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(54) **A process for making high calorie city gas.**

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Description

This invention relates to a process for making high calorie city gas from hydrocarbonic crude materials such as butane, propane, naphtha and the like, and more particularly to an improvement in such a process.

5 In Japan, gas industry plants are located mainly in large cities. These plants have a trend to carburet the calorific value of city gas to convert it to high calorie type city gas classified at 13A (i.e., 11,000 kcal/Nm³) which is so called synthetic natural gas (i.e. SNG) refined from liquefied natural gas (i.e. LNG) as the hydrocarbonic crude materials. The reasons why the gas industries are urged to convert the city gas to SNG having the same components with LNG are as follows:

10 It is intended to (1) unify and standardize the city gas to high calorie type city gas having the combustibility of 13A throughout the whole country; (2) adjust the fluctuation of demand and supply of city gas; (3) reduce the cost of city gas production; and (4) pursue the variety of crude materials, the convenient utility of city gas, and the stability of gas supply throughout the whole country.

15 In the process for making SNG, accordingly the system should have the following characteristics: (1) it should be easy to operate the starting, stoppage and load-change of the plant with high response; (2) the efficiency of gasification and gaseous quality should be high; and (3) it is essential that the plants should be able to operate in a simple manner and with high economic efficiency.

20 It is conventional to operate the process for reforming SNG from hydrocarbonic crude materials such as butane, propane, naphtha and the like by means of the following eight steps: (1) the activation step of sulfur contents from crude gas; (2) the desulfurization step of crude gas; (3) the steam-reforming step of crude gas; (4) the primary methanization step of reformed gas; (5) the secondary methanization step of reformed gas; (6) the wet type decarbonation step of processed gas; (7) the dehydration step of processed gas; and (8) the carburetting step by adding liquefied petroleum gas (LPG). In the above eight steps, they are further classified so that the first five steps, i.e. the steps (1) to (5) are the processing steps of crude gas including 25 the pretreatment step of crude gas; the middle two steps, i.e. the step (6) and step (7) are the refining steps of processed gas; and the last step, i.e. the step (8), is the carburetting step of the processed gas.

According to the conventional process described above, at least five steps are required even when the process is operated to obtain only elementary crude gas, i.e. the five steps comprising of: the five units of vessel or column to cover the first five steps above; two units of heating furnace; and one unit of recycle-gas compressor for the recycle gas containing some hydrogen to decarbonate is proposed. In addition to the above systems, it requires additional back-up systems such as another furnace which is used only during the start-up of the plant with heat-up bypass branched from the furnace; its incidental equipment and the like.

30 Thus, the conventional systems are disadvantageous in that (1) their systems and their operation are relatively complex; (2) due to too many systems, they have a large amount of heat and energy losses, and (3) they lack economical efficiency because of the high cost of gas production. Moreover, (4) in the requirement for SNG refining system, specially as to the start-up response of the whole system, it usually takes at least three days for starting up the whole system during the cold state, and takes half a day even during the hot state. In addition, the load-change of the whole system is also a problem in that the response 40 of the whole system to a load-change takes a long time, for example over one minute per one percent of load-change.

45 In view of the prior art described above including the disadvantages and deficiencies of prior art processes, it is a general object of the present invention to provide an improved process of obtaining a hydrogen-rich gas mixture to be desulfurized and also methane-rich gas by methanizing the hydrocarbonic crude materials such as butane, propane, naphtha and the like, and also hydrogenizing methanol by way of a one step reaction within one unit of a reactor respectively.

It is another object of the present invention to provide a simplified system while improving the efficiency of gasification and gas quality stabilization.

50 It is a further object of the present invention to provide a process for easily operating the start-up, stoppage and load-change of a system within fifteen minutes respectively.

In the process of reforming an elementary feed gas before finally refining the product gas, i.e. SNG from the hydrocarbonic crude materials such as butane, propane, naphtha and the like, the technical means provided by the present invention for achieving the objects described above is to provide a process including the following steps: the step of a methanizing reaction; the step of a desulfurizing reaction; the 55 step of maintaining a predetermined temperature to meet with the reactive condition of activating a catalyst; the step of temperature control; and the step of introducing the heat from an external heat source by way of a heat transfer medium for enabling the transfer of heat between the catalyst and heat source.

Referring now in detail to the desulfurizing reaction.

(1) In order to perform hydrodesulfurization, it employs only a one unit desulfurizing column comprising an integral type heat exchanger having reactive inner tubes with U-shaped passages therein separately filled with nimox catalyst and also zinc oxide within the U-shaped inner tubes respectively.

Regarding the heat transfer medium, it is heated to approximately 350 °C by an external heat source, and introduced into the internal space between the shell drum and U-shaped inner tubes to heat up the catalysts as well as the elementary feed gas to meet with their reactive temperature condition.

Regarding the feed gas obtained by vaporizing the hydrocarbonic crude materials, it is mixed with an amount of hydrogen gas which is produced in the other external producer to produce in turn a hydrogen-mixed feed gas, i.e. the feed gas to be fed into the desulfurizing column.

Regarding the catalytic reaction of the hydrogen-mixed feed gas fed into the U-shaped reaction tubes, in the outward passage with the nimox bed, the hydrogen and inert sulfureous compound react together to produce hydrogen sulfide (i.e. activated sulfureous compound) while passing through the nimox bed. In the return passage containing the zinc oxide bed, the sulfureous content of the activated sulfureous compound is removed by adsorbing it as zinc sulfide through the zinc oxide bed, to obtain a desulfurized hydrogen-mixed feed gas.

(2) In order to perform the steam-reforming, it employs only a one unit methanation column having a shell and tube structure. In more detail, the column comprises an integral type heat exchanger having a plurality of reactive inner tubes filled with a methanation catalyst consisting of an alumina group carrier supported by nickel.

Regarding the feed gas to be fed into the methanation column, this is a mixture of desulfurized hydrogen-mixed feed gas and steam. This feed gas is reacted in an isothermal reaction under specific reactive conditions in a rapid single pass reaction within only a one unit column to produce a methane-rich gas as an elementary feed gas.

Regarding the heat transfer medium to be introduced into the methanation column, it is heated to approximately 320 °C for butane, 315 °C for propane, and 330 °C for naphtha respectively and introduced into the internal space between the shell drum and inner tubes to heat up the catalysts as well as the feed gas while keeping their specified temperatures to meet with their reactive temperature condition.

(3) In order to obtain the hydrogen to be used for the hydrodesulfurization described above, the same methanation column is used as described in paragraph (2) above because this column is designed as a combined use type so that it has another inner tube filled with a hydrogenizing catalyst within the same column in addition to the tubes filled with the methanation catalyst. That is, a one unit column is used for the twin purposes of both methanation and hydrogenization. Regarding the feed gas to be fed into the hydrogenizing tube of the combined use type column, it uses a methanol/water mixture preheated to the same temperature as mentioned in the above paragraph (2) which is then vaporized to form the feed gas to be fed into the hydrogenizing tube of the combined use type column. This feed gas is reacted in an isothermal reaction under specific reactive conditions in a rapid single pass reaction within only a one unit column to obtain a hydrogen-rich mixture gas.

(4) Regarding the composition of the heat transfer medium used for controlling the feed gases as well as the catalyst each at an optimum temperature in order to operate the steam-reforming and hydrodesulfurization, it uses an inorganic salt type heat transfer medium of NaNO₂, NaNO₃ and KNO₃, which is then circulated between these columns and a furnace.

In operation, this heat transfer medium absorbs heat generated by the catalyst in the exothermic reaction zone and reversely releases heat to the catalyst in the endothermic reaction zone. Thus the heat movement is rapidly performed between the heat transfer medium and its object. The heat transfer is performed by two system circulation circuits of the heat transfer medium, such as in the reforming system the accumulated heat within the catalyst bed is absorbed so as to cool the catalyst. In the desulfurizing system the temperature of the catalyst is optionally controlled through shunt-valves.

In the step of refining the elementary feed gas, i.e. the methane-rich gas and also SNG, a well known apparatus for removing carbon dioxide and moisture from a methane-rich gas mixture (i.e. an apparatus of decarbonation and dehydration in continuous gas stream based on PSA method) is used such as described in Japanese patent provisional publication No. Hei 2-281096 filed by the same applicant as the present invention.

From the above, the present invention provides a simplification of the operation of refining SNG comprising the steps of producing, refining and carburetting the elementary feed gas. The process of the present invention improves the efficiency of gasification, to reduce the cost of gas production, and to enable the operation of the start-up, stoppage and load-change of the whole system within fifteen minutes.

IN THE DRAWINGS:

Figure 1 is a schematic flow diagram showing the process of making an elementary feed gas as SNG in the present invention;

5 Figure 2 is a schematic perspective illustration showing the structure of the desulfurizing column of the present invention;

Figure 3 is a schematic perspective illustration showing the structure of the reaction column of the present invention;

10 Figure 4 is a graphical representation showing the catalyst-bed temperature distribution during the methanization of crude butane;

Figure 5 is a graphical representation showing the relationship between the reaction temperature of reforming butane and its gas yield;

Figure 6 is a graphical representation showing the catalyst-bed temperature distribution during the hydrogenizing reaction of methanol; and

15 Figure 7 is a flow sheet showing the process of making SNG, and specifically the partial process of removing the carbon dioxide and moisture performed by the continuous stream PSA method.

Referring now in detail to the process of producing, refining and carburetting the SNG of the present invention based on Figure 1, the hydrocarbonic crude materials such as butane, propane, naphtha and the like are pressurized to around a reaction pressure by a crude material pump (1), and then subsequently heated up and vaporized by a crude material preheater (2) and a crude material evaporator (3). Thereafter, the materials are mixed with a hydrogen-rich mixture gas produced in a reaction column (8) in a crude materials/hydrogen mixer (4), and the temperature of the crude material/hydrogen mixture gas is controlled in a crude material superheater (5) to be about 350 °C and then sent into an integral type desulfurizing column (6) which is operated to activate and adsorb the sulfureous contents of the crude material/hydrogen mixture gas. The sulfureous content in the desulfurizing column (6) is reduced to hydrogen sulfide (H₂S) by the hydrogen additive reaction between the hydrogen and inert sulfureous compounds of the crude material gas through the nimox catalyst bed filled in the outward passage tubes within the desulfurizing column (6). On the other hand, the hydrogen sulfide (H₂S) now contained within the crude material gas reacts when it reaches the zinc oxide bed in the return passage tubes in the manner H₂S + ZnO → ZnS + H₂. The ZnS is adsorbed by an adsorbent ZnO so that the sulfureous content is removed from the crude material/hydrogen mixture gas.

Figure 2 illustrates that the desulfurizing column (6) is in the form of a shell and tube type heat exchanger having fixed tubes with baffle plates (70) therein. The interior of the upper chamber includes a flange and is vertically sub-divided by a partition plate (61) which forms a U-shaped passage with the inlet (62) of the hydrogen-mixed feed gas and also the outlet (63) of the desulfurized hydrogen-mixed feed gas. The inlet (62) communicates with the outward passage (64) filled with the nimox catalyst (65), the outlet (63) communicates with the return passage (66) filled with the zinc oxide (67).

The heat transfer medium previously heated in a heat medium furnace (7) to about 350 °C is forcedly flowed upwardly within the shell side in a zig-zag stream due to the plurality of baffle plates (70) to maintain the catalysts at an activating temperature. The heat transfer medium is flowed into the column (6) through an inlet (68) and out of the column through an outlet (69).

Regarding the relationship of temperature between the hydrogen-mixed feed gas to be fed into the desulfurizing column (6) and the catalysts filled within the U-shaped reaction tubes, their temperatures are under the control of the heat transfer medium. The heat transfer medium has a large heat capacity, and is forcedly flowed in turn from the heat medium furnace (7), to the crude material superheater (5) and then to the desulfurizing column (6) to constantly keep them at a predetermined temperature. This temperature control of the feed gas and catalyst by the heat transfer medium is not only useful in the regular operation of the system but also useful during start-up and load-change. Thus the heat transfer medium is one of the major reasons that the system of this invention can undergo rapid start-up and respond quickly to load-change.

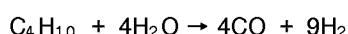
In prior art devices, the temperature difference between the hydrogen-mixed feed gas and the catalysts was difficult to control because the heating was carried out by an internal heating system operated by the heat of the gas. This control was particularly difficult in the start-up stage of the system. In the worst case, this resulted in the catalyst causing the problem of carbonic extraction in a high temperature zone, and reversely causing insufficient desulfurization in a low temperature zone. The present invention solves this disadvantage of prior art devices by providing the external heating means (7) for the heat medium.

Conventionally, regarding the hydrogenizing catalysts such as the nimox bed and zinc oxide, the prior art devices used two units of column separately for each catalyst. In contrast the present invention provides

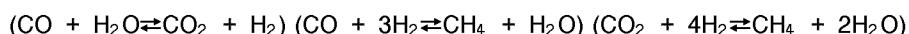
an integral unit column having a minimized surface as illustrated in Fig. 2. This arrangement makes it possible to minimize heat loss through radiation from the desulfurizing device which favourably influences the total plant efficiency.

The reforming and methanizing reaction of the process of the present invention will now be further explained by reference to Figure 3. Desulfurized hydrogen-mixed feed gas is delivered from the desulfurizing column (6) and is mixed with steam in the feed gas/steam mixer (9) to produce a desulfurized feed gas/steam mixture gas. This gas mixture is heated up to a reaction temperature of approximately 320 °C in the feed gas superheater (10). The mixture is then fed into the steam-reforming column (8) in which the feed gas is reacted in an isothermal reforming (i.e. thermal cracking) reaction and also methanizing reaction under specific reaction conditions. This reaction is carried out using a catalyst having a large activation such as an alumina group carrier supported by nickel. The resulting single pass reaction is carried out at high speed within only a one unit column in which a high calorie type fuel gas rich in CH₄ and less CO is reformed.

For example, in the case of butane, the hydrocarbon is thermally cracked by steam on the catalyst and CO and H₂ are formed in accordance with the following chemical equation:



According to the progress of the gasification, it causes the methanation reaction and shift reaction on CO and H₂, and the following synthetic reaction is further progressed:



According to the present invention, the above synthetic reaction can be carried out in a one unit column with a single pass reaction.

In Figure 3, the combined use type methanation column (8) comprises a shell and tube type heat exchanger having fixed tubes with baffle plates therein. The fixed tubes, i.e. the reaction tubes (81), are filled with methanizing catalyst (82), and the heat transfer medium having a temperature of approximately 320 °C is forcedly flowed upward from the heat medium inlet (83) positioned at the lower portion into the space between the shell drum and reaction tubes (81) through the heat medium shunt/control valve (11) [Figure 1] to heat and maintain the catalyst at its effective operating temperature.

Regarding the relationship between the temperature of the desulfurized feed gas/steam mixture gas to be fed into the combined use type methanation column (8) and the catalyst (82) filled within the column (8), this relationship is controlled by the heat transfer medium having a large heat capacity which is forcedly flowed in order through the heat medium shunt/control valve (11), the column (8) and the feed gas/steam superheater (10) to maintain them at a constant predetermined temperature. This temperature control of the feed gas and catalyst by the heat transfer medium is not only useful in the regular operation of the system but also useful during start-up and load-change of the system. Thus the heat transfer medium is one of the major reasons that this system can undergo rapid start-up and respond quickly to load-change as well as the case of the desulfurizing column (6) described previously.

Figure 4 illustrates the relationship between the temperature of the catalyst bed (82) in the combined use type methanation column (8) between the steam-reforming reaction zone (i.e. endothermic reaction) and methanizing reaction zone (i.e. exothermic reaction), and the depth of the catalyst bed. The temperature is determined by a plurality of thermal sensors within the bed.

Figure 4 illustrates that the catalyst-temperature slightly descends initially and then suddenly increases up to around 360 °C in the shallow portion of the bed. This indicates that the beginning of the catalytic reaction occurs near the entrance. This temperature variation is believed to occur due to an endothermic reaction in the steam-reforming zone causing the temperature to dip followed by an exothermic reaction in the methanizing reaction zone causing the temperature to rise to about 360 °C.

With increasing depth, the temperature again descends suddenly from the peak of about 360 °C, and is stabilized at about 320 °C which corresponds with the temperature of the heat transfer medium of about 320 °C. The peak catalyst temperature is rapidly cooled due to the flow of fresh heat transfer medium introduced from the heat medium inlet (83). This is positioned at the lower portion of the reaction column (8) and adopts a counter-flow type heat exchanging method. Consequently the product gas, i.e. the methane-rich gas and also the elementary feed gas, which is produced by the reaction column (8) is sufficiently cooled by the fresh flow of the heat transfer medium so that a relatively high yield of CH₄ can be expected in a lower temperature zone as illustrated in Figure 5.

Figure 5 shows that the lower the temperature, the higher the yield of CH₄. It is theoretically known that the gas composition described above has a thermodynamically equilibrium composition. Therefore, the gas composition can be obtained by theoretical calculation.

Returning to Figure 3, the heat transfer medium flows upwards through baffle plates (84) and absorbs heat from the reaction tubes generated in the exothermic reaction zone. When the temperature of the heat transfer medium reaches the peak temperature, the heat transfer medium then flows into the endothermic zone where it releases its heat to the reaction tubes to heat up the tubes. After passing through the endothermic zone, the heat medium then flows out from the upper portion of the column (8) through outlet (87). This means that the heat transfer medium is heated up in the exothermic reaction zone and the heat transfer medium releases its heat in the endothermic reaction zone after the temperature of the heat transfer medium reaches its peak. The heat transfer in the endothermic reaction zone is performed at high speed due to the wide temperature difference. This results in the acceleration of the endothermic reaction.

The process of the present invention makes use of a one unit column with a single pass reaction as described above because the heat transfer medium can momently absorb a large amount of heat generated in the exothermic reaction zone. Conventional systems make use of a two or three unit column system due to the failure of their heat transfer system to efficiently absorb generated heat.

As previously described, it has been conventional to adopt three steps such as a steam-reforming step, a first methanization step and a second methanization step while adjusting the reactive conditions by providing a plurality of coolers between these steps. The present invention succeeds in solving the multiplied reaction problem of the prior art by providing a simplified reaction device with minimized radiation surface which is energy efficient as described in connection with the desulfurizing column (8).

The present invention gains a small amount of highly concentrated hydrogen for use in the hydrodesulfurization by hydrogenizing the methanol/water mixture to be fed into the hydrogenizing column (8) as described previously. This improves the overall efficiency of the plant and also facilitates start-up and the ability of the system to react to load-change.

Returning to Figure 1, methanol is pressurized to about a reactive pressure by a methanol pump (12), and then mixed with degassified water in a methanol/water mixer (13). The resulting solution is vaporized in a methanol evaporator (14) by heating the methanol/water mixture. Thereafter the vaporized methanol/water mixture gas is further heated in a methanol superheater (15) to approximately 320 °C after which the superheated methanol/water mixture gas is fed into the reaction column (8).

As previously described, the reaction column (8) is of the combined use type, i.e. two system reaction tubes are mounted within a single unit shell drum. One reaction system mounted in the column is used for the steam-reforming and methanation and the other reaction system is used for hydrogenization which will now be explained in detail.

Figure 3 schematically illustrates that a partial tube (86) of the plurality of reaction tubes is filled with a hydrogenizing catalyst (85) and used as the hydrogenizing reaction tube (86).

The methanol/water mixture having the same temperature as the steam-reforming reaction temperature is fed into the hydrogenizing reaction tube (86). The methanol/water mixture undergoes an isothermal reaction on the hydrogenizing catalyst (85) under specific reactive conditions in a high speed single pass reaction, in which the methanol/water mixture is converted into a hydrogen-rich mixture gas which is relatively rich in H₂ and depleted in CO and CH₄ (i.e. CH₃OH + H₂O → 3H₂ + CO₂). The tube (86) is disposed along the center axis line of the column (8) so as to pass through both chambers in the upper and lower portions and this tube is filled with hydrogenizing catalyst (85). As to the direction of flow of the heat transfer medium, the temperature control, the advantage in the start-up and load-change and the like of tube (86), these are generally the same as in the methanizing reaction tube (81).

Regarding the hydrogenizing reaction on the catalyst (85) in the tube (86), this is the reverse reaction of methanol synthesis and thermal cracking. The efficiency of the methanol cracking yield or reforming yield is increased with increased and reduced pressure. It is an endothermic reaction in the thermal cracking reaction (i.e. CH₃OH → 2H₂ + CO), and it is an exothermic reaction in the shift reaction (i.e. CO + H₂O → H₂ + CO). Overall the hydrogenizing reaction is endothermic. Figure 6 shows the temperature variation toward the axis direction during the hydrogenizing reaction of the catalyst (86). The temperature initially descends rapidly but later rises when the catalyst receives heat released from the heat transfer medium and then conforms with the surface temperature. Thus, by momently releasing a large amount of the heat from the flow of the heat transfer medium, it can prevent the definite temperature-drop of the catalyst (85), and can perform the high yield reaction of hydrogen through one piece of the reaction tube (86) in a single pass reaction.

Comparing now the present invention with the prior art regarding the above hydrogenizing reaction, hydrogen has to be fed into the hydrodesulfurization in the prior art. It is presumed that the first step

reaction or the first column in the prior art is a hydrodesulfurization selected from amongst the conventional three stepped reaction of the methanation as previously described. In this technique, it is expected that a partial feed gas is pressurized by a recycle-gas compressor, and then recycled into a desulfurizing device as a hydrogen-mixed feed gas. The hydrogen content of the feed gas will be about 10%. Therefore, this prior art is disadvantageous because it is required to decrease the recycle-gas temperature as 10% of the whole feed gas to the normal temperature, and also to pressurize the recycle gas by the compressor so as to overcome the pressure loss estimated as 70% of the whole system. Thus, the energy loss of the prior art is serious.

In contrast, according to the present invention, it is obviously advantageous that the present invention can reduce radiation heat loss due to the large size of the first column described above, the energy loss consumed by the recycle gas compressor and the double energy loss consumed to cool the recycle gas before the desulfurization and again to heat up the processed gas after the desulfurization. Instead the present invention only consumes a small amount of energy to power the methanol pump (12), and has minimal radiation heat-loss from the integral type column (8) in addition to the highly efficient process of producing the highly concentrated hydrogen from the methanol with the high speed start-up and load-change capabilities of the plant.

According to the present invention, regarding the heat transfer medium, the combination of the hydrodesulfurization and steam-reforming are significant to the present invention. These significant reactions are achieved by maintaining each catalyst at an optimum operating temperature and also by providing the feed gases, i.e. the hydrogen-mixed feed gas, steam-mixed feed gas and methanol/water mixture gas, at an optimum temperature by supplying these from the external heat source through the inorganic salt type heat transfer medium. This heat transfer medium has sometimes been called "heat transfer salt" (i.e. HTS) in the art. This HTS is a eutectic mixture selected from sodium nitrite, sodium nitrate and potassium nitrate.

The advantage of this HTS is that its coefficient of heat transfer is more than 50% higher than oil group heat transfer mediums which are generally used in the art at temperatures of less than 350 °C if it is required to operate a rapid heat transfer, e.g. a reaction temperature between 320 °C and 350 °C used in the present invention, when it is required to transfer heat from the heat transfer medium to a reaction column and/or the interior of a shell drum of a heat exchanger for removing and/or supplying the heat from or to the reaction tubes therein. Thus, it is clear that this advantage of HTS used by the present invention is one of significance to the present invention.

Returning to Figure 1, the flow of HTS in the present system is delivered and pressurized from a heat medium reservoir (16) by a heat medium pump (17) and then the flow of HTS is branched into two streams, i.e. into the desulfurization system and steam-reforming system through a three-way control valve (11).

In the desulfurization system, the flow of HTS is heated up to 352 °C by the heat medium furnace (7) in order to control the desulfurizing temperature at 350 °C as described previously, and then the flow of HTS supplies the heat itself to or reversely absorbs (i.e. in the desulfurizing column only) the heat from each of the inner tubes of respective heat exchanging devices while passing through the shell drum of the crude material superheater (5), desulfurizing column (6), and a secondary water-supply heater (23). Finally the temperature of the HTS drops to about 321 °C and is returned into the heat medium reservoir (16).

In the steam-reforming system, the flow of HTS is branched by the three-way control valve (11) and heated up to a temperature of reforming of about 320 °C, and then the flow of HTS supplies the heat itself to or reversely absorbs (i.e. in the desulfurizing column only) the heat from each of the inner tubes of the respective heat exchanging devices while passing through the shell drum of the reaction column (8), feed gas/steam superheater (10), crude materials evaporator (3) and methanol superheater (15). Finally the temperature of the HTS drops to about 321 °C and is returned to the heat medium reservoir (16).

Regarding the system of controlling the temperatures of the two branched flows of HTS heat-sourced from the heat medium furnace (7) as if they were only one flow, the temperature of each branched flow is controlled by controlling the flow rate of each branched flow through the three-way control valve (11).

According to the necessity of optionally controlling the temperature of each of the branched flows, it is required to adequately arrange in order the heat devices such as the reaction heat-device group (i.e. reaction column or desulfurizing device), heat recovery device group (i.e. evaporator, superheater and the like), and heating device group (i.e. heat medium furnace). This is to ensure that the temperatures of both branched flows of the heat transfer medium as they return to the heat medium reservoir (16) are approximately equal while carefully checking the heat transfer medium inlet-temperature to be fed into the desulfurizing column and also the inlet-temperature into the reaction column by means of controlling the flow ratio between the desulfurizing system flow rate and reforming system flow rate through the three-way control valve (11). This enables the two desired temperatures to be controlled. On the other hand, regarding the temperature control of the heat medium furnace (7), it is controlled by controlling the fuel rate in

response to the inlet-temperature of the heat transfer medium flow into the desulfurizing column. Thus the heat balance of the whole system can be sensitively controlled by the furnace (7).

In the present invention, it is important to control the heat transfer medium temperature at each optimum temperature in the desulfurization and reforming reactions. This control system enables speedy 5 start-up and load-change, and makes it possible to fine-control the whole system.

Regarding the process of producing SNG from the hydrocarbonic crude materials such as butane, propane, naphtha and the like relating to the present invention, in order to satisfy the capabilities (i.e. the specific character of the start-up and load-change) generally required by SNG process, it is not only appropriate to employ the process of making the feed gas of the present invention but also to employ "the 10 apparatus of removing carbon dioxide and moisture from methane-rich gas" (i.e. continuous stream PSA method) which is filed by the same applicant as the present application and published as Japanese patent provisional publication No. Hei 2-281096, and then the product gas is carburetted by hydrocarbonic gas. Regarding the detail of the admitted prior art No. Hei 2-281096, the detailed explanation is omitted from the present description because of its previous publication.

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EXAMPLES

Figure 7 illustrates a preferred practical example of an arrangement for making high calorie type city gas according to the present invention. The composition and characteristics of each gas stream number shown 20 in Figure 7 is set out in Table 1 below. A butane evaporator (27) is provided in the arrangement illustrated in Figure 7 for carburetting the product gas according to the present invention.

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Table 1

Stream	1	2	3	4	5	6	7	8	9
No.	1	2	3	4	5	6	7	8	9
Tempera. °C	318	307	199	370	320	315	30	97	43
Pressure MPa (kg/cm ² G)	1.03 (9.3)	1.06 (9.6)	1.00 (9.0)	1.03 (9.3)	1.00 (9.0)	0.97 (8.7)	0.95 (8.5)	0.95 (8.5)	0.95 (8.5)
Composition (mol%)	H ₂ -	CH ₄ -	CO -	CO ₂ -	C ₂ H ₄ 3.00	iC ₄ H ₁₀ 27.00	nC ₄ H ₁₀ 70.00	CH ₃ OH -	H ₂ O -
	-	-	-	-	47.65 1.83 1.67 3.78 -	0.00 0.00 49.15 96.40 -	22.65 0.87 11.90 0.28 -	3.08 0.23 21.00 2.05 -	0.04 0.26 70.00 5.32 -
	5.095 kg mol/hr	0.765 0.765	20.380 1.020	1.020 26.496	33.785 37.26 0.00 -	17.177 1.414 0.00 -	1.414 18.591 0.00 -	417 -	417
	Nm ³ /h [•]	-	-	-	17	131	475	385	-

According to the above constitution, the present invention provides the following advantages:

(1) it reduces energy consumption of the necessary heat and electrical power compared to conventional arrangements since the hydrogen-additive sulfurization of feed gas is performed in a one unit column and the highly concentrated hydrogen reformed from the crude methanol is used for the hydrogenation,

(2) it can prepare the methane-rich mixture gas with high yield in a one step reaction as one of the reaction means of methanizing the hydrocarbonic materials such as butane, propane, naphtha and the like in accordance with the vapor-phase catalytic cracking reaction in the presence of a catalyst in the reaction column,

(3) it facilitates speedy start-up and load-change since it employs a heat transfer medium able to transfer heat at high speed for adjusting each reaction condition in the hydrogen-additive sulfurization and steam-reforming; the heat transfer medium being heated in an external furnace,

(4) it has a high gasification efficiency since fewer processing devices are necessary, and achieves both a speedy heat transfer from the reaction heat and an effective heat recovery, and

(5) it further facilitates the operation of the total system of the present invention, specially it can operate the start-up, stoppage and load-change (i.e. the changeable span is in range of 100%) within fifteen minutes, if the refining of the elementary feed gas is processed by the continuous stream PSA method.

Claims

1. A process for producing high calorie type city gas from a hydrocarbonic crude gas comprising the steps of:

5 (A) desulfurizing sulfureous compounds present in the hydrocarbonic crude gas by hydrodesulfurization using a desulfurizing column which includes U-shaped passages within a first shell and tube heat exchanger type reactor, the first limb of each U-shaped passage forming a forward reaction tube and being filled with a nimox catalyst and the second limb of each U-shaped passage forming a backward reaction tube and being filled with zinc oxide;

10 (B) methanizing the desulfurized gas to produce a methane-rich feed gas by using a combined-use type reaction column for methanation and methanol steam-reforming within a second shell and tube heat exchanger type reactor, the column housing a plurality of reaction tubes filled with a methanizing catalyst comprising an alumina group carrier supported by nickel;

15 (C) steam-reforming a mixture of methanol and water to produce a hydrogen-rich gas by using said combined-use type reaction column for methanation and methanol steam-reforming within the second shell and tube heat exchanger type reactor, the column further housing a reaction tube filled with a steam-reforming catalyst;

20 (D) refining the methane-rich feed gas by removing carbon dioxide and moisture from it; and

(E) carburetting the refined methane-rich feed gas to form the high calorie type city gas;

25 the process being characterized in that:

(i) the desulfurizing step (A) includes the steps of introducing a heat transfer medium into the shell drum of the first heat exchanger type reactor to keep the temperature of its reaction tubes at approximately 350 °C, mixing the hydrocarbonic crude gas with the hydrogen-rich gas to form a hydrogen-mixed gas, and feeding the hydrogen-mixed gas into said U-shaped passages to desulfurize the hydrogen-mixed gas by allowing hydrogen and sulfureous compounds present in the hydrogen-mixed gas to react on the nimox catalyst present in each forward reaction tube to produce hydrogen sulfide, and absorbing the hydrogen sulfide on the zinc oxide present in each backward reaction tube;

30 (ii) the methanizing step (B) includes the steps of introducing a heat transfer medium into the shell drum of the second heat exchanger type reactor to keep the temperature of its reaction tubes at approximately 320 °C, and feeding a mixture of the desulfurized gas and steam into said reaction tubes filled with the methanizing catalyst where it is methanized in a single pass isothermal reaction to produce the methane-rich feed gas;

35 (iii) the steam-reforming step (C) includes the step of feeding the mixture of methanol and water into the reaction tube filled with the steam-reforming catalyst where it is steam-reformed in a single pass isothermal reaction on the catalyst with the same temperature as the methanation reaction to produce the hydrogen-rich gas for mixing with the hydrocarbonic crude gas; and

40 (iv) maintaining the reaction temperatures of the hydrodesulfurization, methanation and methanol steam-reforming reactions at a constant optimum level by the use of the heat transfer medium which comprises an inorganic salt having high speed heat transferability, the reciprocal heat transferability of circulating said heat transfer medium being adapted to release the necessary heat in an endothermic reaction zone or to absorb the heat generated in an exothermic reaction zone in said various reaction tubes, and which permits the temperature in two branched flows of said heat transfer medium to the first and second shell and tube heat exchanger type reactors to be controlled, both flows being derived from one external heating furnace and being controlled by a three-way flow rate control valve.

45 2. A process for producing high calorie type city gas according to claim 1, wherein the refining step (D) is carried out using the continuous stream PSA method.

Patentansprüche

50 1. Verfahren zur Herstellung eines kalorienreichen Stadtgases aus einem Kohlenwasserstoff-Rohgas, das die Stufen umfaßt:

55 (A) Entschwefelung von schwefelhaltigen Verbindungen, die in dem Kohlenwasserstoff-Rohgas enthalten sind, durch Hydrodesulfurierung unter Verwendung einer Entschwefelungssäule, die U-förmige Durchgänge innerhalb eines ersten Reaktors vom Typ eines Röhrenwärmeaustauschers mit Mantel enthält, wobei der erste Schenkel jedes U-förmigen Durchgangs eine Reaktionsröhre in

Vorwärtsrichtung bildet und mit einem Nimox-Katalysator gefüllt ist, und wobei der zweite Schenkel jedes U-förmigen Durchganges eine Reaktionsröhre in Rückwärtsrichtung bildet, die mit Zinkoxid gefüllt ist;

(B) Methanisierung des entschwefelten Gases, um zu einem methanreichen Betriebsgas zu gelangen unter Verwendung einer kombinierten Reaktionssäule für die Methanisierung und die Methanol-Dampf-Reformierung innerhalb eines zweiten Röhrenwärmeaustauschers mit Mantel, wobei in der Säule eine Vielzahl von Reaktionsröhren angeordnet sind, die mit einem Methanisierungskatalysator gefüllt sind, der einen Nickelgestützten Träger der Aluminiumoxidgruppe umfaßt;

(C) Dampf-Reformierung eines Gemisches aus Methanol und Wasser, um zu einem wasserstoffreichen Gas unter Verwendung der kombinierten Reaktionssäule für die Methanisierung und die Methanol-Dampf-Reformierung innerhalb des zweiten Reaktors vom Typ des Röhrenwärmeaustauschers mit Mantel zu gelangen, wobei die Säule weiterhin eine Reaktionsröhre enthält, die mit einem Dampf-Reformierungskatalysator gefüllt ist;

(D) Reinigung des methanreichen Betriebsgases durch Entfernung von Kohlendioxid und Feuchtigkeit daraus; und

(E) Karburierung des gereinigten methanreichen Betriebsgases, um das kalorienreiche Stadtgas zu bilden;

wobei das Verfahren dadurch gekennzeichnet ist, daß

(i) die Entschwefelungsstufe (A) die Schritte der Einführung eines Wärmeübertragungsmediums in den zylinderförmigen Mantel des ersten Reaktors vom Typ des Röhrenwärmeaustauschers einschließt, um die Temperatur von dessen Reaktionsröhren auf etwa 350 ° C zu halten, Mischen des Kohlenwasserstoff-Rohgases mit dem wasserstoffreichen Gas, um ein Wasserstoff-Mischgas zu bilden und Einführung des Wasserstoff-Mischgases in die U-förmigen Durchgänge, um das Wasserstoff-Mischgas zu entschwefeln durch Ermöglichung einer Reaktion der in dem Wasserstoff-Mischgas enthaltenen Komponenten Wasserstoff und schwefelreiche Verbindungen an dem Nimox-Katalysator, der in jeder Reaktionsröhre in Vorwärtsrichtung vorhanden ist, um Schwefelwasserstoff zu bilden, und Absorption des Schwefelwasserstoffes am Zinkoxid, das in jeder Reaktionsröhre in Rückwärtsrichtung vorhanden ist;

(ii) die Methanisierungsstufe (B) die Stufen der Einführung eines Wärmeübertragungsmediums in den zylinderförmigen Mantel des zweiten Reaktors vom Typ des Röhrenwärmeaustauschers einschließt, um die Temperatur von dessen Reaktionsröhren auf etwa 320 ° C zu halten, und Einführung eines Gemisches des entschwefelten Gases und von Dampf in die Reaktionsröhren, die mit dem Methanisierungskatalysator gefüllt sind, wobei das Gas in einer isothermen Durchlaufreaktion methanisiert wird, um zu methanreichem Betriebsgas zu gelangen;

(iii) die Dampf-Reformierungsstufe (C) die Stufe der Einführung des Gemisches von Methanol und Wasser in die Reaktionsröhre einschließt, die mit dem Dampf-Reformierungskatalysator gefüllt ist, worin die Dampfreformierung in einer isothermen Durchlaufreaktion an dem Katalysator mit der gleichen Temperatur wie die Methanisierungsreaktion erfolgt, um zu dem wasserstoffreichen Gas für das Vermischen mit dem Kohlenwasserstoff-Rohgas zu gelangen;

(iv) Aufrechterhaltung der Reaktionstemperaturen der Hydrodesulfurierungs-, Methanisierungs- und Methanol-Dampf-Reformierungsreaktionen auf einem konstanten optimalen Niveau durch Verwendung des Wärmeübertragungsmediums, das ein anorganisches Salz umfaßt, das eine schnelle Wärmeübertragbarkeit hat, wobei die wechselseitige Wärmeübertragbarkeit der Zirkulierung des Wärmeübertragungsmediums angepaßt ist, um die notwendige Wärme in einer endothermen Reaktionszone freizusetzen oder die in einer exothermen Reaktionszone erzeugte Wärme zu absorbieren in den verschiedenen Reaktionsröhren, und das gestattet, die Temperatur in zwei verzweigten Strömen des Wärmeübertragungsmediums zu dem ersten und dem zweiten Reaktor vom Typ des Röhrenwärmeaustauschers mit Mantel zu steuern, wobei beide Ströme aus einem äußeren Heizofen abgeleitet und über ein die Fließgeschwindigkeit steuerndes Dreiwege-Steuerungsventil gesteuert werden.

2. Verfahren zur Herstellung eines kalorienreichen Stadtgases nach Anspruch 1, worin die Reinigungsstufe (D) unter Einsatz des PSA-Verfahrens im kontinuierlichen Gasstrom durchgeführt wird.

55 Revendications

1. Procédé de production de gaz de ville à haut pouvoir calorifique à partir d'un gaz hydrocarboné brut comprenant les étapes consistant à :

(A) éliminer des composés soufrés présents dans le gaz hydrocarboné brut par hydrodésulfurisation en utilisant une colonne de désulfurisation comprenant des tubes de passage en forme de U dans un premier réacteur de type échangeur de chaleur composé d'une enveloppe et de tubes, la première branche de chaque tube de passage en U formant un tube réactionnel aller rempli d'un catalyseur de type nimox et la deuxième branche de chaque tube de passage formant un tube réactionnel de retour rempli d'oxyde de zinc,

(B) méthanation du gaz désulfurisé pour produire un gaz d'alimentation riche en méthane en utilisant une colonne de réaction de type combiné pour la méthanation et le reformage à la vapeur de méthanol dans un deuxième réacteur de type échangeur de chaleur composé d'une enveloppe et de tubes, la colonne contenant une pluralité de tubes réactionnels remplis avec un catalyseur de méthanation qui est du nickel sur un support de type alumine,

(C) reformage à la vapeur d'un mélange de méthanol et d'eau pour produire un gaz riche en hydrogène en utilisant ladite colonne de réaction de type combiné pour la méthanation et le reformage à la vapeur de méthanol dans le deuxième réacteur de type échangeur de chaleur composé d'une enveloppe et de tubes, la colonne renfermant en outre un tube réactionnel rempli d'un catalyseur de reformage à la vapeur,

(D) raffinage du gaz d'approvisionnement riche en méthane par élimination de dioxyde de carbone et d'humidité,

(E) carburation du gaz d'alimentation riche en méthane raffiné pour former le gaz de ville à haute teneur en calories,

le procédé étant caractérisé en ce que

(i) l'étape de désulfurisation (A) comporte les étapes consistant à introduire un milieu caloporteur dans l'enveloppe cylindrique du premier réacteur de type échangeur de chaleur afin de maintenir la température de ses tubes réactionnels à environ 350 °C, à mélanger le gaz hydrocarboné brut avec le gaz riche en hydrogène pour former un gaz contenant de l'hydrogène, et à envoyer ledit gaz contenant de l'hydrogène dans les tubes de passage en forme de U pour désulfuriser le gaz contenant de l'hydrogène par réaction de l'hydrogène et des composés soufrés présents dans le gaz contenant de l'hydrogène sur le catalyseur nimox présent dans chacun des tubes de passage aller dans le but de former du sulfure d'hydrogène et par absorption du sulfure d'hydrogène sur l'oxyde de zinc contenu dans chacun des tubes de passage retour,

(ii) l'étape de méthanation (B) comporte les étapes consistant à introduire un milieu caloporteur dans l'enveloppe cylindrique du deuxième réacteur de type échangeur de chaleur afin de maintenir la température de ses tubes réactionnels à environ 320 °C, et à envoyer un mélange de gaz désulfurisé et de vapeur dans lesdits tubes réactionnels remplis de catalyseur de méthanation où il subit une réaction isothermique de méthanation en un seul passage afin de produire le gaz d'alimentation riche en méthane,

(iii) l'étape de reformage à vapeur comprend l'étape consistant à envoyer le mélange de méthanol et d'eau vers le tube réactionnel rempli de catalyseur de reformage à la vapeur, où il est reformé à la vapeur en une réaction isothermique par passage unique sur le catalyseur à une température identique à celle de la réaction de méthanation pour produire le gaz riche en hydrogène destiné à être mélangé avec le gaz hydrocarboné brut, et

(iv) en ce que l'on maintient les températures réactionnelles de l'hydrodésulfurisation, de la méthanation et du reformage à la vapeur de méthanol à une valeur constante optimale en utilisant un milieu caloporteur qui est un sel minéral capable de transférer rapidement la chaleur, la capacité de transfert de chaleur réciproque dudit milieu caloporteur étant appropriée pour libérer la chaleur nécessaire dans une zone de réaction endothermique ou pour absorber la chaleur dégagée dans une zone de réaction exothermique dans lesdits tubes réactionnels, et qui permet de réguler la température de deux flux, issus de la division d'un flux de milieu caloporteur, allant vers le premier et deuxième réacteur de type échangeur de chaleur composé d'une enveloppe et de tubes dont il faut réguler la température, les deux flux provenant d'un four externe et étant régulés par une vanne de commande à trois voies.

2. Procédé de production de gaz de ville à haute teneur en calories conforme à la revendication 1 dans lequel l'étape de raffinage (D) est réalisée à l'aide d'un procédé PSA en flux continu.

FIG. I

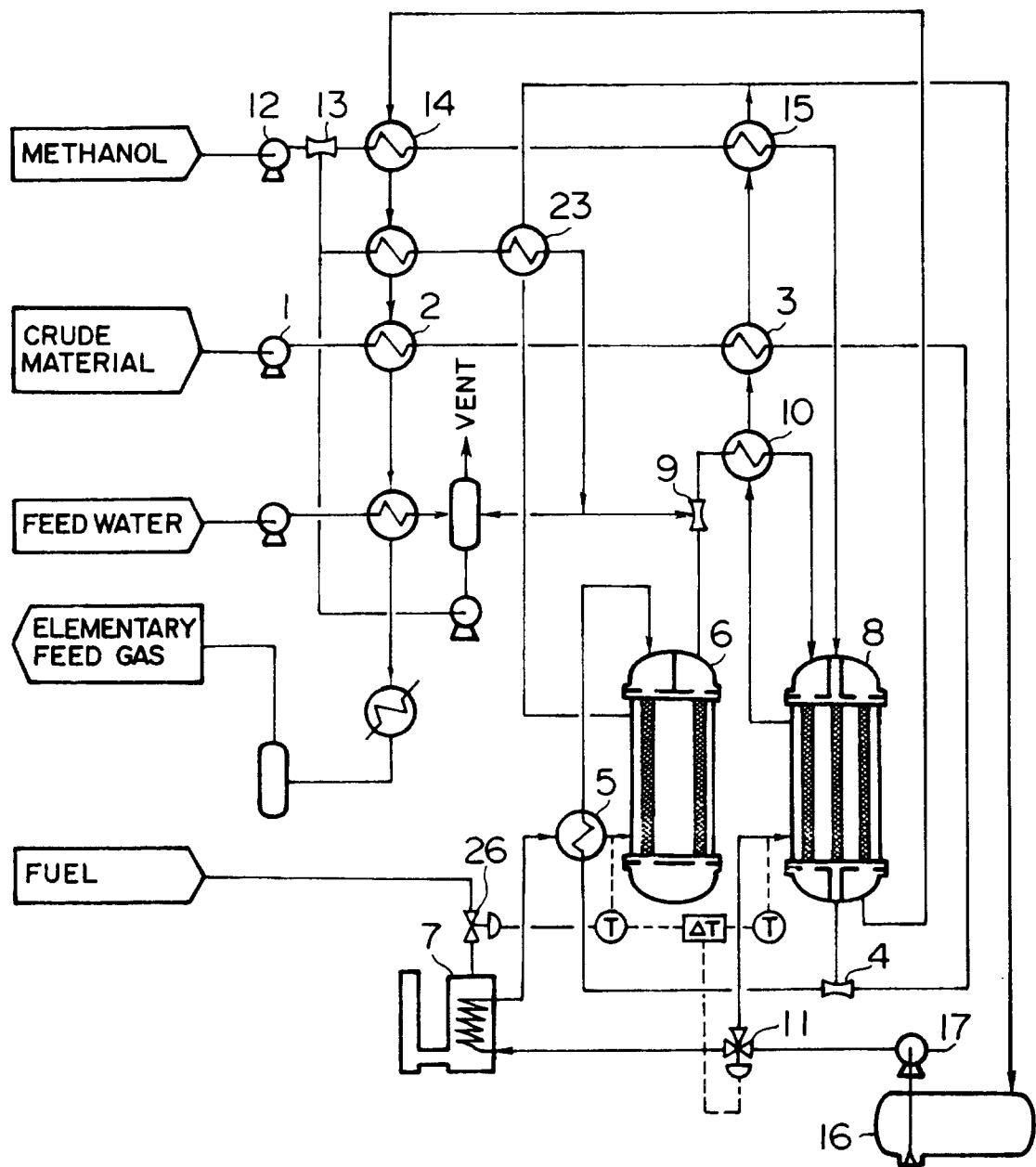


FIG. 2

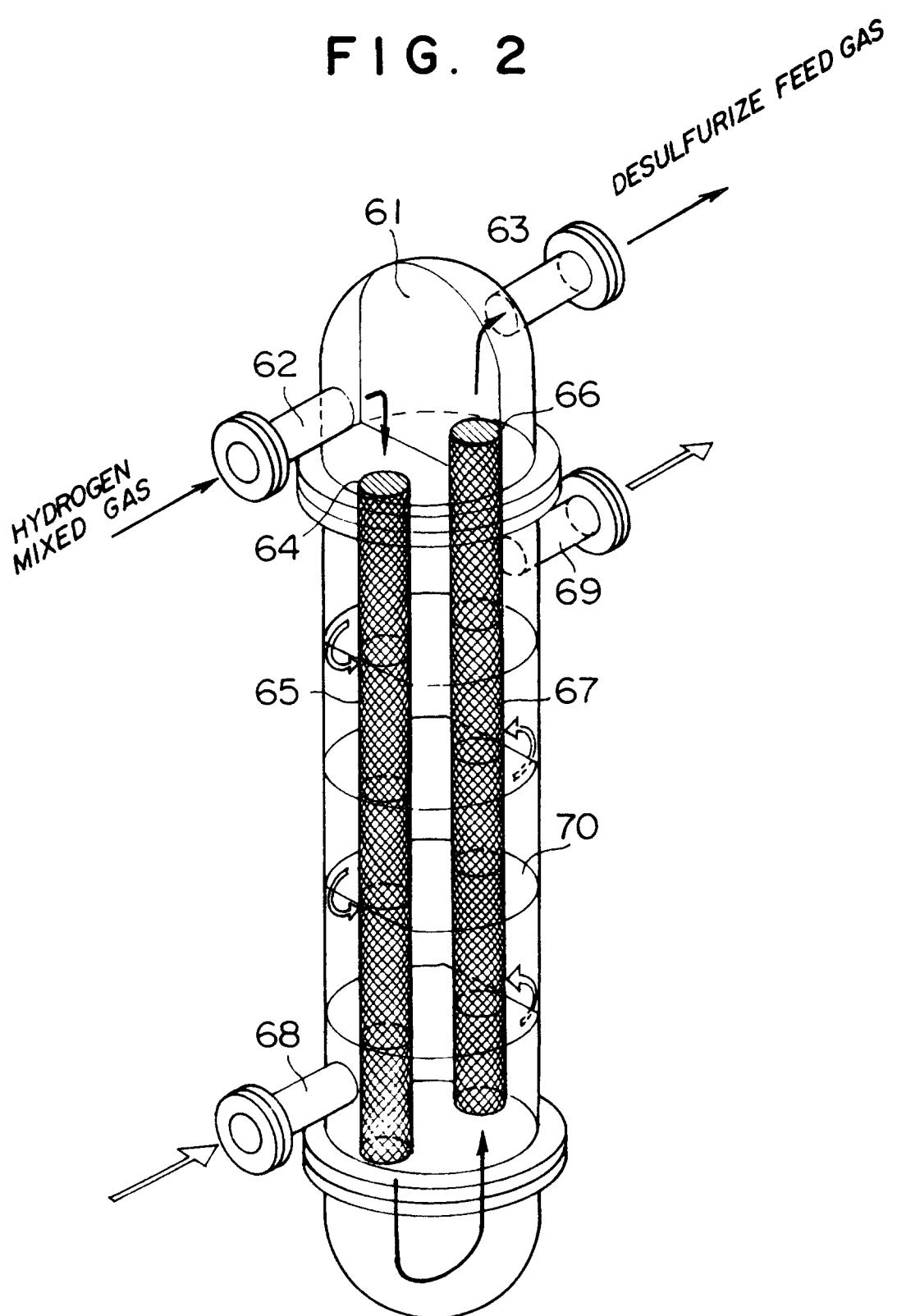


FIG. 3

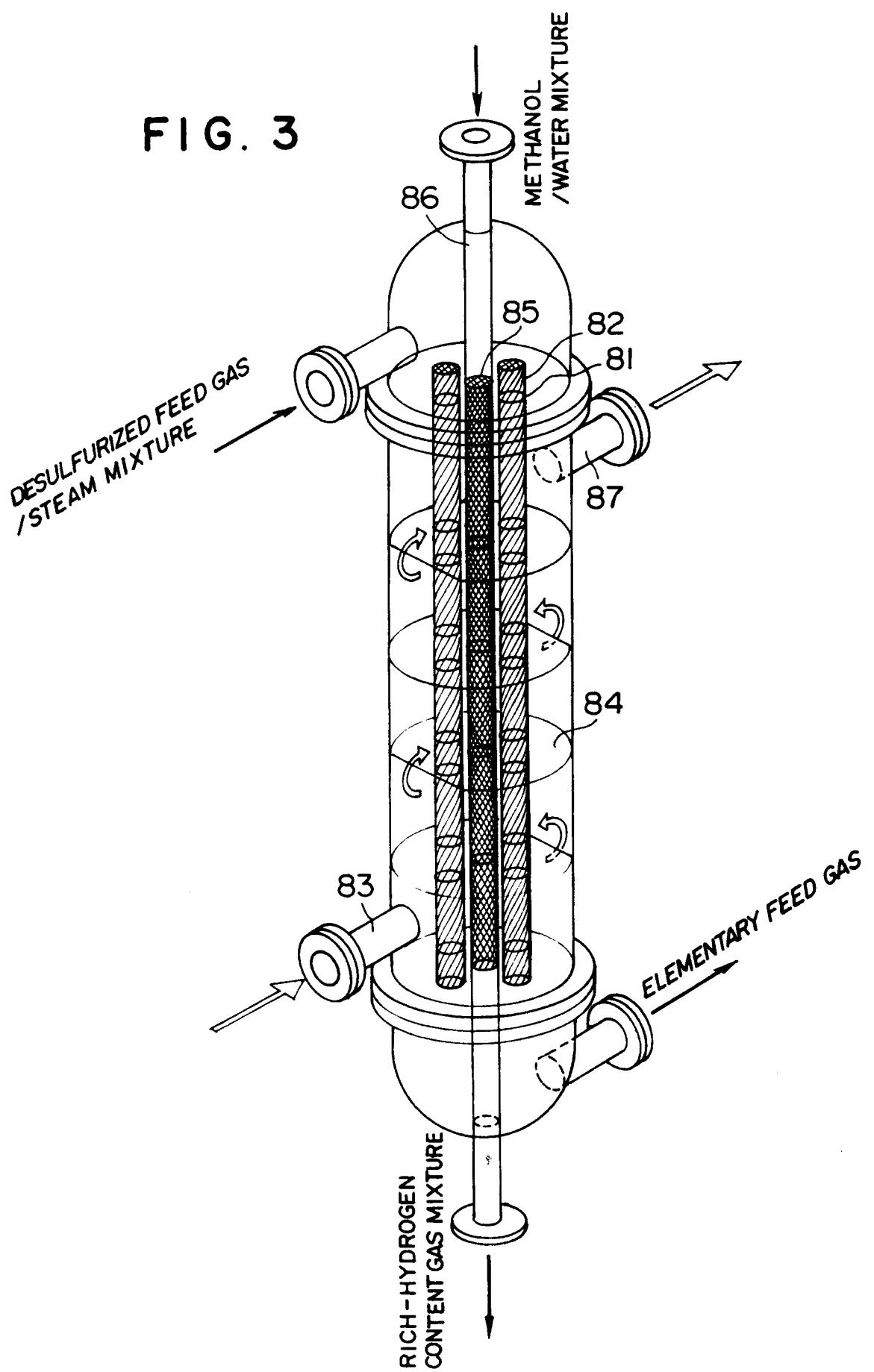


FIG. 4

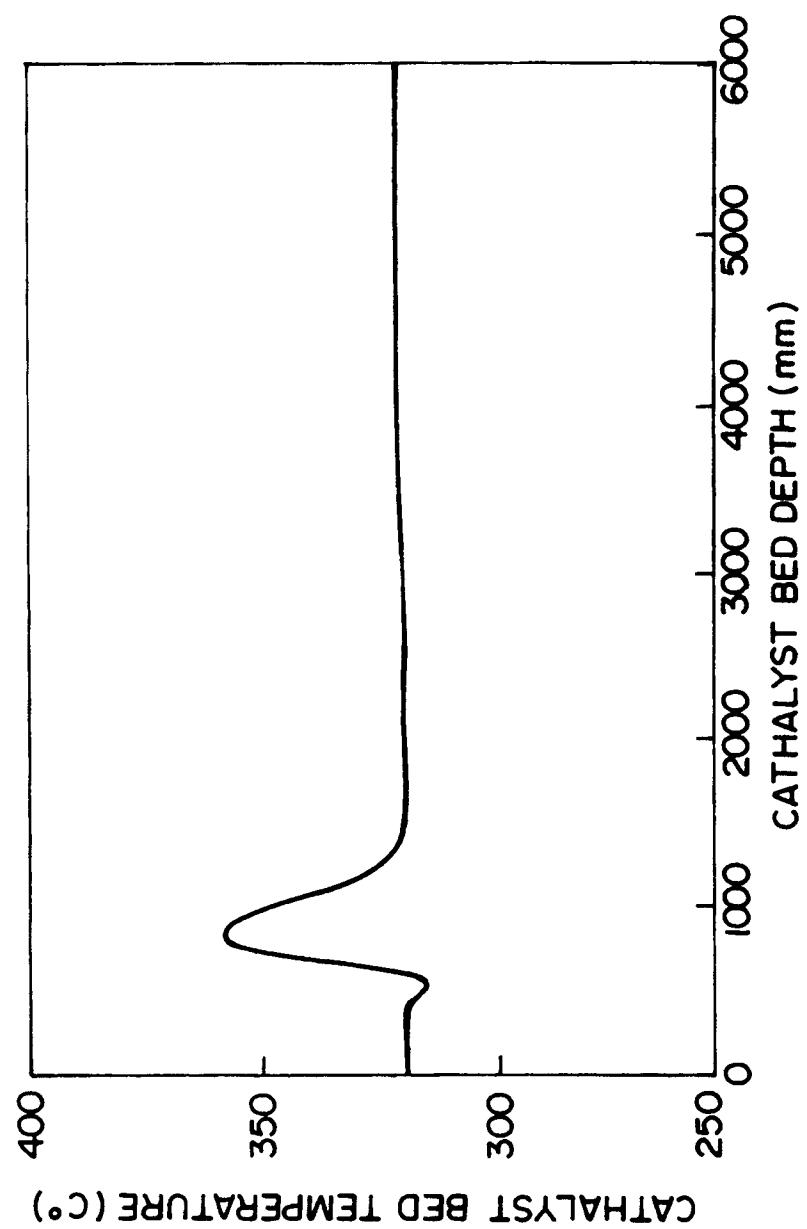


FIG. 5

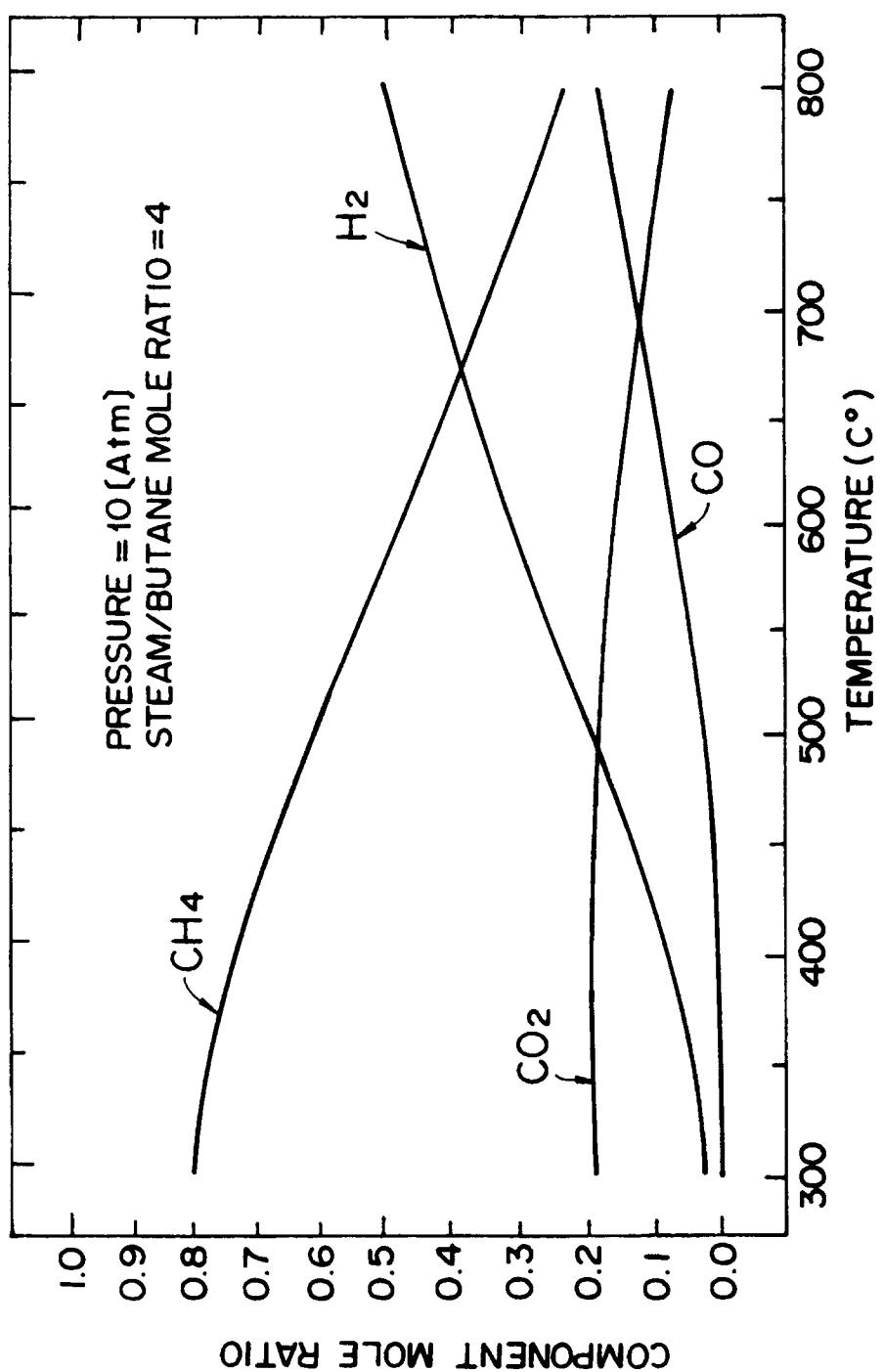


FIG. 6

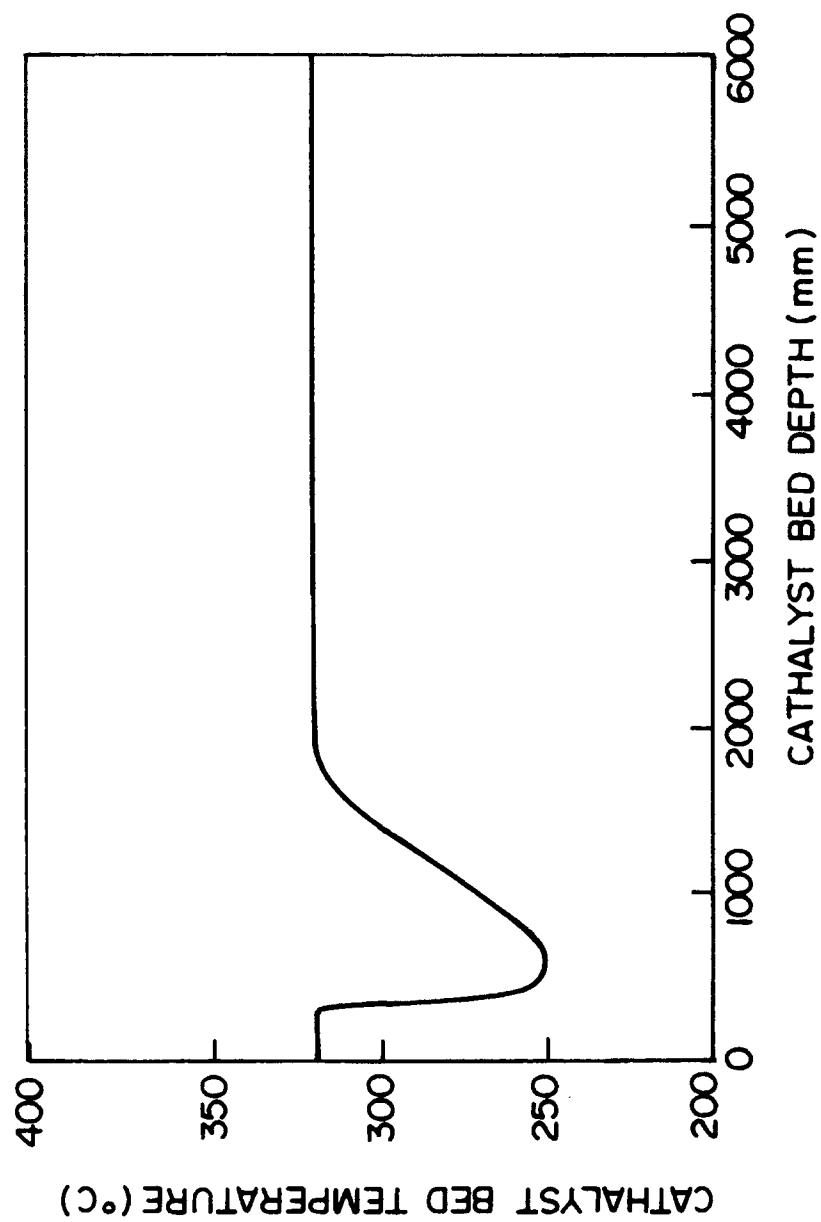


FIG. 7

FIG. 7A

FIG. 7A FIG. 7B

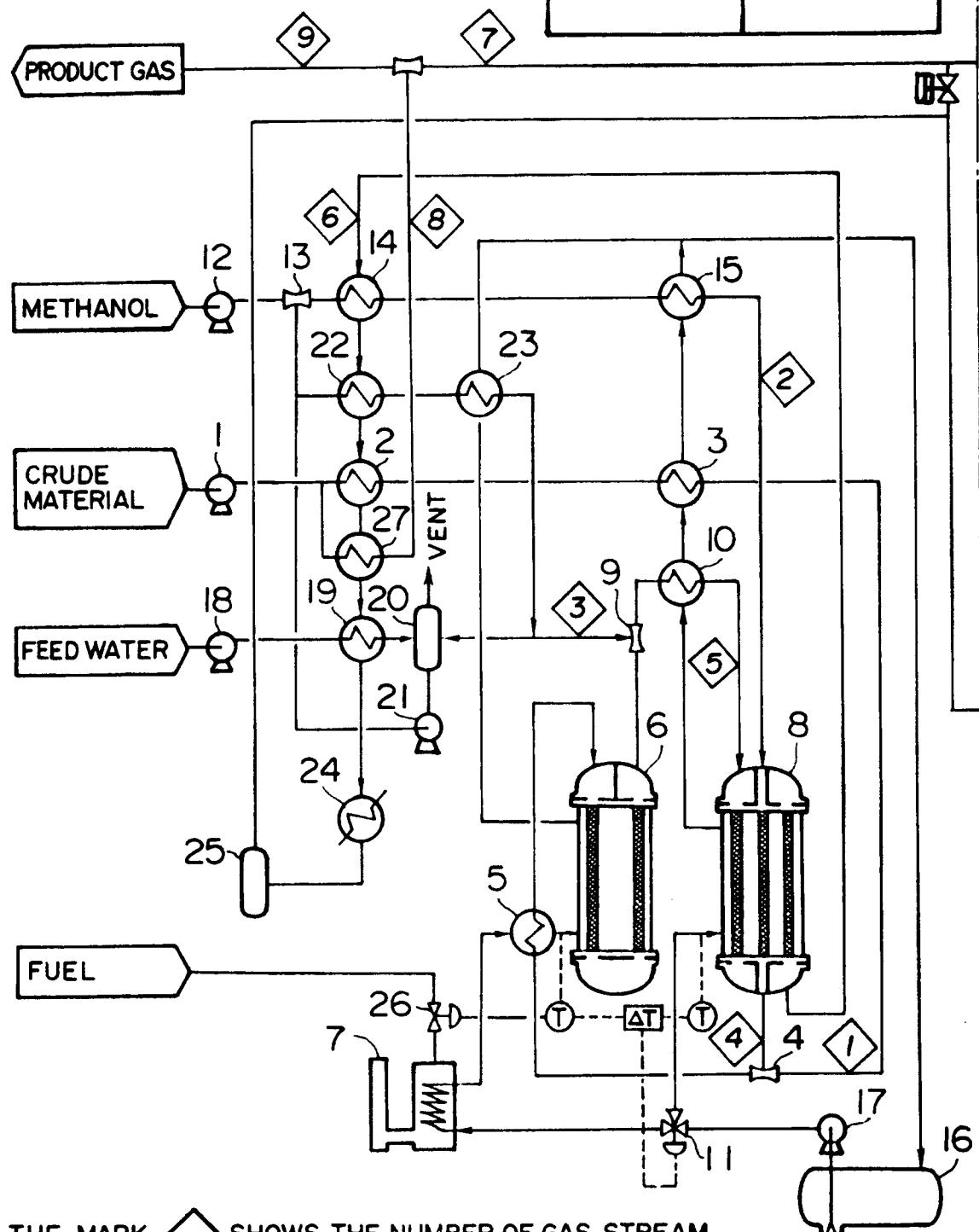


FIG. 7B

