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(54) Process for forming city gas with high heat value from methanol as a crude material.

(57) A process for producing a city gas having a high caloric content wherein a methanol-water mixture is reacted in a one-step reaction to produce a methane-rich gas mixture containing methane, hydrogen, carbon monoxide, carbon dioxide and water. The water is separated from the methane-rich gas mixture and recycled as a water feed. The carbon dioxide is then removed from the methane-rich gas mixture and butane is added to the remaining methane-rich gas to produce a resultant city gas having a heat value of at least about 11,000 Kcal/Nm^3. The total amount of heat required to heat the reactants and sustain the process at steady state conditions is provided by heat that is recovered and recycled from the heat of reaction. A nickel catalyst is used to promote the one-step reaction.

PROCESS FOR FORMING CITY GAS WITH HIGH HEAT VALUE FROM METHANOL AS A CRUDE MATERIAL

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a process for producing city gas having a high calorie content using methanol as a raw material which is available in the liquid state at a convenient temperature range for transportation and storage and the like. The present invention is also directed to a one-step methanation reaction for producing methane-rich gas from methanol which may be used in the process for producing city gas. In addition, the present invention is directed to a catalyst having a low sulfur content for use in promoting the one-step methanation reaction.

2. Discussion of Background Material Information

Recently, in an attempt to increase the caloric content of city gas used in densely populated area, such as megalopolises, it has been proposed to introduce LNG (liquefied natural gas). However, since LNG requires extremely low temperatures, such as minus 162° C., during transportation and storage, city gas facilities in small to medium sized cities have experienced many technical problems with its transportation and storage, which, due to the expense associated with the efforts necessary in this regard; is not particularly economical.

In addition to having none of the above discussed disadvantages associated with LNG, using methanol as the starting material for purposes of the present invention is advantageous because of its consistently lower cost due to the abundance of natural resources, such as coals, natural gases and the like, from which methanol is obtained. Moreover, methanol contains no impurities, such as sulfur, nitrogen, heavy metals, and the like, as do coals, natural gases and the like. Therefore, methanol does not require additional processing to remove such impurities which would add additional costs to the city gas product.

In view of the foregoing, methanol is believed to have a promising future as a raw material for city gas.

Although it is known to produce city gas utilizing methanol, as a raw material as exemplified by Japanese Patent Publication No. Sho 57-24835, this conventional process for producing city gas from methanol includes a reformation step in which a mixture of methanol and water is contacted and reformed on a ruthenium (Ru) based catalyst. The gases produced by the reformation step include hydrogen (H_2), carbon monoxide (CO) and carbon dioxide (CO_2). Next, a methanation step is conducted in which the hydrogen and carbon monoxide gases are converted into methane. After methanation, carbon dioxide gas is removed and the remaining methane rich gases are subjected to a dehydration and caloric adjustment step.

According to the above conventional process for producing city gas from methanol, due to the fact that the gases are first reformed by being contacted with a catalyst in a contact cracking process, followed by a methanation step, the conventional method results in high production costs and low productivity. Moreover, the process system is oversized and complex.

SUMMARY OF THE INVENTION

The object of this invention is to overcome the above discussed disadvantages associated with the previously known conventional process of producing city gas from methane using methanol as a starting material.

In accordance with the present invention, methane-rich gas is first produced from a mixture of methanol and water by means of a one-step reaction process. The one-step methanation reaction process of the present invention is unique in this respect in that it eliminates the need for supplying feed water into the mixture of methanol and water other than in the initial start-up of the process. Once the process is operating on-line, only a methane feed is required.

In addition to the advantage of only needing to add water during the start-up of the process of the present invention, this process of the present invention is also advantageous in that the heat used to heat the heating medium is fully recycled throughout the process steps. Any water, other than that needed for start-up purposes, will be fully recycled by the water which is separated from the methane-rich gases during the reforming process. Likewise, any heat, other than that needed for start-up purposes, will be fully recovered from the heat of reaction which is generated when the methane-rich gas is produced.

In general, the present invention is directed to a process for producing high calorie city gas which involves first preparing a methanol and water mixture; then exchanging heat between a heat medium and the methanol-water mixture in at least one heat exchanger to produce a heated methanol-water mixture having a predetermined reaction temperature; followed by reacting the heated methanol-water mixture in a reactor at a low temperature of less than about 300° C in the presence of a catalyst which includes a nickel component supported on an alumina carrier having a reduced sulfur content and a reduced specific surface area so as to form a methane-rich gas mixture; followed by separating water from the methane-rich gas mixture; prior to removing carbon dioxide gas from the methane-rich gas mixture; and finally adding butane to the methane-rich gas mixture to regulate the caloric content of the methane-rich gas mixture whereby a portion of the water separated from the methane-gas mixture is used in preparing the methanol and water mixture, and wherein at least a portion of heat necessary for heating the heat medium is generated by the heat of reaction during the production of the methane-rich gas mixture.

In addition, the present invention is also directed to a method for producing a methane gas which involves providing a feed stock including methanol; reacting the methanol in the presence of a catalyst including a catalytically active metal substance selected from the group consisting of elemental nickel (Ni) and a nickel compound, and a carrier including alumina material under reaction conditions including a temperature maintained at about 300° C to produce gas containing methane, preferably wherein the reaction conditions include pressures of less than about 9 atm. The gas containing methane is preferably a methane-rich gas mixture, preferably containing at least about 72% CH_4, and more preferably containing at least about 72% CH_4 and less than about 25% CO_2. The methane-rich gas composition may also include about 3% H_2, with the most preferably composition being about 72% CH_4, about 25% CO_2, and about 3% H_2. The methane-rich gas produced in accordance with the previously described procedure has a heat value of at least about 6,900 Kcal/Nm^3.

The present invention is also directed to the catalyst which has been found to be particularly suitable for use in the previously described one-step methanation reaction. The catalyst in accordance with the present invention includes a catalytically active metal substance selected from the group consisting of elemental nickel (Ni) and a nickel compound; and a carrier including alumina material. The catalytically active metal substance is preferably a nickel compound, such as nickel oxide. The aluminum material is preferably a member selected from the group consisting of alumina, alumina hydrate and silica alumina. Preferably the alumina material is selected from the group of alumina materials having a sulfur content of less than about 1.2% by weight, which are preferably selected from the group consisting of alumina and alumina hydrate, which most preferably are pulverized alumina and pulverized alumina hydrate. Another particularly preferred alumina material is silica alumina, and more preferably silica alumina having a specific surface area of less than about 350 M^2/g., in which case the catalytically active metal substance is preferably a nickel compound, and most preferably nickel oxide.

In addition, the present invention as directed to a process for producing a city gas which involves providing a methane-rich gas mixture, preferably in accordance with the previously described procedure; separating at least a portion of any water present in the methane-gas mixture; removing carbon dioxide from the methane-rich gas to form a resultant methane-rich gas having a certain caloric content; dehumidifying the resultant methane-rich gas; and adding butane to carburate the methane-rich gas so as to result with a city gas having a caloric content higher than the certain caloric content of the resultant methane-rich gas, which is preferably about 11,000 Kcal/Nm^3. The resultant city gas also preferably has a Wobbe Index of about 13,340, and a Combustion Potential of between about 41.6 and 41.9 cm/SEC.

In a preferred embodiment of the process for producing city gas, as described above, the feed stock including methanol is provided by mixing a methanol feed with a water feed to produce a methanol-water mixture having a predetermined mole ratio, which is preferably between about 0.3 and 0.7, and most preferably about 0.5, and heating the methanol-water mixture to a temperature which favors a methanation reaction, which, as previously described, is preferably carried out as a one-step methanation reaction in accordance with the present invention.

The details of the process for producing city gas in accordance with the present invention are otherwise described hereinbelow so as to enable anyone skilled in the art to practice the invention.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is a process flow chart illustrating an example practiced in the present invention.

Figure 2 is a block diagram flow chart illustrating a preferred embodiment of the present invention.

Figures 3-7 illustrate processes utilized in start-up procedures.

DETAILED DESCRIPTION OF THE INVENTION

Referring to the drawings, and more particularly to the process flow chart shown in Fig. 1, the process for producing city gas having a high caloric content from methanol as a raw material will now be explained in more detail.

First the methanol is mixed with water to form a liquid methanol-water mixture after which the liquid methanol-water mixture is passed through a series of heat exchangers wherein the methanol-water mixture is gasified and heated to a proper temperature for reaction purposes prior to being fed into a reactor for reaction zone (1).

The series of heat exchangers include a first heat exchanger (2) that functions as a preheater. The heat exchange medium utilized to preheat the liquid methanol-water mixture in the first heat exchanger is the reactant product gases that are produced in the reactor (1). In other words, a portion of the heat of reaction that is absorbed by the product stream that leaves the reactor (1) is utilized to preheat the feed stream that is eventually fed into the reactor. The liquid methanol-water mixture that enters the first heat exchanger is preheated as it passes through the first heat exchanger and is fed into a second heat exchanger (3) in the form of a heated, liquid methanol-water mixture.

The second heat exchanger (3) in the series of heat exchangers is an evaporator in which the preheated liquid methanol-water mixture leaving the first heat exchanger is gasified into a gaseous methanol-water mixture. The heat exchange medium utilized to gasify the preheated liquid methanol-water mixture in the second heat exchanger is a heat exchange medium that is circulated through the reactor (1) in a manner that will be discussed in more detail below. The resultant gaseous methanol-water mixture that exits the second heat exchanger is fed into a third heat exchanger (4).

The third heat exchanger (4) in the series of heat exchangers is a superheater in which the gaseous methanol-water mixture is superheated to a proper reaction temperature. As in the case of the second heat exchanger (3), the heat exchange medium utilized to superheat the gaseous methanol-water mixture in the third heat exchanger is a heat exchange medium that is circulated through the reactor (1).

The first, second and third heat exchangers are arranged in series with respect to the methanol-water feed stream that supplies the methanol and water to the reactor. The second and third heat exchangers are additionally arranged in series with respect to the heat exchange medium that is circulated through the reactor (1) and supplied to both the second and third heat exchangers. As shown in figure 1, the heat exchange medium passes first from the reactor (1) to the third heat exchanger and then to the second heat exchanger. In this manner, there is initially a sufficient amount of heat in the heat exchange medium to superheat the gaseous methanol-water mixture as the heat exchange medium and the gaseous methanol-water mixture pass through the third heat exchanger. Likewise, there is a lower, but sufficient, amount of heat in the heat exchange medium to gasify the preheated liquid methanol water mixture as the heat exchange medium and the preheated liquid methanol-water mixture pass through the third heat exchanger. By this arrangement of the first, second and third heat exchangers and the heat exchange mediums used therein, the full recovery and use of the heat of reaction, as discussed above is accomplished.

The reactor (1) is designed for producing methane-rich gas mixtures by catalytically reacting methanol and water in the gas phase. The type of reactor utilized may be selected from any conventional reactor types suitable for catalytically reacting gas phase reactants. For purposes of the present invention, a tubular reactor will be referred to for exemplary purposes.

The catalyst which is packed in the reactor (1) comprises a nickel based catalyst which is supported on a suitable support means. A preferred support means utilized in the present invention is an alumina carrier which has a reduced sulfur content and/or a reduced surface area. As an example, the catalyst may comprise nickel (Ni) or compounds thereof, including nickel oxide, supported on a carrier of pulverized alumina or pulverized alumina hydrate in which the sulfur content (for example, SO_4^{-2}) has been reduced to less than 1.2 %. In another example, the catalyst may comprise nickel oxide supported on a carrier of silica alumina having a specific surface area of less than $350m^2/g$.

The above discussed catalysts are particularly useful in the present invention because, it has been discovered, they have a high catalytic activity under comparatively lower temperature than catalysts previously utilized in conventional processes to produce city gas from methanol. Moreover, it has been discovered that the catalyst utilized in the present invention are capable of producing methane-rich gases (for example CH_4: 72%, CO_2: 25% and H_2: 3%), from methanol at a high rate. The methane-rich gases produced by the previously described catalysts in accordance with the present invention are produced by a one-step reaction process at reaction temperature's preferably of about 300°C and pressures of about 9 atm. The methane-rich gases produced by the one-step reaction process have heat values of about 6,900

Kcal/Nm^3. After being produced, these methane-rich gases are further processed into city gas having higher caloric content by adding butane to carburate the methane-rich gas, after the separation of water, the removal of carbon dioxide gas and dehumidification.

The separation of water from the methane-rich gases, produced by the previously described one-step methanation reaction, is conducted within a separation tank (5). In the process of feeding the mixed methane-rich gases into the separation tank (5), the potential heat retained in the mixed methane-rich gases as a result of the catalytic reaction in reactor (1) is partially recovered by the methanol-water mixture feed as it passes through preheater (2). Additionally, a further portion of the potential heat is recovered by potassium carbonate that circulates through reboiler (7), illustrated in Figure 1. Before entering separation tank (5), the methane-rich gases pass through a cooler (7) in which their temperature is finally adjusted.

The heat of reaction in the catalyst-based methanation reaction, as performed in the above reactor (1), is an exothermic reaction whereby heat is generated during the reaction. This heat of reaction is recovered by a heat medium that circulates through the reactor and the second and third heat exchangers, whereby the potential heat absorbed by the heat medium is transferred to the methanol-water mixture as the heat medium and methanol-water mixture pass through respective portions of the second and third heat exchangers, which, as discussed above, comprise an evaporator and superheater, respectively.

The heat medium that circulates through the reactor and the second and third heat exchangers is a salt, preferably which is fused at a temperature of 142° C. This fused salt heat medium circulates by means of a pump (9) from a heat medium storage tank (8) through reactor (1), then through the third heat exchanger and finally through the second heat exchanger after which the heat medium returns to the heat medium storage tank through return line A. In operation, the heat of reaction of the methanation process is absorbed by the heat medium as the heating medium passes through the reactor (1), and the absorbed heat of reaction is transferred to the methanol-water mixture as the methanol-water mixture passes through the third and second heat exchangers. In this manner, the methanol-water mixture is heated to the necessary reaction temperature.

The heat of reaction produced by the methanation process and the potential heat possessed by the methane- rich gases will be enough to provide the total amount of heat necessary to sustain the process for producing the methane-rich gas. That is, other than during start-up procedures, i.e., when operating at steady state conditions, the process of the present invention does not require any additional heat input.

Moreover, due to the fact that the heat of reaction generated is excessively beyond the amount of heat required to sustain the methanation process, a temperature controlling device (10), utilized for adjusting the temperature of the heat medium is arranged between the heat medium storage tank (8) and the reactor (1), as illustrated in Figure 1.

The water separated from the methane-rich gases in the separation tank (5) is mixed with the methanol which is fed by a methanol feed-pump (11) from a methanol tank (not illustrated). Since more water is produced during the methanation process than the amount of water needed to be added to the methanol feed to form the methanol-water mixture, excess water is exchanged from the water separation tank (5). In this manner, other than during start-up procedures, i.e., when operating at steady state conditions, the process of the present invention does not require that any additional water be added to the system to form the methanol-water mixture.

The purpose of mixing the water with the methanol is to prevent carbonization from occurring in the reactor (1). For this purpose, it is preferable to adjust the mole ratio between the methanol and water to be at about 0.5. If the mole ratio of water to methanol is set at more than about 0.7, the amount of heat necessary for heating up the methanol-water mixture to a proper temperature for methanation becomes larger to the point at which it is difficult to provide all the necessary heat by merely recovering the heat of reaction as discussed above. Accordingly, a large mole ratio of water to methanol, i.e., greater than about 0.7, is disadvantageous in the production cost of city gas since additional heat will have to be supplied to the system. In contrast, if the mole ratio is smaller than about 0.3, carbonization may occur during operation.

During start-up procedures, there is of course neither water which has been separated from the mixed methane-rich gases, nor the heat of reaction for heating up the heat medium. Accordingly, it is necessary to feed water into the system and heat the heat medium during the start-up procedure. However, once steady state operation is reached, it is not necessary to feed in supplemental water nor further heat the heat medium. The details involved in start-up operations will be discussed herein below.

As noted above, after water is separated from the mixed methane-rich gases, it is necessary to remove carbon dioxide from the gas mixture, to dehumidify the methane-rich gas mixture and to regulate the caloric content of the methane-rich gas mixture by adding butane to the methane-rich gas. These subsequent process steps will now be described.

The methane-rich gases from which the water has been separated in the separation tank (5) is next directed through a carbon dioxide absorption tower in which carbon dioxide is absorbed and removed by the potassium carbonate. After the carbon dioxide has been removed in the carbon dioxide absorption tower (12), the methane-rich gases pass through a series of coolers (13, 14 and 15) and into a purified gas water separation tank (16).

After the elimination of carbon dioxide by means of the carbon dioxide absorption tower, the methane-rich gas will have a caloric content of about 9,200 Kcal/Nm^3. Although the above process for removing carbon dioxide utilizes a carbon dioxide absorption tower, the removal of carbon dioxide could be performed by another process such as the dry method (method of Pressure Swing Adsorption).

As a last step, the methane-rich gas is dehumidified and a required amount of butane is mixed with the refined gas through a mixer (17) wherein the caloric content of the produced city gas is adjusted to around 11,000 Kcal/Nm^3. The necessary heat for evaporating the butane is derived from exchanging heat between the methane-rich gases and the butane feed. For this purpose a heat exchanger is located between the carbon dioxide absorption tower and the first cooler (13). The butane feed is gasified as a result of passing through this heat exchanger.

Figure 2 shows a flow chart for the production of city gas by the previously described process wherein city gas having a high caloric content is produced from a feed of methanol.

As discussed in detail above, the process for producing city gas according to the present invention includes the following sequence of steps:

(a) a mixing step in which a methanol feed is mixed with a water feed to produce a methanol-water mixture;

(b) a heating step in which the methanol-water mixture is heated to temperature at which a methanation reaction can occur;

(c) a reaction step in which the methanol-water mixture is reacted to form a methane-rich gas mixture comprising methane, carbon monoxide, carbon dioxide, hydrogen and water;

(d) a water separation step in which water is separated from the methane-rich gas mixture;

(e) a carbon dioxide removal step in which carbon dioxide is removed from the mixed methane-rich gas mixture to form another methane-rich gas; and

(f) a caloric adjustment step in which the caloric content of the methane-rich gas is increased to produce a city gas having a high caloric content.

The process according to the present invention, as discussed above, is advantageous in that during steady state operation, the water feed of step (a) comprises a portion of the water separated from the methane-rich gas mixture in step (d). In other words, a portion of the water separated in step (d) provides all the necessary feed water for step (a) and, furthermore, this separated or recovered water already contains an amount of heat, so that it does not require as much heating as an external source of feed water would.

The process according to the present invention, as discussed above, is advantageous in that during steady state operation the heating step (b) utilizes heat recovered from the heat of the reaction of step (c) by transferring the recovered heat to the methanol-water mixture. This transferring of heat is performed by means of a heat exchange medium that absorbs the heat of reaction from step (c) and transfers the heat to the methanol-water mixture.

In recovering and transferring the heat, the heat exchange medium first passes through a reactor wherein the reaction step (c) occurs, then through a third heat exchanger wherein the methanol-water mixture is superheated, and then through a second heat exchanger wherein the methanol-water mixture is gasified. While the heat exchange medium passes through the second and third heat exchangers in one direction the methanol-water mixture pass through the second and third heat exchangers in an opposite direction, so that the methanol-water mixture is first gasified then superheated. Accordingly, the methanol-water mixture first passes through a first heat exchanger wherein the methanol-water mixture is preheated by exchanging heat with the mixed methane-rich gas produced in the reactor, then through the second heat exchanger wherein the methanol-water mixture is gasified and then through the third heat exchanger wherein the gasified methanol-water mixture is superheated before entering the reactor.

The one-step methanation process according to the present invention is accomplished by maintaining the temperature at which the reaction occurs in step (c) at a temperature of about 300 °C and maintaining the pressure at which the reaction occurs in step (c) at a temperature of less than about 9 atm.

In addition it is necessary to use a catalyst capable of promoting this one-step methanation reaction. The particular catalyst developed for the present invention comprises a nickel catalyst which is supported on an alumina carrier. The nickel catalyst may be nickel or an oxide of nickel. The alumina may be selected from alumina, alumina hydrate or silica alumina. The preferred alumina utilized as a carrier in the present invention comprises a low sulfur alumina which has a sulfur content of less than about 1.2 % by weight. The alumina utilized in the present invention may also have a reduced specific surface area of less than about 350m^2/g.

In accordance with the trade-offs between possibility of carbonization occurring in the reactor if too little water is mixed with the methanol feed in step (a) and in considering that the amount of heat input required is dependent of the amount of water added to the methanol feed in step (a), it has been determined that the mole ratio of water to methanol in step (a) should be maintained between about 0.3 and 0.7. More preferably, the mole ratio of water to methanol should be about 0.5.

The process according to the present invention adjusts the final caloric content of the city gas in the caloric adjustment step (f) by dehydrating the methane-rich gas and adding a sufficient amount of butane to the methane-rich gas to provide a city gas having a heat value of about 11,000 Kcal/Nm^3.

The city gas produced in accordance with the process of the present invention, in addition to having a heat value of about 11,000 Kcal/Nm^3, has a Wobbe Index of about 13,340, and a Combustion Potential of between about 41.6 to 41.9 cm/sec.

The start-up procedure for the above process of producing city gas having a high caloric content from a methanol will now be explained.

During start-up, water, preferably pure water, that is to be mixed with the methanol to form the methanol-water mixture is fed from a water supply tank by a feed-water pump (18) as illustrated in Figure 1. The initial heating of the heat medium is performed in the heat medium circulation channel which comprises the reactor (1), the third heat exchanger (4), the heat medium heating furnace (19), the heat medium storage tank, including its heater (20) and the return line A. For purposes of initial heating during start-up procedures, the heat medium circulation channel is dividable into three by-pass circuits which are illustrated in Figures 3 to 7. As shown in Figure 3, these by-pass circuits include a first circulation system (a) that includes a by-pass that is positioned between the inlet and outlet of the heat medium storage tank; a second circulation system (b) that is located between the inlet and outlet of the heat medium storage tank and further includes the temperature controlling device (10) and the heat medium heating furnace (19); and a third circulation system (c) that is located between the inlet and outlet of the heat medium storage tank and further includes the temperature controlling device (10), the heat medium heating furnace (19), the third heat exchanger (4), and the second heat exchanger (3). Also illustrated in Figure 3 is a fourth circulation system (d) that connects the inlet and outlet of the start-up blower (21) to the first heat exchanger (2), the second heat exchanger (3), the third exchanger (4), the reactor (1), the first heat exchanger (2), the reboiler (6) and the water separation tank (5).

In starting up the previously described system, the heat medium is circulated along the first circulation system (a) by pump (9) while the heat medium is heated by the heater (20) within the heat medium storage tank (8), as shown in Figure 4. During this initial heating, the temperature of the heat medium is heated to about 170° C.

After the heating medium reaches a temperature of about 170° C, the circulating heat medium is directed to flow through the second circulation system (b), as shown in Figure 5. While flowing through the second circulation system (b), the heat medium is heated in the heat medium heating furnace (19) to a temperature of about 250° C. The heat medium heating furnace is heated by combusting a fuel source therein or, alternatively, an electrical heating means.

After the heating medium reaches a temperature of about 250° C, the circulating heat medium is directed to flow through the third circulation system (c) as shown in Figure 6.

After the heating medium is directed to flow through the third circulation system, nitrogen (N_2) is fed into the fourth circulation system (d) by means of a start-up blower (21), whereby the nitrogen is circulated through the fourth circulation circuit (d), as shown in Figure 7.

The circulating nitrogen is heated by heat exchanged from the heat medium as the nitrogen is circulated through the second and third heat exchangers. The nitrogen is heated to the necessary temperature of reaction of about 250° C for the methanol-water mixture in the reactor (1).

When the previously described start up procedures are accomplished, the flow of the heat medium is directed through the third circulation system and the methanol-water mixture is fed into the reactor (1).

According to the above operations, both the heat of reaction generated during the methanation and the heat that is retained by the water as it passes through the separation tank (5) contribute to the heat necessary to sustain the methanation reaction in the reactor (1). Accordingly, once steady state conditions are reached by the above procedures, both the fuel supply to the heat medium heating furnace and the water from the feed-water source are stopped.

EXAMPLES

The following illustrate examples of city gas having high caloric content, produced according to the process of the present invention, utilizing the system as illustrated in Figure 1.

Example No. 1

This example was conducted in the reactor (1) under the following test conditions:

Mole ratio (water/methanol): 0.5
Reaction temperature: 305 °C
Reaction pressure: 9.0 Kg/cm^2 G

As a result of the above reaction conditions, the produced gas has the following properties:

Heat value: 11,00 Kcal/Nm^3
Specific gravity: 0.68
WI (Wobbe Index): 13340
CP (Combustion Potential): 41.9 cm/sec.

In the above test, the values in each stream, identified in Figure 2, are shown in Table No. 1.

Example No. 2

This example was conducted in the reactor (1) under the following test conditions:

Mole ratio (water/methanol): 0.5
Reaction temperature: 299 °C
Reaction pressure: 8.9 Kg/cm^2 G

As a result of the above reaction conditions, the produced gas has the following properties:

Heat value: 11.000 Kcal/Nm^3
Specific gravity: 0.68
WI (Wobbe Index): 13340
CP (Combustion Potential): 41.6 cm/sec.

In the above test, the values in each stream, identified in Figure 2, are shown in Table No. 2

Example No. 3

This example was also conducted in the reactor (1) under the following test conditions:

Mole ratio (water/methanol); 0.5
Reaction temperature: 280 °C
Reaction pressure: 9.0 Kg/cm^{2}G

As a result of the above reaction conditions, the produced gas has the following properties:

Heat value: 11.180 Kcal/Nm^3
Specific gravity: 0.691
WI(Woble Index): 13440
CP(Combustion Potential) 40.2 cm/sec.

In the above test, the values in each stream, identified in Fig. 2, are shown in Table No. 3.

Although the invention has been described with reference to particular means, materials and embodiments, from the foregoing description, one skilled in the art can easily ascertain the essential characteristics of the present invention, and various changes and modifications may be made to adapt to various usages and conditions, without departing from the spirit and scope of the present invention as described in the claims that follow.

(Table 1)

Stream number	Temp. ℃	Pressure kg/cm²G	Composition (mol %)								Flow rate	
			H_2	CO	CO_2	CH_4	C_3H_8	C_4H_{10}	CH_3OH	H_2O	Kgmol/hr	Nm³/hr
1	—	—	—	—	—	—	—	—	100	—	18. 18	—
2	—	—	—	—	—	—	—	—	—	100	9. 09	—
3	295	9. 0	—	—	—	—	—	—	66. 7	33. 3	27. 27	—
4	295	8. 6	1. 4	0. 1	12. 8	36. 7	—	—	—	49. 0	36. 64	—
5	100	8. 6	2. 5	0. 2	22. 4	64. 2	—	—	—	10. 7	20. 93	—
6	100	8. 5	3. 3	0. 2	1. 5	84. 2	—	—	—	10. 8	15. 96	—
7	—	—	—	—	—	—	3	97	—	—	1. 28	—
8	34	8. 5	3. 5	0. 2	1. 5	86. 5	0. 2	8. 1	—	0. 0	15. 54	348

(Table 2)

Stream number	Temp. ℃	Pressure kg/cm²G	Composition (mol %)								Flow rate	
			H_2	CO	CO_2	CH_4	C_3H_8	C_4H_{10}	CH_3OH	H_2O	Kgmol/hr	Nm³/hr
1	—	—	—	—	—	—	—	—	100	—	18. 18	—
2	—	—	—	—	—	—	—	—	—	100	9. 09	—
3	290	8. 9	—	—	—	—	—	—	66. 7	33. 3	27. 27	—
4	294	8. 5	1. 3	0. 1	12. 8	36. 9	—	—	—	48. 9	36. 64	—
5	100	8. 5	2. 4	0. 1	22. 4	64. 3	—	—	—	10. 8	21. 01	—
6	100	8. 4	3. 1	0. 2	1. 5	84. 2	—	—	—	11. 0	16. 03	—
7	—	—	—	—	—	—	3	97	—	—	1. 27	—
8	32	8. 4	3. 2	0. 2	1. 5	86. 9	0. 2	8. 0	—	0. 0	15. 54	348

(Table 3)

Stream number	Temp. ℃	Pressure kg/cm²G	Composition (mol %)								Flow rate	
			H_2	CO	CO_2	CH_4	C_3H_8	C_4H_{10}	CH_3OH	H_2O	Kgmol/hr	Nm³/hr
1	—	—	—	—	—	—	—	—	100	—	21.84	—
2	—	—	—	—	—	—	—	—	—	100	10.94	—
3	280	9.0	—	—	—	—	—	—	66.6	33.4	32.78	—
4	280	8.6	0.8	0.0	12.7	37.1	—	—	—	49.4	43.88	—
5	100	8.6	1.5	0.0	22.2	65.2	—	—	—	11.1	24.97	—
6	105	8.5	2.2	0.0	1.5	82.7	—	—	—	13.6	19.79	—
7	—	—	—	—	—	—	1	99	—	—	1.78	—
8	37	8.5	2.3	0.0	1.6	87.0	0.1	8.9	—	0.1	18.71	417

Claims

1. A process for producing city gas which comprises:

preparing a methanol and water mixture;

exchanging heat between a heat medium and the methanol-water mixture in at least one heat exchanger to produce a heated methanol-water mixture having a desired temperature;

reacting the heated methanol-water mixture in a reactor at a temperature of less than about 300°C in the presence of a catalyst which comprises a nickel component supported on an alumina carrier having a reduced sulphuric component content and a reduced specific surface area, to thereby forming a methane-rich gas mixture;

separating water from said methane-rich gas mixture;

removing carbon dioxide gas from said methane-rich gas mixture; and

adding butane to said methane-rich gas mixture to regulate the caloric content of said methane-rich gas mixture, whereby a portion of the water separated from said methane-rich gas mixture is used in preparing said methanol and water mixture and wherein said heat medium is heated by heat generated by the heat of reaction during the production of said methane-rich gas mixture.

2. A method for producing a gas comprising:

providing a feed stock comprising methanol; and reacting said methanol in the presence of a nickel catalyst based on an alumina carrier under reaction conditions comprising a temperature maintained between about 280°C and 305°C to produce gas containing methane.

3. The method in accordance with claim 2, wherein said reaction conditions comprise pressures of less than about 9 atm.

4. The method in accordance with claim 2, wherein said gas containing methane is methane-rich gas.

5. The method in accordance with claim 4, wherein said methane-rich gas has a composition comprising at least about 72% CH_4.

6. The method in accordance with claim 5, wherein said composition comprises at least about 72% CH_4 and less than about 25% CO_2.

7. The method in accordance with claim 6, wherein said composition comprises about 3% H_2.

8. The method in accordance with claim 7, wherein said composition comprises about 72% CH_4, about 25% CO_2, and about 3% H_2.

9. The method in accordance with claim 4, wherein said methane-rich gas has a heat value of at least about 6,900 Kcal/Nm³.

10. The method in accordance with claim 4, wherein said nickel catalyst comprises a nickel compound.

11. The method in accordance with claim 10, wherein said nickel compound is nickel oxide.

12. The method in accordance with claim 2, wherein said alumina is a member selected from the group consisting of alumina, alumina hydrate, and silica alumina.

13. The method in accordance with claim 12, wherein said alumina is selected from a group consisting of alumina materials having a sulfur content of less than about 1.2% by weight.

14. The method in accordance with claim 13, wherein said alumina materials having a sulfur content of less than about 1.2% by weight are selected from the group consisting of alumina and alumina hydrate.

15. The method in accordance with claim 14, wherein said alumina and alumina hydrate are pulverized.

16. The method in accordance with claim 12, wherein said alumina material is silica alumina.

17. The method in accordance with claim 16, wherein said silica alumina has a specific surface area of less than about 350 M^2/g.

18. The method in accordance with claim 16, wherein said nickel catalyst comprises a nickel compound.

19. The method in accordance with claim 18, wherein said nickel compound is nickel oxide.

20. A process for producing city gas comprising:

a) providing a methane-rich gas mixture;

b) separating at least a portion of any water present in said methane-rich gas mixture;

c) removing carbon dioxide from said methane-rich gas to form a resultant methane-rich gas having a certain caloric content;

d) dehumidifying said resultant methane-rich gas; and

e) adding butane to said methane-rich gas to produce a city gas having a caloric content higher than said certain caloric content of said resultant methane-rich gas.

21. The process for producing a city gas in accordance with claim 20, wherein the caloric content of said city gas is adjusted to at least about 11,000 Kcal/Nm^3.

22. The process for producing a city gas in accordance with claim 21, wherein said city gas has a Wobbe Index of at least about 13,340.

23. The process for producing a city gas in accordance with claim 21, wherein said city gas has a Combustion Potential of between about 40.2 and 41.9 cm/sec.

24. The process for producing a city gas in accordance with claim 23, wherein said city gas has a Combustion Potential of between about 40.2 and 41.9 cm/sec.

25. The process for producing a city gas in accordance with claim 20, wherein said providing a methane-rich gas mixture comprises reacting methanol in the presence of a catalyst under reaction conditions comprising a temperature maintained at less than about 300°C to produce a methane-rich gas.

26. The process in accordance with claim 25, wherein said reaction conditions comprise pressures of less than about 9 atm.

27. The process in accordance with claim 26, wherein said resultant methane-rich gas has a composition comprising at least about 72% CH_4.

28. The process in accordance with claim 27, wherein said composition comprises at least about 72% CH_4 and less than about 25% CO_2.

29. The process in accordance with claim 28, wherein said composition comprises about 3% H_2.

30. The process in accordance with claim 29, wherein said composition comprises about 72% CH_4, about 25% CO_2, and about 3% H_2.

31. The process in accordance with claim 25, wherein said resultant methane-rich gas has a heat value of at least about 6,900 Kcal/Nm_3.

32. The process for producing city gas in accordance with claim 25, further comprising providing a feedstock of said methanol by mixing a methanol feed with a water feed to produce a methanol-water mixture having a predetermined mole ratio; and heating the methanol-water mixture to temperature which favors a methanation reaction wherein said reacting comprises reacting said methanol-water mixture in a reaction zone under reaction conditions including a heat of reaction to produce a methane-rich gas mixture comprising methane, carbon monoxide, carbon dioxide, hydrogen and water.

33. The process in accordance with claim 32, wherein said resultant methane-rich gas comprises methane, carbon dioxide, carbon monoxide and hydrogen.

34. The process according to claim 32, wherein the water feed comprises at least a portion of the water separated from the methane-rich gas mixture.

35. The process according to claim 32, wherein said heating comprises recovering heat from the heat of reaction and transferring recovered heat to the methanol-water mixture.

36. The process according to claim 35, wherein said transferring the recovered heat comprises absorbing the heat of reaction by means of a heat exchange medium and exposing the methanol-water mixture to the heat transfer medium.

37. The process according to claim 36, further comprising passing the heat exchange medium through the reaction zone prior to superheating the methanol-water mixture to form a superheated methanol-water mixture.

38. The process according to claim 37, further comprising gasifying the superheated methanol-water mixture.

39. The process according to claim 37, wherein the methanol-water mixture is first preheated in a first heat exchanger by exchanging heat with the methane-rich gas mixture produced in the reaction zone, then gasified in a second heat exchanger and subsequently superheated in a third heat exchanger.

40. The process according to claim 32, wherein said reaction conditions comprise a pressure maintained at less than about 9 atm.

41. The process according to claim 40, wherein said reaction conditions comprise a temperature maintained between about 280° C and 305° C.

42. The process according to claim 41, wherein said methanation reaction is a one-step methanation which comprises exposing the methanol-water mixture in a reaction zone to said catalyst.

43. The process according to claim 42, wherein said catalyst comprises a nickel catalyst supported on an alumina carrier.

44. The process according to claim 43, wherein said alumina carrier is selected from the group consisting of alumina, alumina hydrate and silica alumina.

45. The process according to claim 44, wherein said alumina carrier has a sulfur content of less than about 1.2 % by weight.

46. The process according to claim 44, wherein said alumina carrier has a specific surface area of less than about 350 M^2/g.

47. The process according to claim 32, wherein the mole ratio of water to methanol is between about 0.3 and 0.7.

48. The process according to claim 47, wherein the mole ratio of water to methanol is about 0.5.

49. A catalyst comprising catalytically active metal substance selected from the group consisting of elemental nickel (Ni) and a nickel compound; and a carrier comprising alumina material.

50. The catalyst in accordance with claim 49, wherein said catalytically active metal substance is a nickel compound.

51. The catalyst in accordance with claim 50, wherein said nickel compound is nickel oxide.

52. The catalyst in accordance with claim 49, wherein said alumina material is a member selected from the group consisting of alumina, alumina hydrate, and silica alumina.

53. The catalyst in accordance with claim 52, wherein said alumina material is selected from the group of alumina materials having a sulfur content of less than about 1.2% by weight.

54. The catalyst in accordance with claim 53, wherein said alumina materials having a sulfur content of less than about 1.2% by weight are selected from the group consisting of alumina and alumina hydrate.

55. The catalyst in accordance with claim 54, wherein said alumina and alumina hydrate are pulverized.

56. The catalyst in accordance with claim 52, wherein said alumina material is silica alumina.

57. The catalyst in accordance with claim 56, wherein said silica alumina has a specific surface area of less than about 350 M^2/g.

58. The catalyst in accordance with claim 57, wherein said catalytically active metal substance is a nickel compound.

59. The catalyst in accordance with claim 58, wherein said nickel compound is nickel oxide.

60. A city gas having at least one property selected from the group consisting of a heat value of at least about 11,000 $Kcal/Nm^3$, a Wobbe Index of at least about 13,340, and a Combustion Potential of between about 40.2 and 41.9 cm/sec.

61. The city gas in accordance with claim 60, wherein said at least one property is a heat value of at least about 11,000 $Kcal/Nm^3$.

62. The city gas in accordance with claim 60, wherein said at least one property is a Wobbe Index of at least about 13,340.

63. The city gas in accordance with claim 60, wherein said at least one property is a Combustion Potential of between about 41.6 to about 41.9 cm/sec.

64. The city gas having a heat value of at least about 11,000 $Kcal/Nm^3$.

65. The city gas in accordance with claim 64, wherein said heat value is at least about 11,000 $Kcal/Nm^3$.

66. The city gas in accordance with claim 65, having a Wobbe Index of at least about 13,340.

67. The city gas in accordance with claim 65, having a Combustion Potential between about 40.2 and about 41.9 cm/sec.

68. The city gas in. accordance with claim 66, having a Combustion Potential between about 40.2 and 41.9 cm/sec.

69. A methane-rich gas having a composition comprising at least about 72% CH_4.

70. The methane-rich gas in accordance with claim 69, wherein said composition comprises at least about 72% CH_4, and up to about 25% CO_2.

71. The methane-rich gas in accordance with claim 70, wherein said composition comprises about 3% H_2.

72. The methane-rich gas in accordance with claim 71, wherein said composition comprises about 72% CH_4, about 25% CO_2, and about 3% H_2.

73. The methane-rich gas in accordance with claim 69, wherein said methane-rich gas has a heat value of at least about 6,900 Kcal/Nm^3.

FIG. 1A

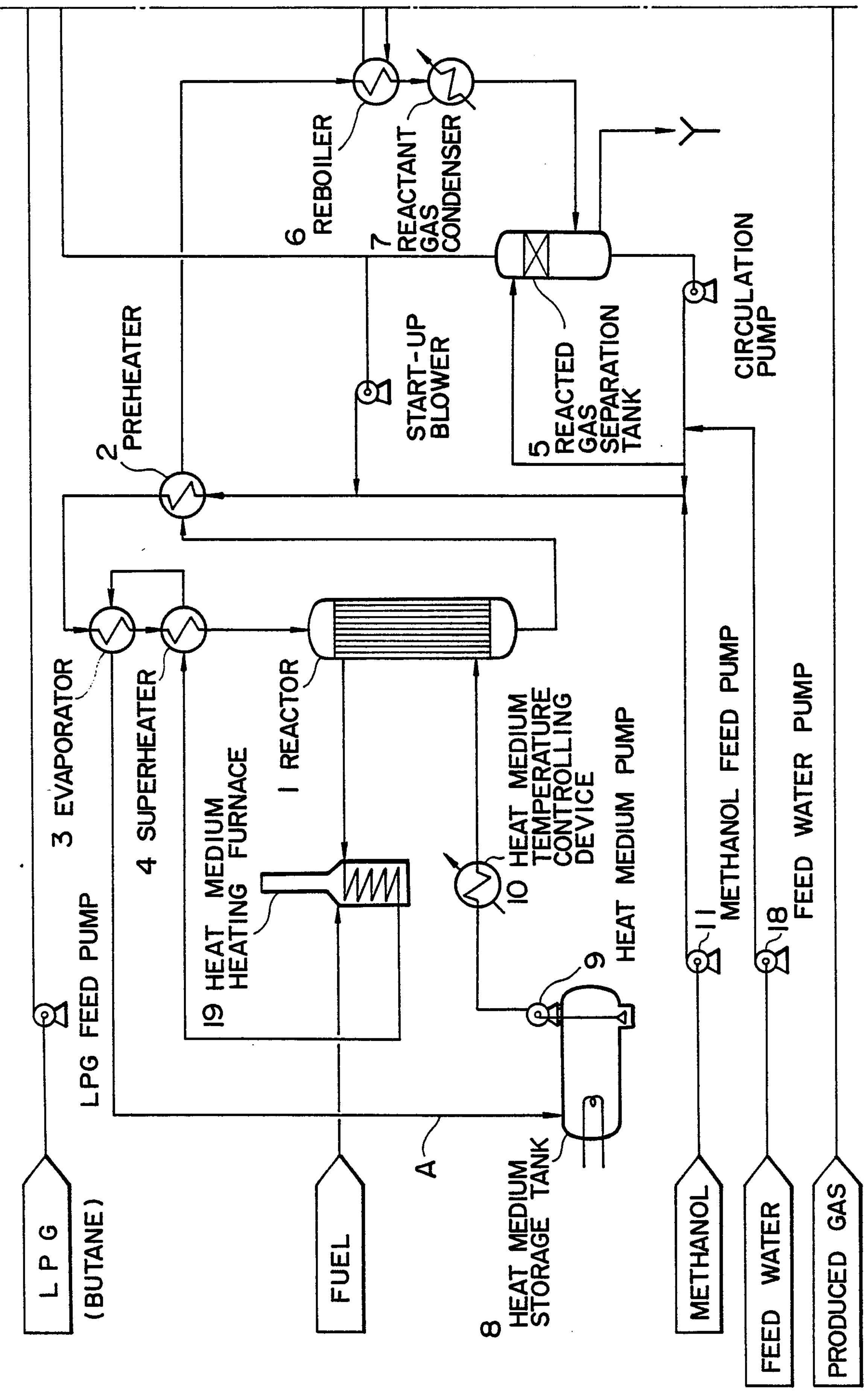
LPG
(BUTANE)
FUEL
A
8 HEAT MEDIUM STORAGE TANK
METHANOL
FEED WATER
PRODUCED GAS
LPG FEED PUMP
19 HEAT MEDIUM HEATING FURNACE
9 HEAT MEDIUM PUMP
10 HEAT MEDIUM TEMPERATURE CONTROLLING DEVICE
11 METHANOL FEED PUMP
18 FEED WATER PUMP
3 EVAPORATOR
4 SUPERHEATER
1 REACTOR
2 PREHEATER
START-UP BLOWER
5 REACTED GAS SEPARATION TANK
CIRCULATION PUMP
6 REBOILER
7 REACTANT GAS CONDENSER

FIG. 1B

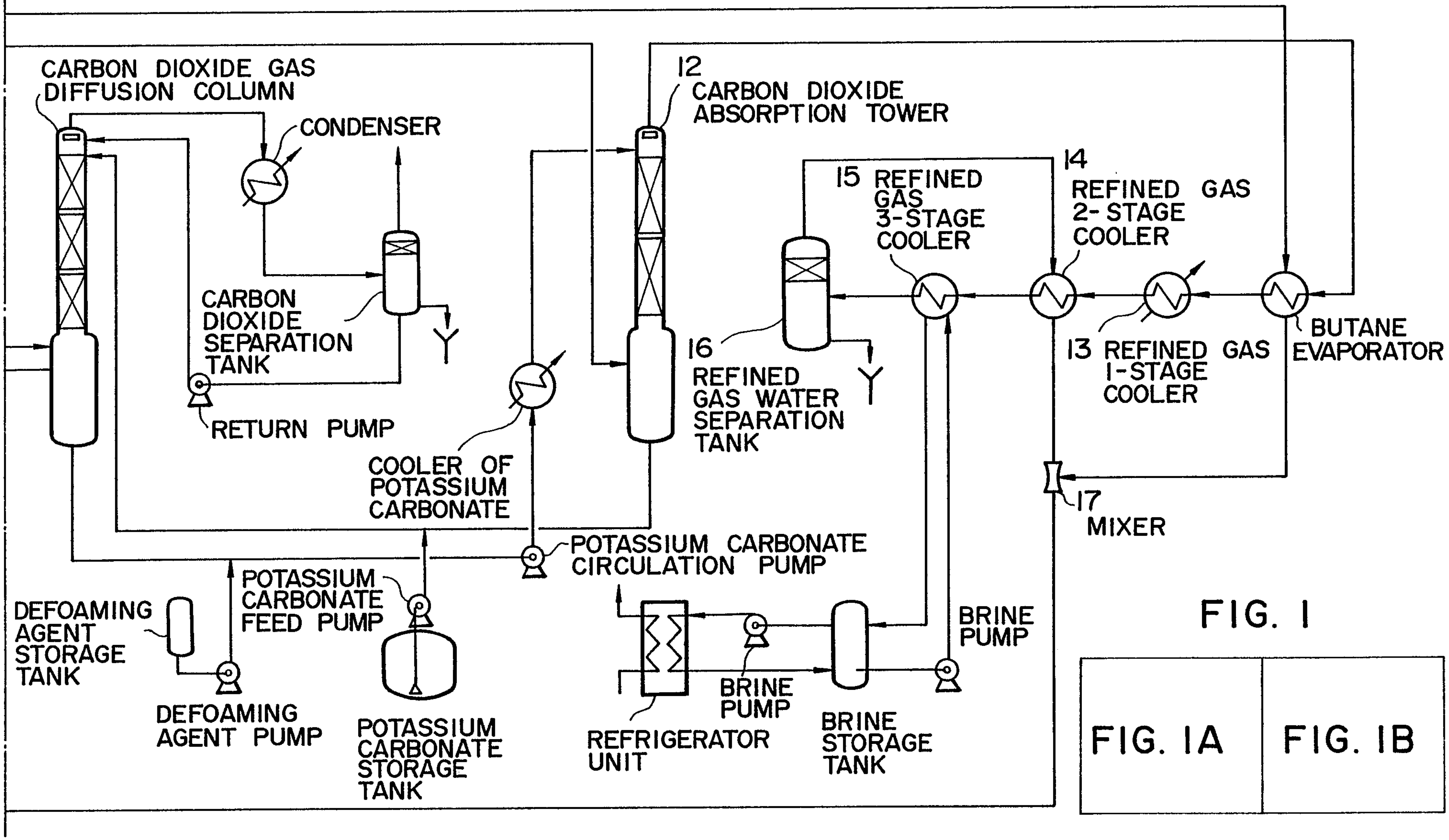
CARBON DIOXIDE GAS DIFFUSION COLUMN
CONDENSER
CARBON DIOXIDE SEPARATION TANK
RETURN PUMP
12
CARBON DIOXIDE ABSORPTION TOWER
COOLER OF POTASSIUM CARBONATE
POTASSIUM CARBONATE CIRCULATION PUMP
POTASSIUM CARBONATE FEED PUMP
POTASSIUM CARBONATE STORAGE TANK
DEFOAMING AGENT STORAGE TANK
DEFOAMING AGENT PUMP
15 REFINED GAS 3-STAGE COOLER
16
REFINED GAS WATER SEPARATION TANK
14
REFINED GAS 2- STAGE COOLER
13 REFINED GAS 1-STAGE COOLER
BUTANE EVAPORATOR
17
MIXER
BRINE PUMP
BRINE PUMP
BRINE STORAGE TANK
REFRIGERATOR UNIT
FIG. 1A
FIG. 1B

FIG. 1

FIG. 2

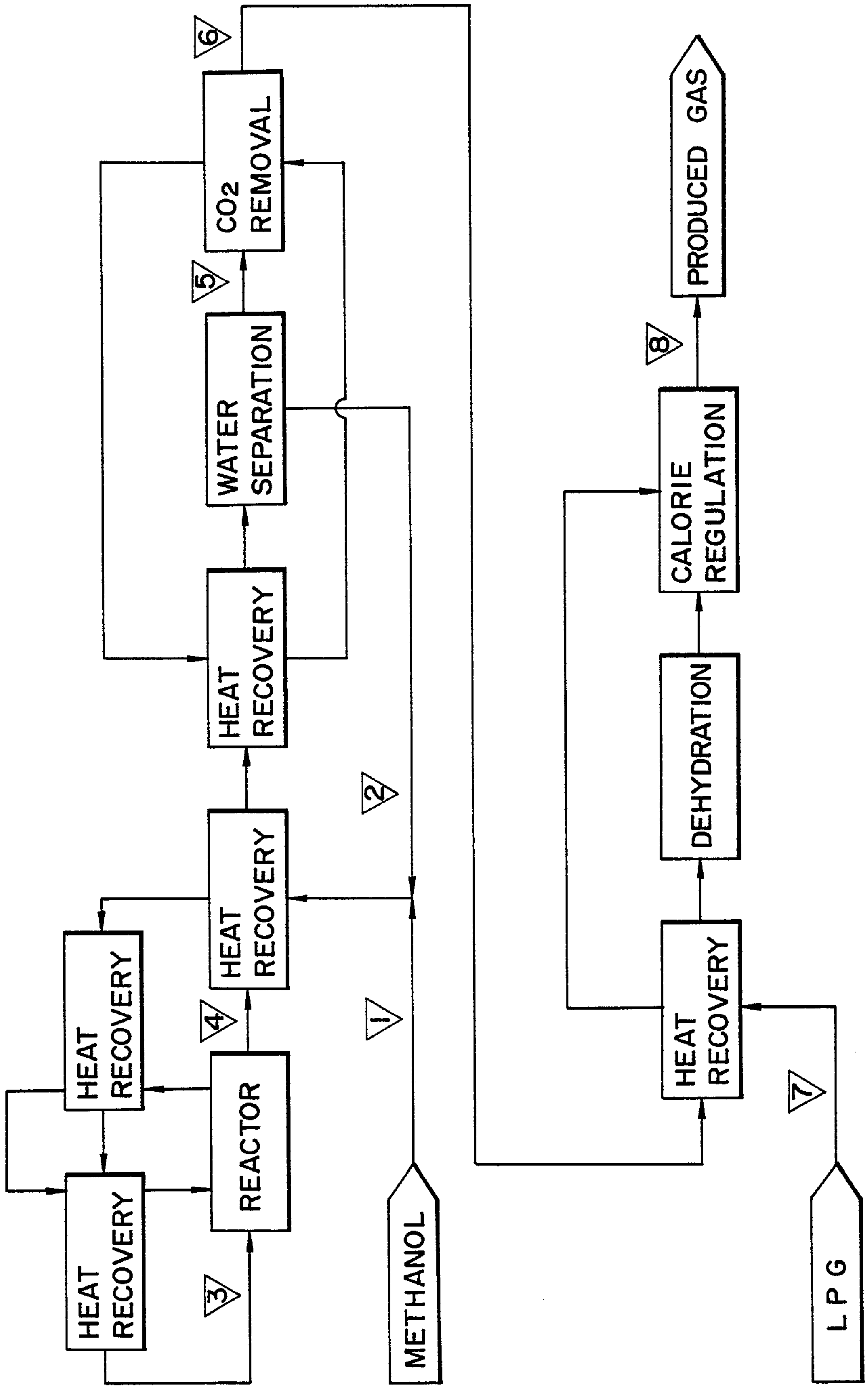
METHANOL
1
2
3
4
5
6
7
8
REACTOR
HEAT RECOVERY
HEAT RECOVERY
HEAT RECOVERY
HEAT RECOVERY
WATER SEPARATION
CO2 REMOVAL
LPG
HEAT RECOVERY
DEHYDRATION
CALORIE REGULATION
PRODUCED GAS

FIG. 3A

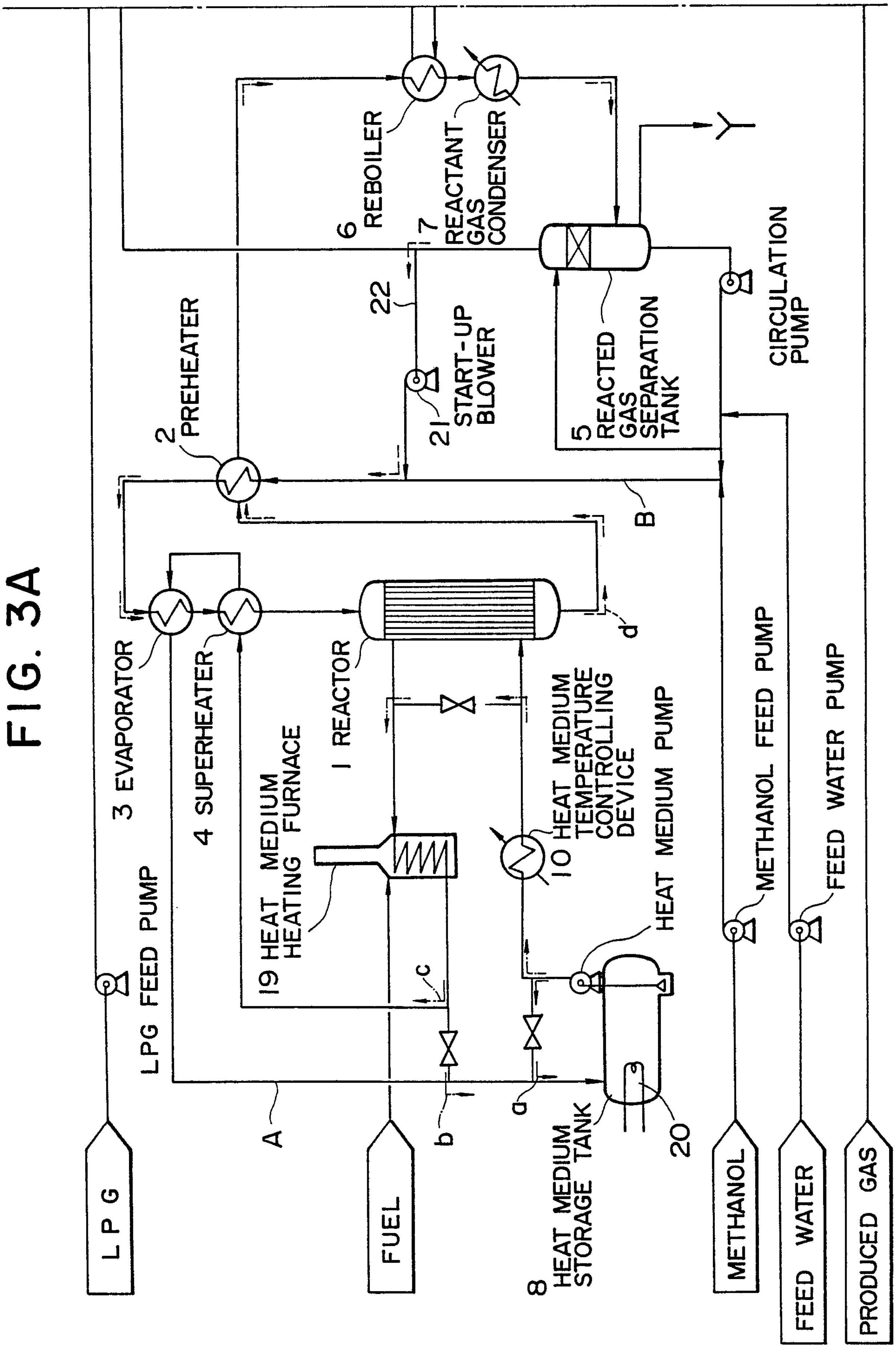
LPG
FUEL
METHANOL
FEED WATER
PRODUCED GAS
LPG FEED PUMP
A
b
a
c
d
B
8 HEAT MEDIUM STORAGE TANK
20
HEAT MEDIUM PUMP
10 HEAT MEDIUM TEMPERATURE CONTROLLING DEVICE
19 HEAT MEDIUM HEATING FURNACE
3 EVAPORATOR
4 SUPERHEATER
1 REACTOR
2 PREHEATER
21 START-UP BLOWER
22
6 REBOILER
7 REACTANT GAS CONDENSER
5 REACTED GAS SEPARATION TANK
CIRCULATION PUMP
METHANOL FEED PUMP
FEED WATER PUMP

FIG. 3B

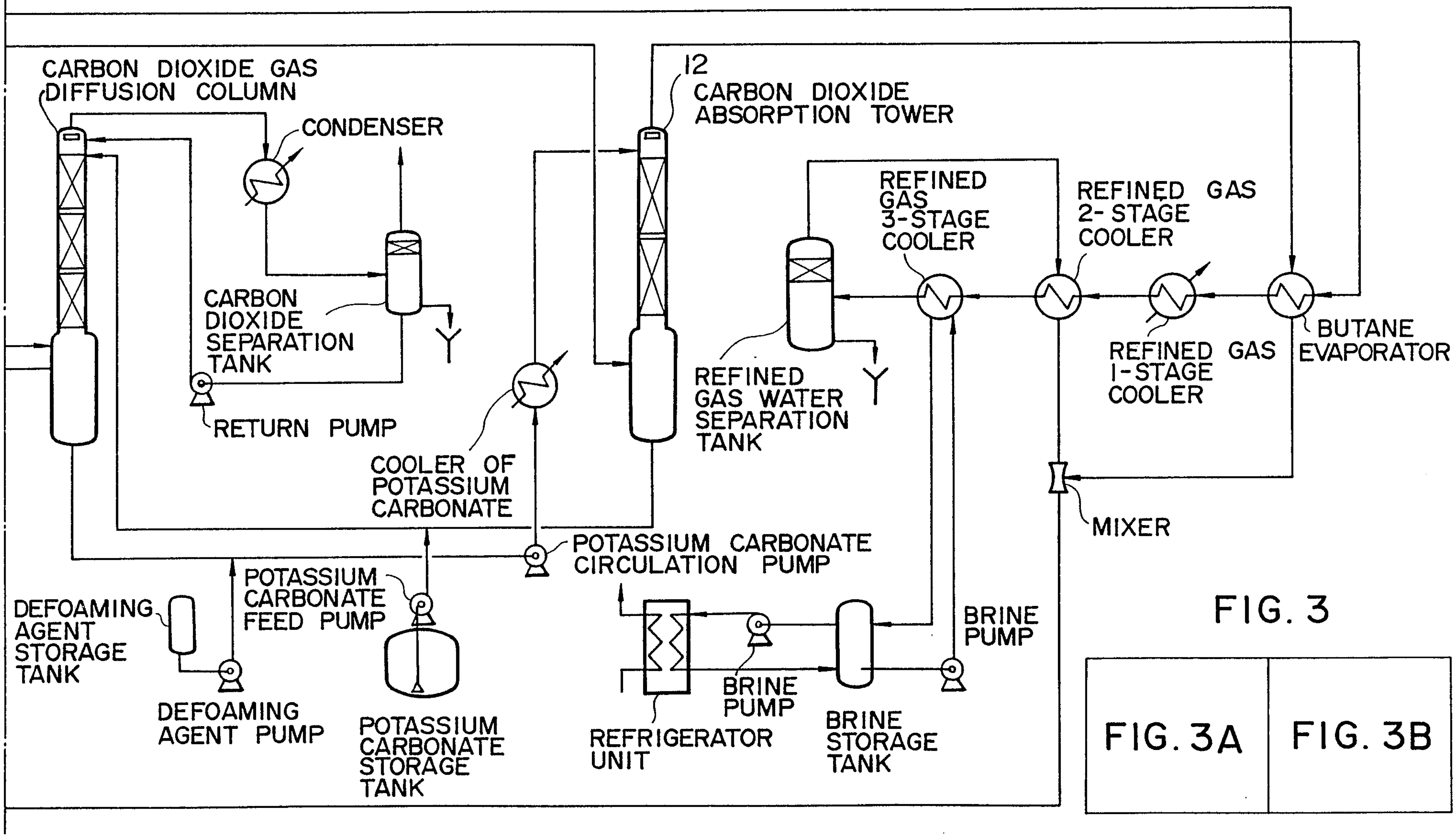

FIG. 3

FIG. 3A	FIG. 3B

FIG. 4A

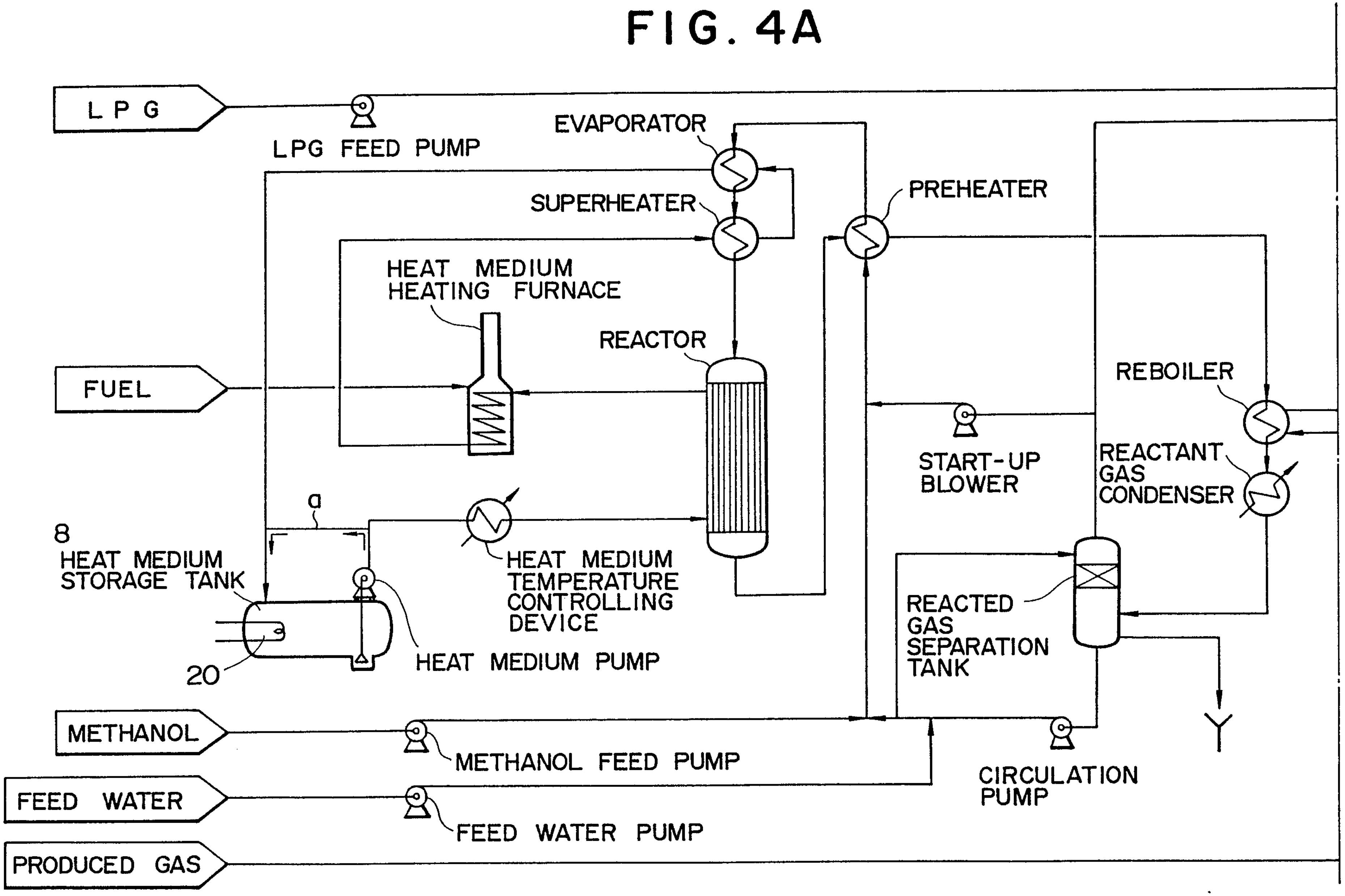
LPG
LPG FEED PUMP
EVAPORATOR
SUPERHEATER
PREHEATER
HEAT MEDIUM HEATING FURNACE
REACTOR
FUEL
REBOILER
START-UP BLOWER
REACTANT GAS CONDENSER
a
8
HEAT MEDIUM STORAGE TANK
HEAT MEDIUM TEMPERATURE CONTROLLING DEVICE
REACTED GAS SEPARATION TANK
20
HEAT MEDIUM PUMP
METHANOL
METHANOL FEED PUMP
CIRCULATION PUMP
FEED WATER
FEED WATER PUMP
PRODUCED GAS

FIG. 4B

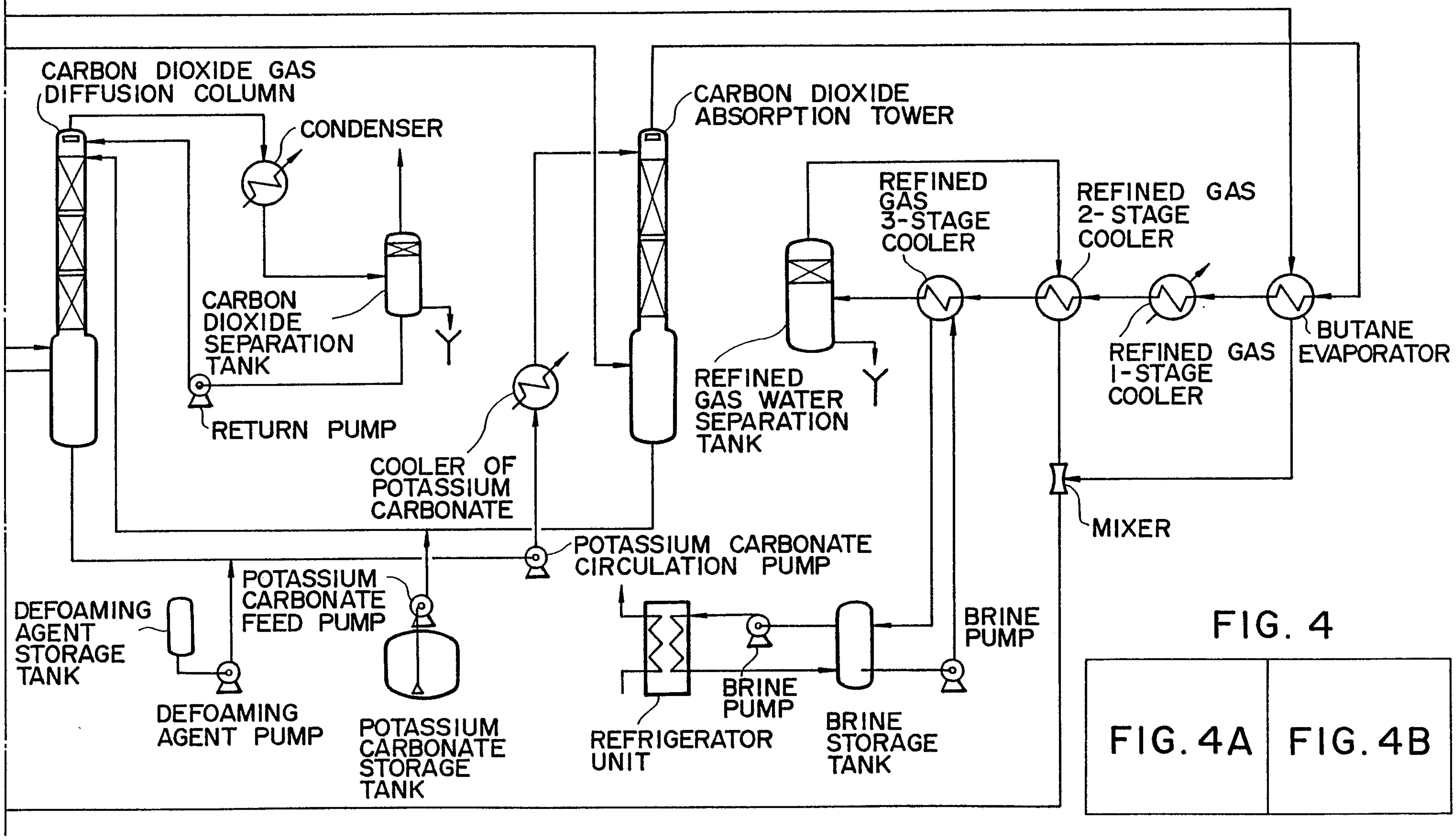
CARBON DIOXIDE GAS DIFFUSION COLUMN
CONDENSER
CARBON DIOXIDE SEPARATION TANK
RETURN PUMP
CARBON DIOXIDE ABSORPTION TOWER
REFINED GAS 3-STAGE COOLER
REFINED GAS 2-STAGE COOLER
REFINED GAS 1-STAGE COOLER
BUTANE EVAPORATOR
REFINED GAS WATER SEPARATION TANK
COOLER OF POTASSIUM CARBONATE
MIXER
POTASSIUM CARBONATE CIRCULATION PUMP
POTASSIUM CARBONATE FEED PUMP
DEFOAMING AGENT STORAGE TANK
DEFOAMING AGENT PUMP
POTASSIUM CARBONATE STORAGE TANK
REFRIGERATOR UNIT
BRINE PUMP
BRINE STORAGE TANK
BRINE PUMP
FIG.4A
FIG.4B

FIG. 4

FIG. 5A

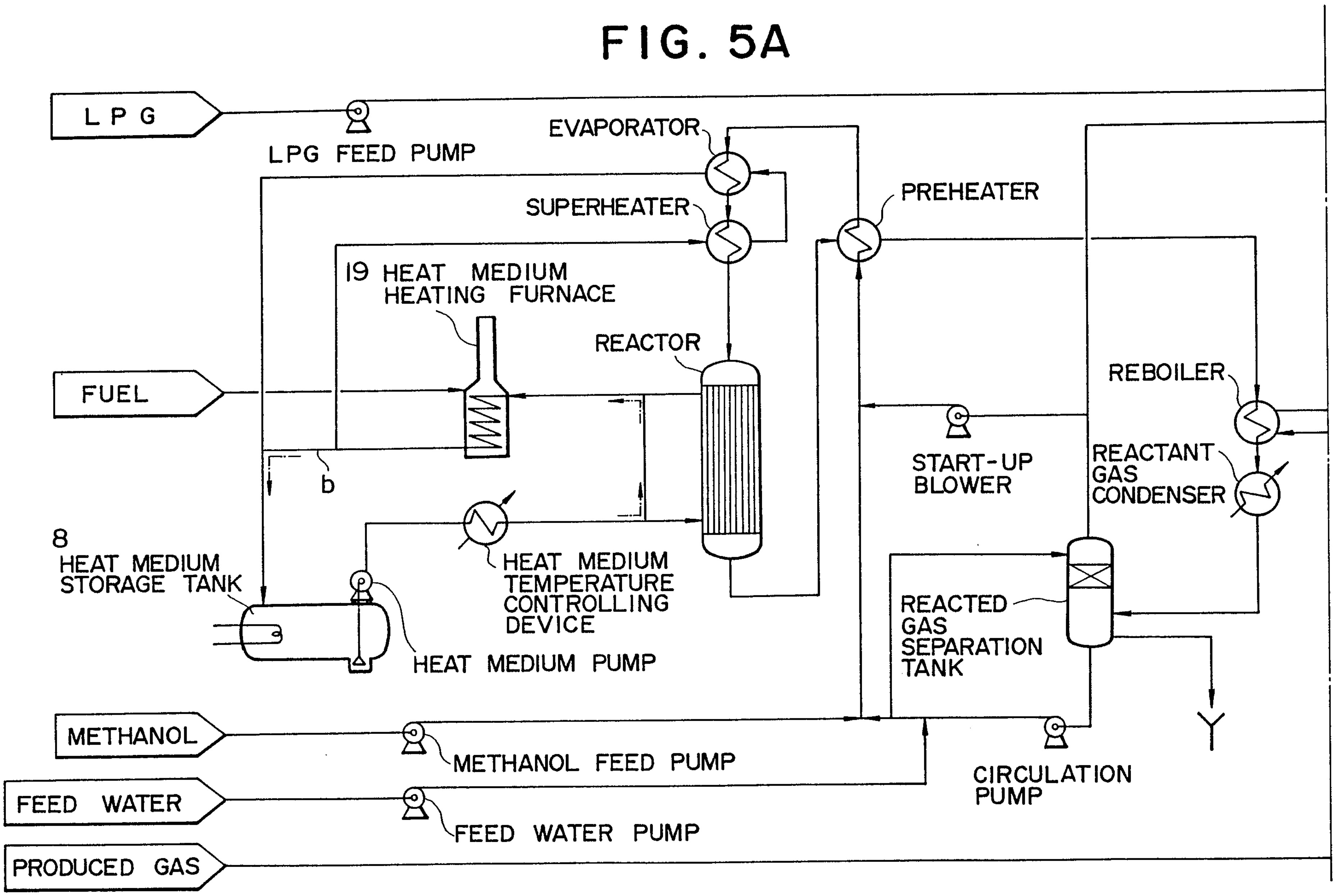
LPG
LPG FEED PUMP
EVAPORATOR
SUPERHEATER
PREHEATER
19 HEAT MEDIUM HEATING FURNACE
REACTOR
FUEL
REBOILER
START-UP BLOWER
REACTANT GAS CONDENSER
b
8
HEAT MEDIUM STORAGE TANK
HEAT MEDIUM TEMPERATURE CONTROLLING DEVICE
HEAT MEDIUM PUMP
REACTED GAS SEPARATION TANK
METHANOL
METHANOL FEED PUMP
CIRCULATION PUMP
FEED WATER
FEED WATER PUMP
PRODUCED GAS

FIG. 5B

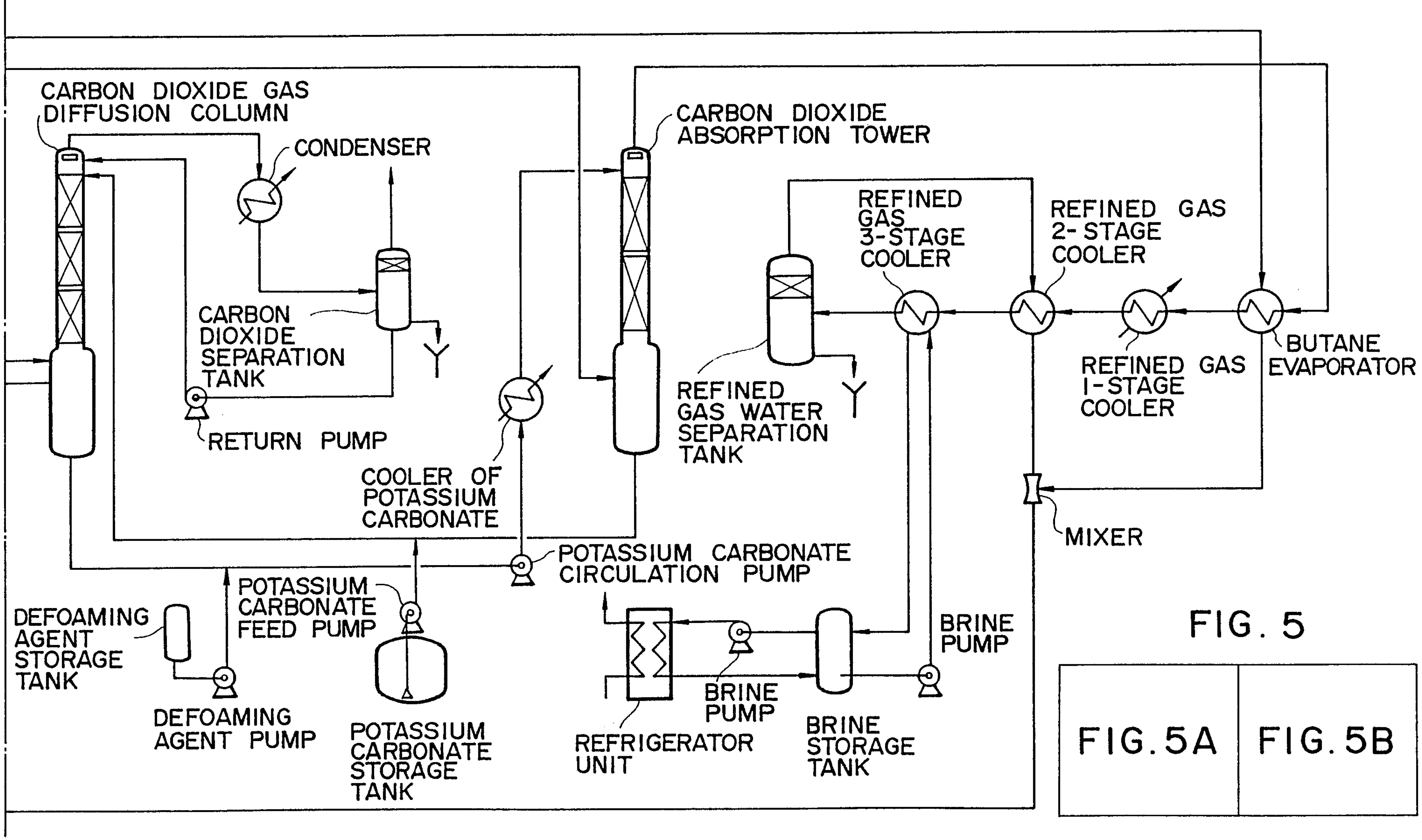
CARBON DIOXIDE GAS DIFFUSION COLUMN
CONDENSER
CARBON DIOXIDE SEPARATION TANK
RETURN PUMP
CARBON DIOXIDE ABSORPTION TOWER
COOLER OF POTASSIUM CARBONATE
REFINED GAS 3-STAGE COOLER
REFINED GAS 2-STAGE COOLER
REFINED GAS 1-STAGE COOLER
BUTANE EVAPORATOR
REFINED GAS WATER SEPARATION TANK
MIXER
POTASSIUM CARBONATE CIRCULATION PUMP
DEFOAMING AGENT STORAGE TANK
DEFOAMING AGENT PUMP
POTASSIUM CARBONATE FEED PUMP
POTASSIUM CARBONATE STORAGE TANK
REFRIGERATOR UNIT
BRINE PUMP
BRINE STORAGE TANK
BRINE PUMP
FIG.5A
FIG.5B

FIG. 5

FIG. 6A

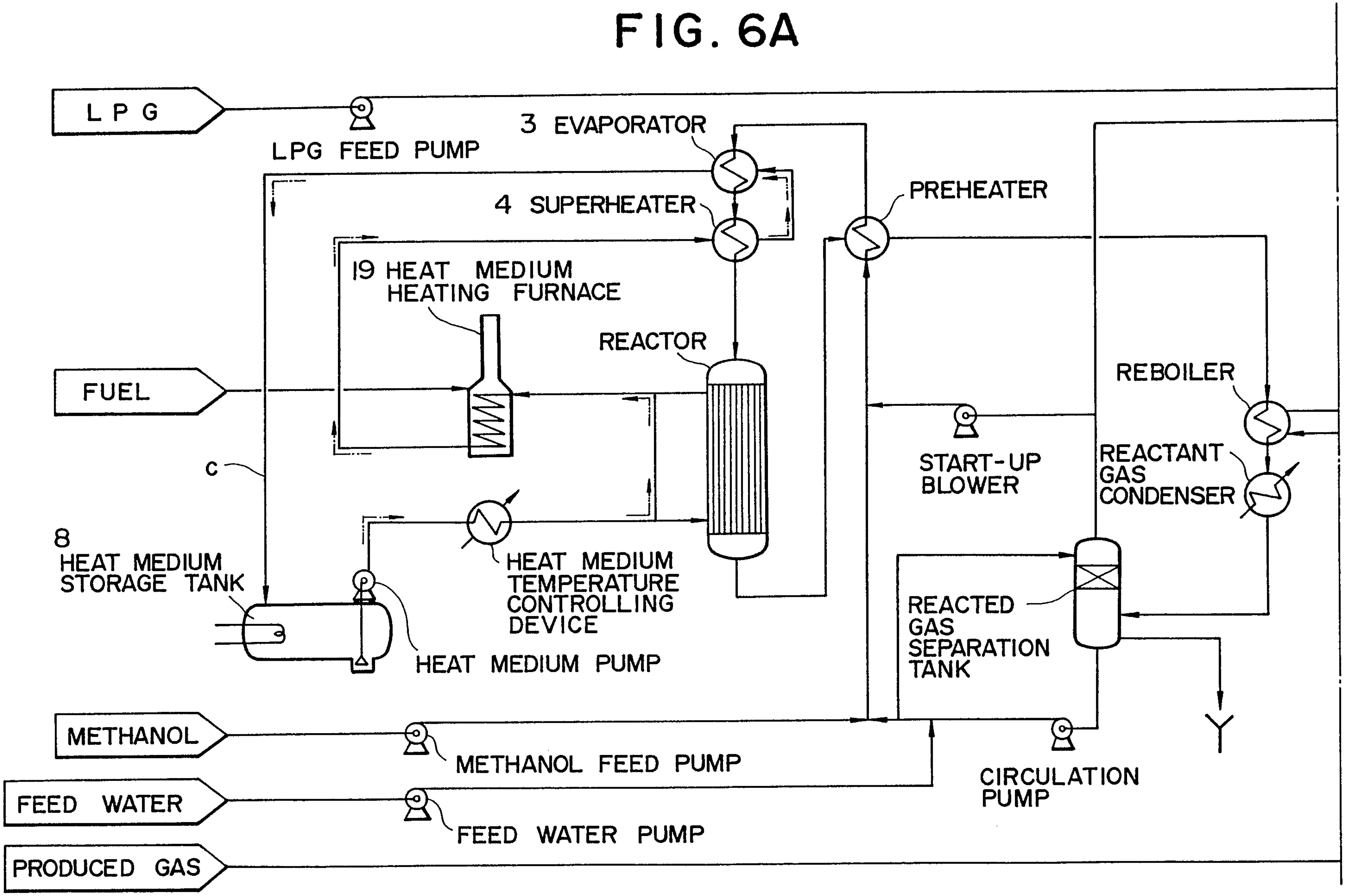
LPG
LPG FEED PUMP
3 EVAPORATOR
4 SUPERHEATER
PREHEATER
19 HEAT MEDIUM HEATING FURNACE
REACTOR
FUEL
c
8 HEAT MEDIUM STORAGE TANK
HEAT MEDIUM PUMP
HEAT MEDIUM TEMPERATURE CONTROLLING DEVICE
START-UP BLOWER
REBOILER
REACTANT GAS CONDENSER
REACTED GAS SEPARATION TANK
CIRCULATION PUMP
METHANOL
METHANOL FEED PUMP
FEED WATER
FEED WATER PUMP
PRODUCED GAS

FIG. 6B

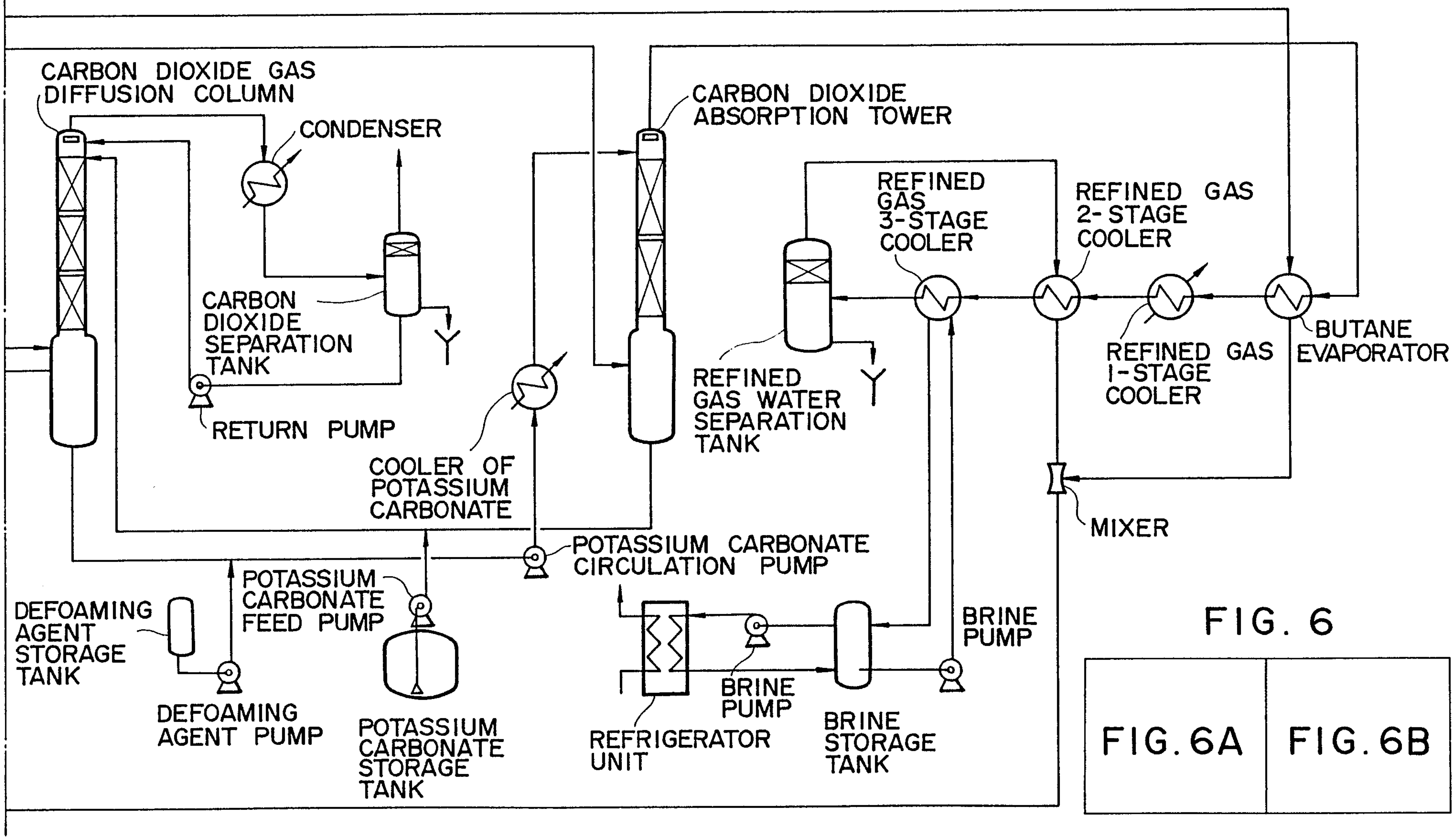
CARBON DIOXIDE GAS DIFFUSION COLUMN
CONDENSER
CARBON DIOXIDE SEPARATION TANK
RETURN PUMP
CARBON DIOXIDE ABSORPTION TOWER
REFINED GAS 3-STAGE COOLER
REFINED GAS 2-STAGE COOLER
REFINED GAS WATER SEPARATION TANK
REFINED GAS 1-STAGE COOLER
BUTANE EVAPORATOR
MIXER
COOLER OF POTASSIUM CARBONATE
POTASSIUM CARBONATE CIRCULATION PUMP
POTASSIUM CARBONATE FEED PUMP
DEFOAMING AGENT STORAGE TANK
DEFOAMING AGENT PUMP
POTASSIUM CARBONATE STORAGE TANK
REFRIGERATOR UNIT
BRINE PUMP
BRINE STORAGE TANK
BRINE PUMP
FIG.6A
FIG.6B

FIG. 6

FIG. 7A

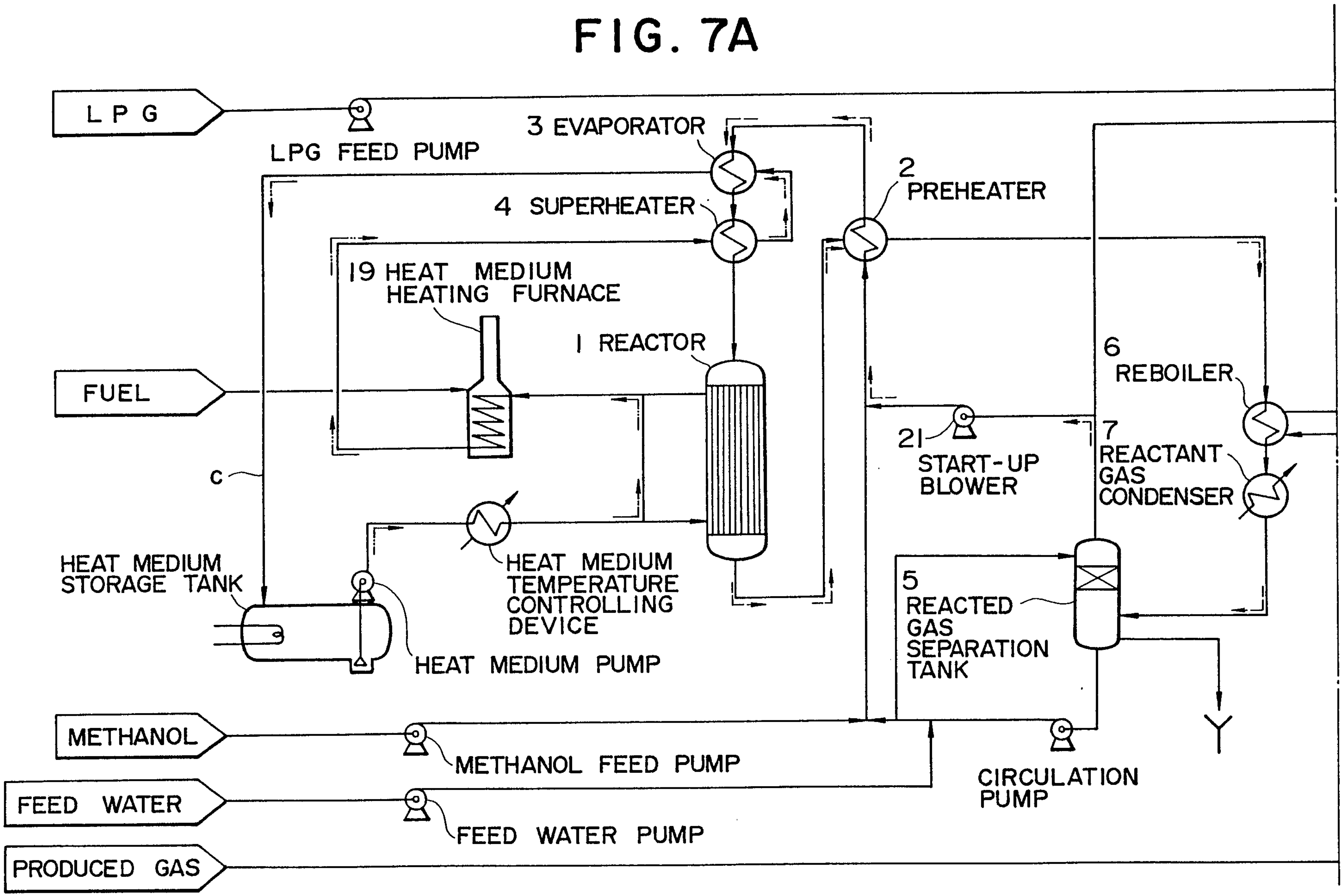
LPG
LPG FEED PUMP
3 EVAPORATOR
4 SUPERHEATER
2 PREHEATER
19 HEAT MEDIUM HEATING FURNACE
1 REACTOR
6 REBOILER
FUEL
21 START-UP BLOWER
7 REACTANT GAS CONDENSER
C
HEAT MEDIUM STORAGE TANK
HEAT MEDIUM TEMPERATURE CONTROLLING DEVICE
5 REACTED GAS SEPARATION TANK
HEAT MEDIUM PUMP
METHANOL
METHANOL FEED PUMP
CIRCULATION PUMP
FEED WATER
FEED WATER PUMP
PRODUCED GAS

FIG. 7B

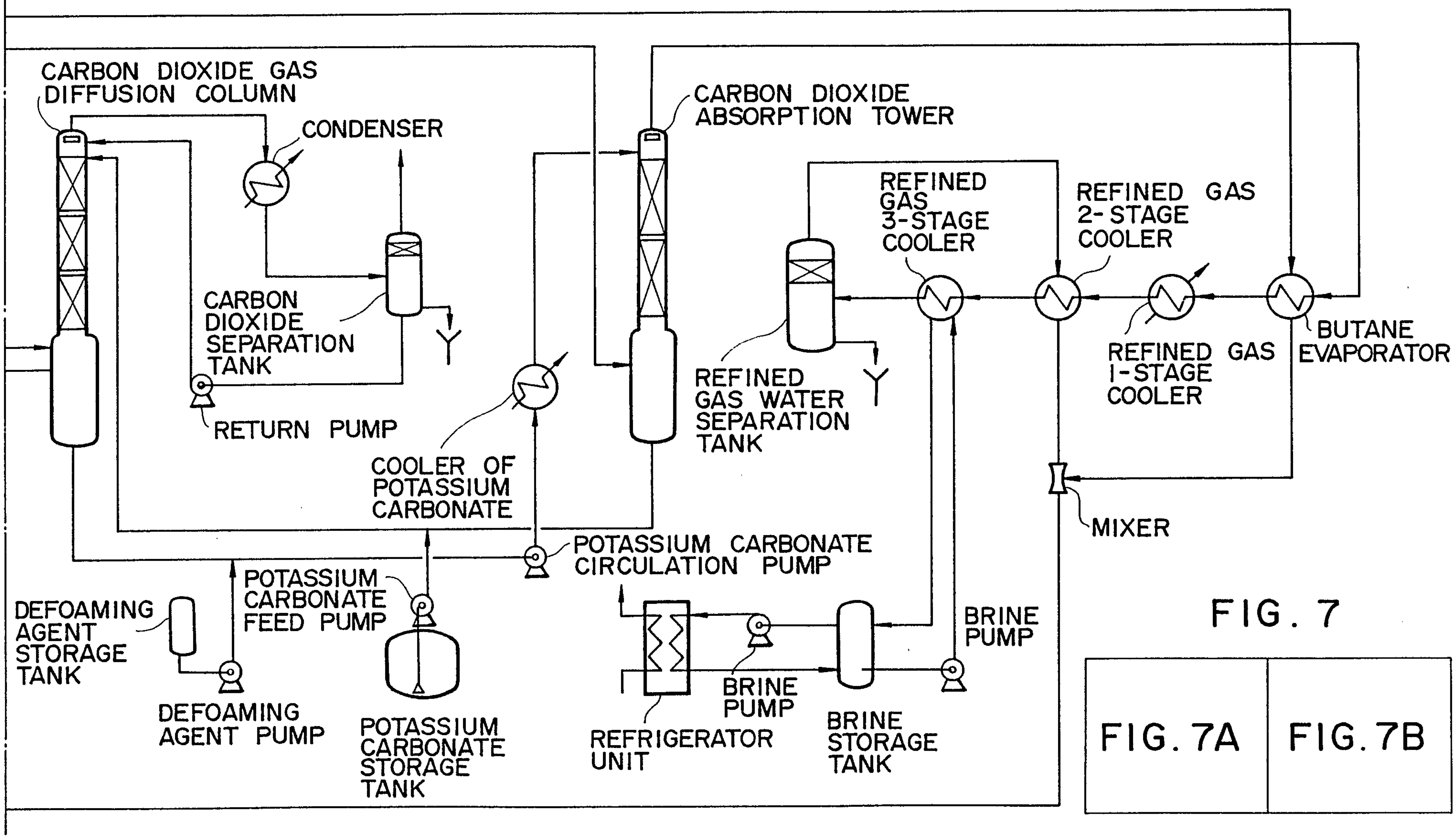
CARBON DIOXIDE GAS DIFFUSION COLUMN
CONDENSER
CARBON DIOXIDE SEPARATION TANK
RETURN PUMP
COOLER OF POTASSIUM CARBONATE
CARBON DIOXIDE ABSORPTION TOWER
REFINED GAS 3-STAGE COOLER
REFINED GAS 2-STAGE COOLER
REFINED GAS WATER SEPARATION TANK
REFINED GAS 1-STAGE COOLER
BUTANE EVAPORATOR
MIXER
POTASSIUM CARBONATE CIRCULATION PUMP
DEFOAMING AGENT STORAGE TANK
POTASSIUM CARBONATE FEED PUMP
DEFOAMING AGENT PUMP
POTASSIUM CARBONATE STORAGE TANK
REFRIGERATOR UNIT
BRINE PUMP
BRINE STORAGE TANK
BRINE PUMP
FIG. 7A
FIG. 7B

FIG. 7