tubes are said to be fitted in parallel, and their physical arrangement may be of a linear or zigzag configuration in a plan view. The side wall burner may be arbitrarily designed so as to be of uniform heat generating capacity, or of a smaller capacity for the upper portion thereof and a larger capacity for the lower portion thereof.

Example 3

Under the same conditions described in Example 1 and 2, the side wall burners in Figure 3 were so arranged that the combustion gas outlet temperature (at inlet of the duct 13) is 800°C. The amount of fuel consumed was reduced to 56% the amount in Example 1, while the amount in Example 2 was reduced to 69% the amount in Example 1. That is, the amount of fuel consumed in Example 3 was reduced to 81% the amount in Example 2.

The following embodiment employs a heat conductive packing, for example, inert balls such as alumina balls packed at the outlet of the radiation heat transfer portion of the combustion gas in order to improve heat transfer therein. Alternative means to encourage heat transfer can be fins fitted on the outer side wall of the adjacent portion of the reaction tube. Further saving of fuel in the heating furnace may be attained by lowering the temperature of combustion gas discharged from the furnace as much as possible. However, as the combustion gas temperature is lowered, radiation heat transfer is remarkably reduced and convection heat transfer becomes predominant, so that the rate of heat transfer is greatly reduced. As a result, fuel consumed may be saved, but it becomes necessary to lengthen the expensive reaction tube or to increase the number of reaction tubes in order to increase the heat transfer area. The present inventors made many studies on lowering the temperature of the combustion gas discharged from the furnace while maintaining the rate of heat transfer at a high level so as to save fuel consumed, and as a result devised this embodiment which is shown in Figure 4. In this embodiment, the flow of the hydrocarbon-steam mixture into the reaction tube 1 and of the formed gas therefrom are in the opposite direction to that in Figure 3. The lower or downstream half of the formed gas conduit 6 which traverses the bed 2 is a coiled tube 8 instead of the linear tube shown in Figure 3. The rate of heat transfer is remarkably improved by providing an inert ball-packed portion

14 and by means of the coiled tube 8. The solid, packed heat transfer medium represented by the balls is packed around the tubes in the region of their alkaline solid packing beds, and fills at least part of the space between the tubes and the inner walls of the furnace. The inert balls of an appropriate shape and size can be made of a material with resistance to heat and a good heat conductivity. Figure 5 shows a variation of the apparatus shown in Figure 4, in which fins 15 are fitted to a portion of the outer side wall of the portion of tube 1 containing the alkaline solid packing bed, in order to improve the rate of heat transfer. The fins 15 may be plate-like or rod-like projections, but studs or other formations capable of increasing heat transfer area could be substituted.

Example 4

The same conditions as in Example 3 were employed for an apparatus fitted with plate-like, vertical fins as shown in Figure 5. The amount of fuel consumed is reduced by 11% compared with that in Example 3.

CLAIMS

1. A process for reforming hydrocarbons, in which a gaseous mixture of sulfur-containing hydrocarbon and a hydrocarbon reforming oxidizing agent is brought into contact with a catalyst to be reformed into a mixed gas containing hydrogen and carbon monoxide, and wherein the gaseous mixture is heated to a temperature of above 800°C during passage through an alkaline solid packing bed containing alkali metal and/or alkaline earth metal, and the heated gaseous mixture is then passed through a nickel-containing catalyst bed at a temperature above 800°C to reform the mixture into the said mixed gas.

2. The process claimed in Claim 1, wherein the heated mixture is passed through the nickel-containing catalyst bed at a temperature of from 900 to 1,000°C.

3. The process claimed in Claim 1 or Claim 2, wherein the alkaline solid packing is composed of alkali metal oxide and/or alkaline earth metal oxide, and aluminium oxide.

4. The process claimed in Claim 1, 2 or 3, wherein the nickel containing catalyst is composed of at least one metal oxide selected from the oxides of beryllium, magnesium, calcium, strontium, barium and aluminium and nickel incorporated therein.

5. The process claimed in any of Claims 1 to 4, wherein the mixed gas discharged from the catalyst bed flows countercurrently with respect to the flow of the gaseous mixture into a zone passing through the alkaline solid packing bed and the catalyst bed, so that heat contained by the mixed gas supplies part of the heat of reaction for reforming and part of the heat needed for heating up the gaseous mixture.

6. A process as claimed in Claim 5, including the step of extracting heat from the mixed gas exiting a reaction tube in which the two beds are packed by heat transfer means and supplying the extracted heat to the alkaline solid packing.

7. A process as claimed in any of Claims 1 to 6, in which the feedstock hydrocarbon is sulfur-containing heavy petroleum distillate.

8. A process for reforming hydrocarbons sub-

stantially as herein described with reference to the accompanying drawings.

9. A process for reforming hydrocarbons according to any one of Examples 1 to 4.

10. An apparatus for reforming hydrocarbons, comprising a heating furnace having a radiation heat transfer zone in which there is a plurality of reaction tubes, each tube containing an alkaline solid packing bed and a nickel-containing catalyst bed built therein and the tubes being fitted vertically and in parallel in the said zone, the heating furnace being provided on at least one sidewall thereof with a plurality of burners for heating portions of the reaction tubes containing the catalyst bed.

11. The apparatus claimed in Claim 10, wherein a solid bed of an inert, solid heat transfer medium is packed around the tubes adjacent to the alkaline solid packing bed region in at least a part of the space between the reaction tube and the side wall of the furnace.

12. The apparatus claimed in Claim 10, wherein a plurality of fins are fitted to the outer wall of the reaction tubes in the region thereof containing the alkaline solid packing bed.

13. The apparatus claimed in Claim 10, 11 or 12, wherein a reformed gas conduit leads from the catalyst bed *via* the catalyst bed and through the alkaline solid packing bed to a gas discharge exit.

14. The apparatus claimed in Claim 13, wherein the conduit section traversing the alkaline solid packing bed is in the form of a coil.

15. Apparatus for reforming hydrocarbons substantially as herein described with reference to Fig. 1 or Fig. 2 of the accompanying drawings.

16. Apparatus for reforming hydrocarbons substantially as herein described with reference to and as shown in Fig. 3 or Fig. 4 or Figs 3 or 4 when modified as shown in Fig. 5 of the accompanying drawings.

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