
(12) **UK Patent Application** (19) **GB** (11) **2 123 027 A**

(21) Application No **8317153**
(22) Date of filing **24 Jun 1983**
(30) Priority data
(31) **57/108540**
(32) **25 Jun 1982**
(33) **Japan (JP)**
(43) Application published
25 Jan 1984
(51) **INT CL³**
C01B 3/36

(52) Domestic classification
C5E 101 122 124 126 AT

(56) Documents cited
WOA 8202547
GB 1480549
GB 1212817
GB 1185450
GB 1168726

(58) Field of search
C5E

(71) Applicant
Toyo Engineering Corporation (Japan), 2—5 Kasumigaseki 3-chome, Chiyoda-ku, Tokyo, Japan

(72) Inventors
Mituyuki Jinnouchi, Shinkichi Nozawa

(74) Agent and/or Address for Service
W. P. Thompson and Co., Coopers Building, Church Street, Liverpool L1 3AB

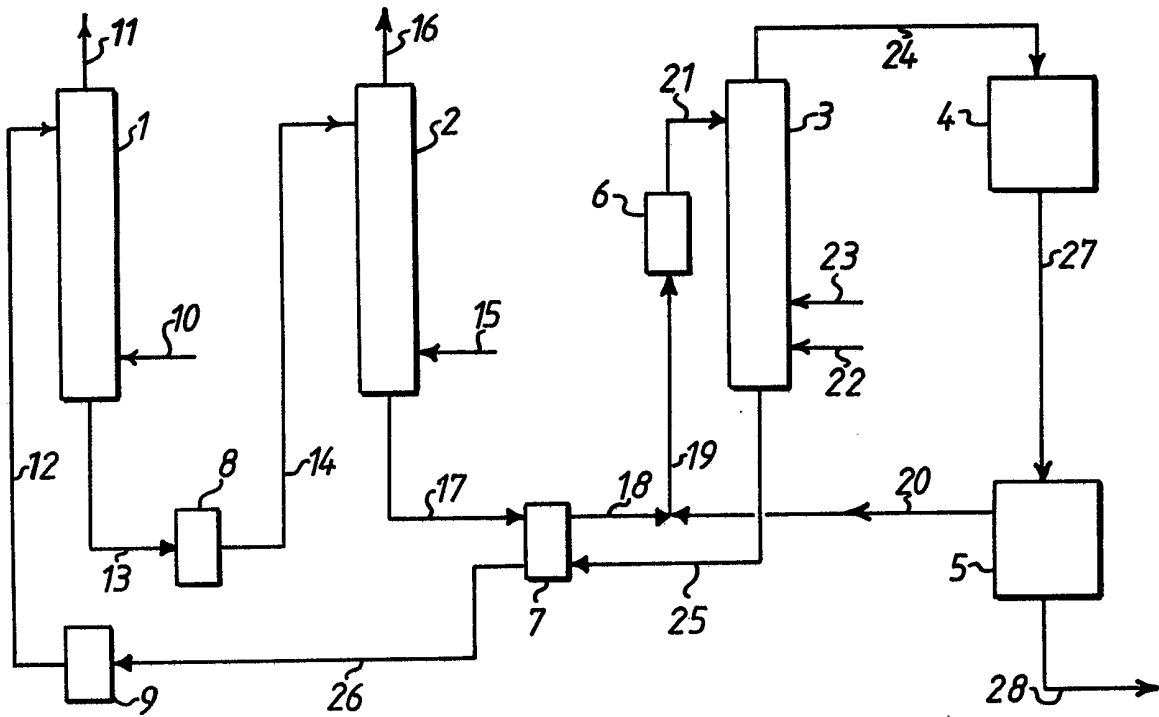
(54) **Process for producing a synthesis gas having an enriched content of carbon oxides**

(57) In a process wherein gaseous raw materials containing a large amount of hydrocarbons are steam reformed a carbon dioxide containing solution prepared by the contact of an aqueous carbon dioxide absorbent solution with a carbon dioxide containing gas is allowed to contact at high temperatures said gaseous raw

materials and/or said steam, each of which is flowing into said reforming reaction, or said synthesis gas which is flowing out of said reforming reaction to strip carbon dioxide from said carbon dioxide containing solution into the gas; and said absorbent solution from which carbon dioxide is stripped is allowed again to contact said carbon dioxide containing gas to prepare said carbon dioxide containing solution which is recycled to be used in the process.

GB 2 123 027 A

//

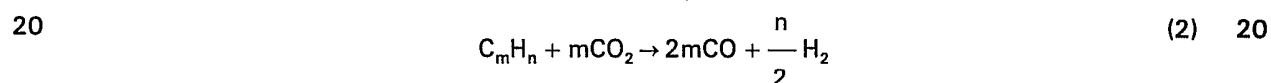
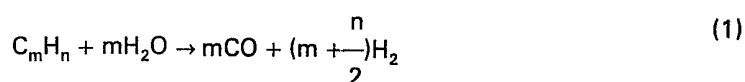


SPECIFICATION

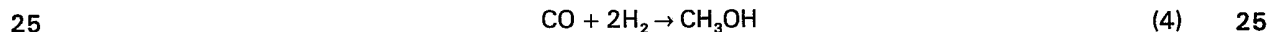
Process for producing a synthesis gas having an enriched content of carbon oxides

5 This invention relates to a process for enriching the carbon oxides content in a synthesis gas having a high content of hydrogen and carbon oxides and produced by a steam reforming reaction in which hydrocarbons are processed with steam in the presence of catalysts at high temperatures. The synthesis gas having a high content of hydrogen and carbon oxides has been produced on a large scale by the steam reforming reaction (referred to as the reforming reaction hereafter) whereby hydrocarbons such as natural gas, liquified petroleum gas, or naphtha, with steam added, are processed in contact with catalysts at high temperatures, as a means of supplying raw synthesis gas for manufacturing methanol, higher alcohols, chemicals through oxo synthesis, or ammonia, or reducing gas for use in direct reduction of iron ores. In the present invention, the term synthesis gas set forth below, which means a gas produced by way of the steam reforming reaction of hydrocarbons, should not be limited in its use to the chemical synthesis of more complex compounds and also the term synthetic reaction should be interpreted in the same manner.

15 The forming reaction of hydrocarbons as described above takes place usually under conditions of temperatures between 600°C and 1050°C and of pressures up to 50 atmospheres (absolute pressure; the same applies hereafter) in the presence of catalysts so as to produce a synthesis gas according to the following equations (1), (2) and (3):



where the equation (1) acts as a main reaction, and the equation (2) and (3) as side reactions. Methanol synthesis, on the other hand, as an example of the synthesis reaction utilizing the synthesis gas as raw material includes the chemical reactions expressed by the equation (4) and (5);



of which equation (4) takes place as a main reaction and equation (5) as a side reaction in the presence of catalysts at temperatures of 210°—450°C and under pressures above 50 atmospheres. Thus, in the case of methanol synthesis, the most preferred value of hydrogen/carbon oxides ratio (referred to as mol ratio hereafter) in the synthesis gas to be used, expressed by the following formula,

$$30 \quad R = \frac{\text{mol\% of hydrogen} - \text{mol\% of carbon dioxide}}{\text{mol\% of carbon monoxide} + \text{mol\% of carbon dioxide}}$$

settles down to 2.0. On the other hand, the "mol ratio" R of the synthesis gas obtained, according for the most part to the equation (1), from lower or medium saturated aliphatic hydrocarbons mainly used as industrial raw materials, such as methane, natural gas, liquified petroleum gas or naphtha, lies in the range from 2.1 to 3.0. Consequently, the use of the synthesis gas obtained from steam reforming of these hydrocarbons for the production of methanol gives rise to an excess of hydrogen, and the presence of this excess hydrogen leads to an uneconomical and decreased production of methanol; in other words, an increased amount of synthesis gas is consumed per ton of product methanol, and eventually larger production facilities are required as compared with the case using a synthesis gas without excess hydrogen. These disadvantages can be eliminated by increasing the carbon oxides content in the synthesis gas obtained from the "reforming reaction" and similar cases are found in the production of higher alcohols, high hydrocarbons by way of the Fisher-Tropsch process, sponge iron from direct reduction of iron ore, and other products than methanol. Although the optimum value of the "mol ratio" R is different in each case, it is necessary to correct the excess of hydrogen by increasing the carbon oxides content in the synthesis gas in all the cases. It is an object of the present invention to provide a novel process of increasing the carbon oxides content in the synthesis gas to correct the excess of hydrogen therein, and the following explanation is made using, for the most part, methanol synthesis as an example.

It is well known in the art to add carbon dioxide to the upper or downstream side of the "reforming reaction" to correct the excess of hydrogen mentioned above. And it is well known, as a first prior art

process, to obtain said carbon dioxide to be added by the combined steps comprising (a) washing a carbon dioxide containing gas, for example, a flue gas obtained from burned fuel in the course of supplying reaction heat required for the "reforming reaction", with absorbent solution such as an aqueous solution of ethanolamines or potassium carbonate to absorb carbon dioxide in the flue gas, (b) boiling the carbon dioxide contained solution obtained by step (a) under approximately atmospheric pressure to obtain a mixture of carbon dioxide gas and steam, (c) cooling said gaseous mixtures of carbon dioxide and steam to condense the steam and separate concentrated carbon dioxide gas from said gaseous mixture, and then (d) compressing the concentrated carbon dioxide gas to combine it with the gas flowing in the upper or downstream side of said steam reforming reaction which is taking place at an elevated pressure. And it is also known as a second prior art process for a similar purpose as disclosed in Japanese Patent Laid-Open No. 87304/1978 to obtain the hydrocarbons enriched with carbon dioxide and to be reformed by the steps comprising (a) washing a residual gas from the methanol synthesis described above which contains carbon dioxide with crude methanol under conditions of low temperature and high pressure to dissolve carbon dioxide in the residual gas into the crude methanol in order to obtain a crude methanol containing carbon dioxide, and (b) reducing the pressure of said crude methanol containing carbon dioxide to cause it to contact a raw hydrocarbon gas which is undergoing the "reforming reaction", at a low temperature so as to release carbon dioxide from the crude methanol into the hydrocarbon gas. It is possible in both of the prior art processes to add carbon dioxide to a gas which flows into or out of the "reforming reaction" and also to convert it to carbon monoxide depending on the equation (2) and (3) when the carbon dioxide is added to the gas which is flowing into the "reforming reaction". These prior art processes, however, include serious disadvantages, although the excess of hydrogen in said synthesis gas can be actually eliminated by these processes. The first prior art process includes two major disadvantages which demand (a) a heat quantity as large as 3500—4500 Kcal per Nm³ of carbon dioxide recovered while recovering the concentrated carbon dioxide by heating said carbon dioxide containing solution under atmospheric pressure and (b) power for compressing the recovered carbon dioxide. These two disadvantages result in a greatly increased cost of recovered carbon dioxide so that the process may not serve to compensate the aforementioned uneconomical production caused by the excess of hydrogen in the synthesis gas. The second prior art process includes a number of disadvantages such as (a) losing a portion of methanol by vaporization while contacting a carbon dioxide containing solution with a gas which flows into or out of the "reforming reaction" to release carbon dioxide in it, due to the relatively high vapor pressure of methanol, or (b) incurring the cost of washing the gas containing some methanol vapor and the carbon dioxide with water to recover the lost methanol and for separating the methanol from the aqueous methanol solution obtained in the said washing. Moreover the impossibility of applying high temperature in releasing the carbon dioxide, due to the same reason, makes it impossible to release the carbon dioxide where hydrocarbons having the liquid state at ordinary temperatures are used as a raw material for the "reforming reaction"; the inevitability of applying a relatively low releasing pressure of carbon dioxide makes it impossible to recover carbon dioxide in a carbon-dioxide-containing gas of which the partial pressure of carbon dioxide is low; the low solubility of carbon dioxide in methanol at approximately ordinary temperatures makes it necessary to use a large amount of low temperature methanol in the washing; and the high solubility of hydrocarbons such as propane and butanes in methanol makes it difficult to use these hydrocarbons as the raw material in the second prior art process. Consequently, these prior art processes have never been applied economically as a means of increasing carbon oxides content in the synthesis gas, and methanol synthesis has so far been practiced in the presence of excess hydrogen in the synthesis gas (this present state is referred to as the present process hereafter).

As a result of the inventors' examination, the uneconomical first prior art process which recovers carbon dioxide by boiling a carbon dioxide-containing solution (referred to as the containing solution hereafter) at atmospheric pressure is due to the fact that water vapor generated in boiling the "containing solution" is used only to lower the partial pressure of released carbon dioxide by dilution and to accelerate the release of carbon dioxide in the "containing solution" to be stripped, but not used as steam for the "reforming reaction", with the result that most of the heat energy consumed for the boiling of the containing solution is dissipated, and in view of the above, the present invention is based on the discovery that the aforementioned energy loss can be prevented, if heat-releasing of carbon dioxide is carried out in direct contact with a gas which flows into or out of the "reforming reaction" under approximately the same pressure as that of the "reforming reaction". The gist of the present invention is (a) to use, as an absorbent solution and "containing solution", an aqueous solution from which no component other than carbon dioxide and water vapor is evolved on heating; (b) to subject the "containing solution under approximately the same pressure as that of the "reforming reaction" to direct contact with gaseous (or vaporised) raw hydrocarbons and/or steam for the reforming which are in the course of raising temperature in order to undergo the "reforming reaction", or with synthesis gas at high temperatures, which is in the course of cooling after the "reforming reaction" (these gases subjected to the direct contact with the containing solution are referred to as diluent gas hereafter and the release of carbon dioxide from the containing solution in said direct contact is referred to as regeneration); (c) to make the aforementioned dilution effect in the "regeneration" to be largely dependent on these "diluent gases";

and to utilize the evolved water vapor from the containing solution for increasing the dilution effect and for use as steam for the reforming if water vapor is generated from the "containing solution" during said direct contact, all of which lead to a number of advantages including (a) a saving of a large amount of energy supplied for the regeneration of the "containing solution"; (b) effective use of supplied energy; (c) no evaporation loss of absorbent from the "containing solution"; and (d) utilization of hydrocarbons which are liquid at ordinary temperatures as a raw material for the reforming, thus making the present invention a novel process with many advantages as mentioned above, with the result that compression of carbon dioxide evolved and separated in the first prior art process is no longer required.

In the accompanying drawing, the single figure is an example of the process of the present invention. The reference numerals in the drawing have the following meaning:

- | | | |
|----|------------------------------------|----|
| | 1. first carbon dioxide absorber | |
| | 2. second carbon dioxide absorber | |
| | 3. containing solution regenerator | |
| | 4. steam reformer | |
| 15 | 5. synthesis gas cooler | 15 |
| | 6. containing solution heater | |
| | 7. heat exchanger | |
| | 8. absorbent solution pump | |
| | 9. absorbent solution cooler | |
| 20 | 10—28. connecting pipe | 20 |

An embodiment of the present invention is then explained using a process example illustrated in the Figure. The Figure shows a process example of producing a synthesis gas for methanol production enriched with carbon oxides in which a mixed gas comprising pressurized natural gas and steam for reforming before undergoing a "reforming reaction" as a "diluent gas" is directly contacted with a "containing solution" to transfer carbon dioxide therein to said mixed gas and then subjected to the "reforming reaction". In the Figure, a raw natural gas processed by necessary treatments (e.g. desulfurization, preheating, humidifying, compression, etc.) and steam are supplied through pipe 22 and 23 to the lower part of a containing solution regenerating tower 3 and caused to contact with a carbon dioxide containing solution which has been heated in a containing solution heater 6 and is supplied through a pipe 21 to the top of the containing solution regenerator 3. By the contact, carbon dioxide in the "containing solution" is transferred into the mixture of the natural gas and the steam, and the carbon dioxide enriched mixed gas is sent through a pipe 24 to a steam reformer 4. The lower part, lower than the inlet of the steam, of the regenerator 3 plays a function of humidifying and preheating the natural gas supplied through pipe 22 by means of the contact of said natural gas with said "containing solution" which has been almost regenerated and is still under high temperature conditions. In the steam reformer 4, the mixed gas if necessary, after an adjustment of temperature and pressure has been made to some extent, is subjected to the "reforming reaction" based on the aforementioned reaction equations in the presence of catalysts. As a result of the "reforming reaction", the mixed gas is converted into a synthesis gas which is supplied through a pipe 28 to a next process after being cooled by a synthesis gas cooler 5. On the other hand, the containing solution which has released carbon dioxide and lost some water content by vaporization in the containing solution regenerator 3 turns into an absorbent solution which is sent through a pipe 25 to a heat-exchanger 7 where it is cooled in heat exchanging relationship content with the carbon dioxide containing solution to be supplied to the containing solution regenerator 3, then sent through a pipe 26 to an absorbent solution cooler 9 for cooling, and sent through a pipe 12 to a first carbon dioxide absorber 1. In the first carbon dioxide absorber 1, a first carbon dioxide containing gas (referred to simply as "first gas" hereafter) supplied through a pipe 10, such as a flue gas, for example, from the steam reformer 4 in which a fuel is burned to supply heat for the steam reforming reaction, is caused to flow, and the absorbent solution from the pipe 12 is contacted with the "first gas" to absorb carbon dioxide in the first gas. As a result of the contact, the "first gas" reduced in carbon dioxide content is sent through a pipe 11 to a following process or discharged in the air in the case of flue gas. The absorbent solution which has absorbed carbon dioxide in the first carbon dioxide absorber 1 is taken out through a pipe 13, raised in pressure by an absorbent solution pump 8, and introduced to a second carbon dioxide absorber 2, where it is subjected to contact with a second carbon dioxide containing gas (referred to simply as a second gas

hereafter) supplied through a pipe 15, such as a residual gas having a high pressure condition and carbon dioxide from methanol synthesis for which, for instance, a synthesis gas from a pipe 28 is used, so as to absorb carbon dioxide in the "second gas" and then to convert the absorbent solution to a "containing solution". After the contact, the "second gas" reduced in carbon dioxide content is sent through a pipe 16 to a next step, and the "containing solution" which has absorbed carbon dioxide is taken out through a pipe 17, raised in temperature in the heat-exchanger 7 described above with the high temperature absorbent solution flowing out of the regenerator 3 for preheating before further heating in the containing solution heater 6, and recycled to the containing solution regenerator 3 where it is caused to release carbon dioxide as mentioned above and regenerated to an absorbent solution with carbon dioxide absorbing ability. An equivalent amount of hot water produced in the synthesis gas cooler 5 to that of water evaporated from the "containing solution" in the containing solution regenerator 3, is fed through a pipe 20 to join with the preheated containing solution to be supplied to the regenerator 3.

The most important point in the present invention process as described above is that it is not essential to boil the "containing solution" and transfer a large amount of water vapor to a gas phase in the containing solution regenerator 3 in order to lower the partial pressure of carbon dioxide in the gas phase by dilution with the water vapor, evaporated from the containing solution, as required in the aforementioned first prior art process. In other words, the dilution in the present invention process is more efficiently carried out, without the evaporation of water vapor from the "containing solution" as a large amount as required in the prior art process, by a much larger amount of "dilution gas" than that of the water vapor evaporated in the prior art process. And the vaporization of water from the "containing solution" to the "diluent gas" can also be reduced to zero or minimized by the presence of steam in the "diluent gas" which is supplied through pipe 23 in the Figure. Therefore, the temperature of the "containing solution" supplied to the regenerator 3 is acceptable if it reaches a temperature at which the equilibrium partial pressure of carbon dioxide emitted from the containing solution is high enough to release carbon dioxide from the solution to the diluent gas already enriched with carbon dioxide to some extent and may preferably be its boiling temperature of slightly below the boiling temperature of the "containing solution" under the total pressure of the regenerator 3. The boiling temperature of the "containing solution" in the present invention process is defined hereafter as a temperature at which the sum of the equilibrium partial pressure of carbon dioxide and that of water vapor emitted from the solution is substantially equal to the total pressure in the regenerator 3. The water vapor evolved from the "containing solution" and transferred to the gas phase does not constitute a loss because it is utilized as steam for the "reforming reaction", regardless of whether the "containing solution" is boiled or not in the regenerator. These points contribute mainly to the great saving of heat energy required for releasing carbon dioxide in the present invention process compared with the first prior art. Consequently, such composition of the "containing solution" is not desired, as evolves any other component than water vapor and carbon oxide (e.g. methanol in the second prior art process) to the extent that can not be neglected at temperatures in the regenerator 3. That is because the vapor other than water vapor and carbon dioxide has to be recovered or removed since it constitutes a loss or disturbs the "reforming reaction", eventually resulting in a large waste and uneconomy.

The second important point of the present invention, as compared with the prior art processes, which is boiling the containing solution at approximately atmospheric pressure, lies in the fact that the higher regeneration temperature up to the boiling temperature of the containing solution under a pressure substantially equal to that of the reforming can be used in the present invention process, and consequently the equilibrium partial pressure of carbon dioxide emitted from the "containing solution" at that temperature is being raised to cause carbon dioxide to be released more easily. In other words, "reforming reaction" is carried out at least under atmospheric pressure, usually under a total pressure from 2 to 50 atmospheres and the regenerator in the present invention process is operated under a total pressure close to that of the "reforming reaction", hence it becomes possible to increase the temperature of the "containing solution" to the boiling temperature at that solution under the total pressure of the "reforming reaction" and to raise extremely the equilibrium partial pressure of carbon dioxide emitted from the solution of this kind, in contrast to the first prior process which only applies a boiling temperature under atmospheric pressure. It is a well known fact that the equilibrium partial pressure of carbon dioxide emitted from the solution of this kind increases exponentially with increased temperature of the solution, and releasing of carbon dioxide is made easier by this principle. As a result, releasing of carbon dioxide by a much smaller regenerator as well as the abovementioned satisfactory dilution effect can be realised.

The third important point is that increased regeneration temperature of the "containing solution" as mentioned above makes it possible to use hydrocarbons which have such boiling temperatures as those to the extent of naphtha under atmospheric pressure and are liquid at ordinary temperature as raw hydrocarbons supplied to the regenerator and so the present invention has another advantage compared with the second prior art process in this respect. And the fourth important point is that the "diluent gas" contacting with the "containing solution" in the regenerator, regardless of whether it is a raw hydrocarbon gas (or vapor), steam, a mixture of both, each of which flows into the "reforming reaction", or a synthesis gas which flows out of the "reforming reaction", can have nearly the same

dilution effect. In the present invention, the "diluent gas" which can be used to lower the partial pressure of carbon dioxide in the gas phase of the containing solution regenerator is a gas selected from a group consisted of a raw hydrocarbon gas (or vapor), steam added for the reforming, a mixture of the raw hydrocarbon gas (or vapor) and the steam for the reforming above described, each of which is supplied to the "reforming reaction", and a synthesis gas which flows out of the "reforming reaction".

The present invention includes a number of embodiments which can be classified into two slightly different categories according to the principle of carbon dioxide absorption, that is, to whether the carbon dioxide is being absorbed by the "absorbent solution" with a mechanism accompanied by chemical reactions between carbon dioxide and an absorbent used or with a mechanical of simple physical dissolution not accompanied by chemical reactions. The detailed explanations of some embodiments concerning two categories abovedescribed are made hereafter with conditions to be applied for this invention.

The "absorbent solution" which accompanies chemical reaction when carbon dioxide is absorbed by the solution includes aqueous solutions comprising two components of potassium carbonate and potassium hydrogen carbonate, and aqueous solutions of ethanolamines as mentioned above, and in addition, aqueous solutions comprising two components of sodium carbonate and sodium hydrogen carbonate, aqueous solutions comprising alcohol amines such as mono-ethanol amine tri-ethanol amine, or mono, di and tri-isopropanol amines and these carbonates, or mixed aqueous solutions of these aqueous solutions. These aqueous absorbent solutions generally are used at low temperatures ranging from room temperature to about 120°C for the absorption of carbon dioxide and are used at higher temperatures than those used in the absorption for the regeneration of the "containing solution". Consequently, the total pressure in the absorption of carbon dioxide by an absorbent solution of this kind and that in the regeneration of the "containing solution" can be set arbitrarily as desired, usually at pressures ranging from atmospheric pressure to several hundreds of atmospheres, so far as the abovementioned temperature relationship between the absorption and the regeneration is maintained.

And in using the absorbent solution of this kind, there is no limitation as regards the kind and number of the carbon dioxide containing gas to be subjected to the absorption, so that many kinds of carbon dioxide containing gases can be used jointly. Although both a flue gas and a residual gas of methanol synthesis are used in the explanation of the process example in the aforementioned Figure, for instance, only either one of both may also be used in this case, and contrary to this, a carbon dioxide removal process in the production of ammonia can also be applied and combined with the example in the Figure. In utilizing carbon dioxide in many kinds of carbon dioxide containing gases, the contact of a regenerated absorbent solution with the carbon dioxide containing gases may better be arranged in the series from lower to higher carbon dioxide partial pressures of both the containing gas and the absorbent solution in the absorption of carbon dioxide. In other words, the contact of the regenerated absorbent solution with the carbon dioxide containing gas in the said series can contribute to the increased carbon dioxide content in the "containing solution", which eventually leads to the transfer of a large amount of carbon dioxide from the "containing solution" to the dilution gas, that is, upper stream gases of the "reforming reaction" or to a synthesis gas in the downstream of the "reforming reaction". If the partial pressure of carbon dioxide in the carbon dioxide containing gases is as low as less than 0.005 absolute atmosphere, however, it is impossible to utilize a sufficient amount of carbon dioxide due to too little content of carbon dioxide to be absorbed by the absorbent solution.

And there are also many selections in the operation conditions of the regenerator for releasing carbon dioxide from the "containing solution" which has absorbed carbon dioxide in the manner as mentioned above to the dilution gases. It is preferable, as the operating temperature in the regeneration of the "containing solution", to select high temperatures which are close to the boiling temperature of the "containing solution" under the total pressure in the regenerator in the manner as described above, in order to increase the rate of releasing of carbon dioxide from the "containing solution" to the dilution gases and to make efficient use of the carbon dioxide. In the regeneration of the "containing solution" of this kind, the heat of decomposition of carbonates and that of vaporization of water are consumed. Therefore, if supply of this heat depends only on a holding sensible heat of the "containing solution" flowing into the regenerator, the temperature of the containing solution falls rapidly, and the rate of regeneration decreases. And if the temperature of a "diluent gas" which contacts the "containing solution" is largely below that of the "containing

solution", a similar phenomenon occurs. Because this phenomenon makes the regenerator to be larger in size than is necessary, it is preferable to control the temperature of "diluent gas" in such a way that the temperature of the "diluent gas" is equal to or higher than that of the "containing solution" in a place where the regeneration is taking place very rapidly in the regenerator, and also to heat the "containing solution" by allowing it to flow down along a heating surface in the regenerator and to contact the "diluent gas". And it is possible to utilize the bottom part of the regenerator as a place where the contact occurs between the "absorbent solution" which has almost completed regeneration and is still high in temperature and the hydrocarbon gases of which the temperature has not yet been raised sufficiently, i.e. as a place where cooling of the "absorbent solution" and humidification and temperature increase of the hydrocarbon gas occurs simultaneously. And it is also possible to utilize the regenerator as a place where a part of the heat energy contained in hot water is produced by

condensation of excess steam under pressure in the synthesis gas cooler 5 of the Figure is directly recovered, and in this case, the abovementioned hot water fed through a pipe 20 may well be introduced into the upper or middle part of the regenerator. And as another means of recovering heat energy contained in the "absorbent solution" which is still high in temperature after the regeneration and in the abovementioned hot water and cooling both liquids, it is also preferred that either one of the liquids or both are reduced in pressure adiabatically and stepwisely to allow water vapor to evaporate and the liquid phase to be cooled with each reduction in pressure and that then the water vapor evolved is pressurized by a well known method (e.g. steam ejector etc.) and allowed to join to the "diluent gas" in the regenerator or in any other place. The "reforming reaction" is often carried out at temperatures between 750°C and 1000°C, and it is easy to select a gas which is suitable with regard to temperature for using the abovementioned "diluent gas" among the raw hydrocarbon gases (vapor), the steam, a mixture of the raw hydrocarbon gases (vapor) and the steam, each of which is being raised in temperature up to the abovementioned reaction temperature of this "reforming reaction", and the synthesis gas which is being reduced in temperature after the "reforming reaction", and to introduce all or a portion of the gas as "diluent gas" to the containing solution regenerator. The hydrocarbon gas (or vapor) and the steam among the abovementioned "diluent gas" can be used separately or as a mixture for the dilution gas. There is no interference in attaining the effect of carbon oxides enrichment by the process of the present invention, even though these "diluent gases" contain carbon dioxide to the extent of 6% wet basis before the enrichment of carbon dioxide according to this invention is applied in the case of methanol synthesis, for example. And it is not necessarily required to introduce the total amount of gas in the upper or downstream side of the "reforming reaction" to the containing solution regenerator as a "diluent gas" and if the amount of carbon dioxide to be released from the "containing solution" to the diluent gas is relatively small, a part of either one of the four "diluent gases" mentioned above may well be introduced to the containing solution regenerator. Consequently, the quantitative ratio of the "containing solution" to the "diluent gas" in the regenerator depends largely on the concentration of absorbent and carbon dioxide in the "containing solution", the concentration of carbon dioxide in the "diluent gas", and the amount of carbon dioxide to be released. And the number of containing solution regenerators is by no means limited to one as illustrated in the Figure. That is, two or more containing solution regenerators can be used in series or in parallel, or in a combined manner of both. For example, it is possible that two absorbent solutions which contain different absorbents independently are used in the first carbon dioxide absorber and the second carbon dioxide absorber respectively, as an alternative to the method in the Figure and "containing solutions" obtained from the two absorbent solutions are regenerated separately in two containing solution regenerators installed in parallel or in series in regard to "diluent gas", and carbon dioxide thereby released is transferred to the abovementioned "diluent gas". Although there is no particular limitation in the pressure applied in the containing solution regenerator, it is desirable to use pressures which are close to the operating pressures of the "reforming reaction" because the "diluent gas" is not required to increase or decrease in pressure beyond necessity and the regeneration temperature can be raised to the extent as practically high as possible, hence pressures from 2 to 50 atmospheres generally applied in the "reforming reaction" are particularly preferred in the regeneration. In a case where hydrocarbons which are liquid at ordinary temperatures and under atmospheric pressure are used as a raw material of the "reforming reaction" however, it is necessary to regulate the temperature and the pressure in the containing solution regenerator to the temperatures and partial pressure of said hydrocarbons at which said hydrocarbons are maintained in a gaseous state.

In the present invention, in the case where a hydrocarbon gas, stream, or a mixture of a hydrocarbon gas and steam in the upper stream of the "reforming reaction" is used as a "diluent gas", a synthesis gas enriched by carbon monoxide is obtained, and on the contrary, in the case where a synthesis gas in the downstream of the "reforming reaction" is used as a "diluent gas", a synthesis gas enriched by carbon dioxide is obtained.

The above is the explanation of the embodiments which applies such absorbent solution as involving the absorption mechanism accompanied by chemical reactions in absorbing carbon dioxide by the "absorbent solution". On the other hand it is also possible in the present invention to use "absorbent solutions" which absorb carbon dioxide by a simple physical dissolution in the absence of chemical reactions. These "absorbent solutions" include water, an aqueous solution of lower or medium alkylether or lower or medium polyalkylene glycol such as the dimethylether of polyethylene glycol among which the vapor pressure of the organic matters is small and a mixture thereof. In order to dissolve carbon dioxide into the "absorbent solution" of this kind, it is necessary in general to apply temperatures as low as -10 ~ 50°C and to contact these absorbent solutions with the carbon dioxide containing gas having a high partial pressure of carbon dioxide, while on the contrary, in order to release carbon dioxide from the "containing solution" of this kind ("containing solution"), it is necessary to contact with a dilution gas having a partial pressure of carbon dioxide below that of the "containing solution", at approximately the same temperature as in the absorption, or to contact with a dilution gas at a higher temperature than that of the "absorption" under approximately the same total pressure as in the absorption. In the present invention, therefore, it is possible that, as step (a), carbon dioxide in a carbon dioxide containing gas which is under pressures nearly equal to or higher than the total pressure applied in the "reforming reaction" is absorbed at low temperatures by the "absorbent solution" of this

kind to prepare a "containing solution" and as step (b) the carbon dioxide is released from the "containing solution" to the diluent gas at higher temperatures than those in the absorption by contact with the diluent gas. This, for example, corresponds to the case where methanol of higher alcohols are synthesized under pressure approximately equal to or higher than those of a "reforming reaction" from a synthesis gas obtained by the "reforming reaction" and a residual gas from said synthesis is utilized as a carbon dioxide containing gas. As the residual gas from the synthesis of methanol or higher alcohols contains carbon dioxide, it becomes possible to utilize it as a carbon dioxide containing gas in such a manner that as step (a) the residual gas which has been subjected to the condensation and separation of methanol and others by cooling and is still before pressure reduction, is allowed to contact the aforementioned physical absorbent solution dissolve carbon dioxide thereof into the solution so as to prepare a "containing solution", and as step (b) the "containing solution" is heated and introduced to a containing solution regenerator under approximately the same pressures as those in the "reforming reaction" to contact with a "diluent gas" so as to release and recover the carbon dioxide dissolved in the manner as described in step (a). This method can be used, as an example in the case where the first carbon dioxide absorber 1 in the Figure and the contained solution regenerator 3 are used as an independent recycle root isolated from the second carbon dioxide absorber 2 for an "absorbent solution" which accompanies chemical reactions and the second carbon dioxide absorber 2 and another containing solution regenerator (not shown in the Figure) are used as an independent recycle root for the physical "absorbent solution", and said another containing solution regenerator (not shown) is installed in parallel or in series to the containing solution regenerator 3 in the Figure as regards the "diluent gas", so that the recycle root of the physical "absorbent solution" can be separated from that of the chemical "absorbent solution" which is used to recover the carbon dioxide contained in carbon dioxide containing gas having a low total pressure. A similar method can be applied as a means of utilizing carbon dioxide which is produced but not necessary in ammonia production for a source of carbon oxides for the synthesis of methanol. But even in the case of physical "absorbent solution", it is much the same as described above in that the vapor pressure or organic matter must be low to a negligible extent. As clearly recognized in the explanation above described for this invention, the temperature of the "containing solution" in the containing solution regenerator varies with the kind and composition of the "absorbent solution". In this invention, it is preferably to select the temperature to be used in the containing solution regenerator in a range of from 100°C to 250°C approximately. As the composition of "absorbent solution" for this invention, most of the well-known compositions satisfying the condition previously described and used in the prior art processes can be applied.

In the present invention, the upper limit of the concentration of carbon dioxide in the "diluent gas" which has been concentrated with the "containing solution" at high temperatures and enriched with released carbon dioxide mainly depends on the partial pressure of carbon dioxide in a carbon dioxide containing gas and an amount ratio of "diluent gas" and "containing solution" in the regenerator. For instance, a "containing solution" prepared by the contact of an "absorbent solution" and a carbon dioxide containing gas of which the concentration of carbon dioxide is 50 mol% or more and the total pressure is 100 atmospheres or more, contains a very large amount of carbon dioxide, and the equilibrium partial pressure of carbon dioxide emitted from the "containing solution" at high temperatures reaches as high as 20 atmospheres or more, so that it is relatively easy to raise the concentration of carbon dioxide in the "diluent gas" to be 70 mol% or more on wet basis by contacting a large amount of the "containing solution" with a relatively small amount of the "diluent gas" under relatively low total pressures and at high temperatures, and it is easier to raise it lower than said concentration, 70 mol%, of carbon dioxide. But it is difficult as described earlier in this invention to transfer a sufficient amount of carbon dioxide to the "diluent gas" in the case where the partial pressure of carbon dioxide in the carbon dioxide containing gas is 0.005 atmosphere or less, because the equilibrium partial pressure of carbon dioxide emitted from the resultant "containing solution" is low even at high temperatures.

The fundamental advantage of the present invention lies in the fact that (a) the energy required for recovering carbon dioxide from a "containing solution" can be reduced to 800 ~ 850 Kcal from 3500 ~ 4500 Kcal of the prior art process per Nm³ of carbon dioxide because of the large reduction in the amount of water vapor simultaneously evolved in the releasing of carbon dioxide from the "containing solution" in order to eliminate hydrogen excess in the aforementioned synthesis gas and of the utilization of the water vapor evolved in the "reforming reaction", and (b) a compressor for the carbon dioxide is no longer required. As a result, this advantage has made possible the decrease in the aforementioned mol ratio with low cost. As a final result, for example, the amount of energy consumed in the synthesis of methanol from natural gas can be improved as described in table 1. In table 1, the energy consumption for each case of ① the present invention process shown in the Figure, ② the prior art process, and ③ the present process explained above, and ④ the case of introducing highly concentrated carbon dioxide under atmospheric pressure from the outside for reference are described as a consumption of the combustion heat of natural gas used for one metric ton of methanol produced. And in the table 1, the raw natural gas means a natural gas supplied for the "reforming reaction" and the fuel natural gas means a natural gas used as a fuel for external heating in said "reforming reaction". And the reason for a small amount of fuel natural gas consumption in case ③ is that methanol synthesis

using a synthesis gas which contains excess hydrogen generates a large amount of residual gas which is used as an alternative fuel for the "reforming reaction", and resulting in the decrease in the consumption of fuel natural gas.

TABLE 1

	① Present invention process	② Prior art process	③ Present process	④ Case of introducing highly concentrated carbon dioxide from outside
Raw natural gas: unit MMKcal/ton of methanol	5.80	5.80	7.17	5.70
Fuel natural gas: unit MMKcal/ton of methanol	1.04	1.94	0.15	1.14
Total	6.84	7.74	7.02	6.84
Value R applied	2.1	2.1	2.9	2.0

5 The other advantage of the present invention is that an elimination of the presence of excess hydrogen in a synthesis gas makes possible the decrease in size of instruments and equipments used in a process plant for any one of applications using the resultant synthesis of the applications described below in using the gas which has appropriate hydrogen content in resultant synthesis gas in said applications. When excess hydrogen contained in a synthesis gas using any application is simply extracted, valuable components such as carbon oxides are accompanied in the extracted excess hydrogen, generally, with the result that the amount of synthesis gas consumed in said applications increases compared with a case in which excess hydrogen does not exist, while on the other hand, by way of the process according to the present invention, it becomes possible to prevent the increase in the amount of synthesis gas consumed, due to the elimination of the presence of excess hydrogen. This is another advantage of the present invention. In the present invention, it is possible to apply well-known gas-liquid contacting equipment such as (a) a static gas-liquid contacting equipment like a plate column, packed column, or spray column and (b) dynamic gas-liquid contacting equipment which disperses gas and/or liquid by means of a rotating device, for the carbon dioxide absorber, and the containing solution regenerator. And it is preferably to apply counter-current gas-liquid contact to both the absorber and the regenerator in the use of said static gas-liquid contacting equipment. And there are many well-known absorbent solutions as described above which can be used in the present invention. Although only principal constituents are described above, these absorbent solutions generally show corrosion behaviour to steels to some extent, so that it is customary to add well-known additives to the absorbent solutions so as to prevent corrosion, and similarly deterioration inhibitors of absorbent are frequently added and used in the solutions; then these additives are preferably used as additives for the absorbent and containing solution of this invention. Among a number of these absorbent solutions, which can be used in this invention, aqueous potassium carbonate solution is particularly preferable, because it causes no evaporation loss of absorbent and is inexpensive as well as being usable as an aqueous solution of high concentration. There is no particular limitation in the present invention with regard to carbon dioxide containing gas which can be used as a supply source of carbon dioxide so long as it contains carbon dioxide of which the partial pressure is 0.005 atmosphere or more, so that the following gases can be used as additional examples in this invention besides the gases above mentioned, a natural gas which contains carbon dioxide before being burned as a fuel in a "reforming reaction"; a residual gas resulting, for instance, from direct reduction of iron ore or from synthesis reactions of many organic substances to which a gas containing hydrogen and carbon oxide is applied; a part or all of synthesis gas after being subjected to a "reforming reaction" in the case where a gas or gases before the "reforming reaction" are used as a "diluent gas" in this invention; a flue gas from a fuel which is burned independently of said "reforming reaction"; a gas which contains hydrogen and carbon dioxide produced by other process

(e.g. partial oxidation of hydrocarbons, coals, etc.): a residual gas resulted from applications for which the gas just mentioned is used for the same purposes as described above. Among a number of these carbon dioxide containing gases already described, a gas which contains carbon monoxide can be used as a diluent gas of this invention after enrichment of carbon dioxide in such a way that all or a part of this gas is subjected to the conversion reaction from carbon monoxide to carbon dioxide in the presence of steam and catalyst. It is also desired that the "diluent gas" and a carbon dioxide containing gas used in the present invention are made previously using a treatment of suitable desulfurization if needed before utilization. The present invention is available as a means of producing synthetic gas for the synthesis of methanol, higher alcohols, synthetic gasoline, and ammonia, for the direct reduction of iron ore, and for the production of other organic substances from natural gas or liquified petroleum gas as raw material, and as a means of producing synthesis gas for the production of the products above mentioned other than synthetic gasoline from naphtha as starting material.

EXAMPLE

An example of the present invention is described hereinafter.

This example is an example where the present invention is examined in a methanol synthesis plant using natural gas as a starting material according to the process example illustrated in the Figure. A flue gas of 279000 Nm³/H under a pressure of 0.05 Kg/cm²G (gauge) and a temperature of at 46°C, for which a part of natural gas is burned to heat a steam reformer, is introduced through the pipe 10 into a first carbon dioxide absorber 1. The flue gas contains the following constituents.

20	CO ₂	7.72 mol%	20
	N ₂	78.34 mol%	
	Ar	1.00 mol%	
	O ₂	3.44 mol%	
	H ₂ O	9.50 mol%	

The gas is contacted counter-currently in the first carbon dioxide absorber with a carbon dioxide absorbent solution introduced through the pipe 12 into the said absorber, and carbon dioxide in the gas is absorbed by the absorbent solution. The flue gas reduced in carbon dioxide content at the first carbon dioxide absorber is discharged through the pipe 11 into the air. The carbon dioxide absorbent solution introduced to the first carbon dioxide absorber is an aqueous solution of potassium carbonate and potassium hydrogen carbonate with the following composition and having a temperature of 50°C.

K ₂ CO ₃	2.350 gram mol/litter
KHCO ₃	1.032 gram mol/litter

The absorbent solution which has absorbed carbon dioxide in the first carbon dioxide absorber 1 is discharged through the pipe 13 from the absorber with the following composition and temperature of 56°C.

K ₂ CO ₃	1.490 gram mol/litter
KHCO ₃	2.751 gram mol/litter

The absorbent solution is then pressurized by the absorbent solution pump 8 and introduced to the second carbon dioxide absorber 2. A gas of 30790 Nm³/H under a pressure of 35 Kg/cm² G and at 179°C with the composition described below, for the production of which a residual gas from a methanol synthesis plant (not shown) is processed in a carbon monoxide conversion plant, is introduced through the pipe 15 into the second carbon dioxide absorber 2.

45	CO ₂	8.68 mol%	45
	CO	0.50 mol%	
	H ₂	54.09 mol%	
	CH ₄	21.81 mol%	
	H ₂	1.41 mol%	
	H ₂ O	13.51 mol%	

The absorbent solution having absorbed more carbon dioxide in contact counter-currently with the gas in the second carbon dioxide absorber 2 turns into a "containing solution" with the following composition and a temperature of 63°C and is discharged through the pipe 17.

	K_2CO_3	1.303 gram mol/litter	
5	$KHCO_3$	3.125 gram mol/litter	5

The absorbent solution introduced in the first and second carbon dioxide absorbers 1 and 2 is an absorbent solution which contains 30 wt% of potassium carbonate in a state under which carbon dioxide is completely released (potassium hydrogen carbonate is completely converted to potassium carbonate). The introducing rate of this solution to the absorber is 728000 Kg/H as a solution converted to the state described hereinabove. The absorbent solution absorbs 12937 Nm³/H of carbon dioxide as a sum of carbon dioxide absorbed in the first and second carbon dioxide absorbers 1 and 2. The "containing solution" is heated in the heat-exchanger 7, mixed with a required amount of condensed hot water which is formed in a synthesis gas cooler 5 and supplied through a pipe 20, heated further in the containing solution heater 6 to 213°C, and introduced through the pipe 21 to the containing solution regenerator 3. A raw natural gas for the steam reformer is introduced at the rate of 54850 Nm³/H through the pipe 22 into the containing solution regenerator 3 under 24.3 Kg/cm² G and at 213°C. The raw material gas has the following composition.

	CO_2	0.90 mol%	
	N_2	0.74 mol%	
20	CH_4	92.78 mol%	20
	C_2H_6	5.24 mol%	
	C_3H_8	0.33 mol%	
	C_4H_{10}	0.01 mol%	

And 68700 Kg/H of steam for the steam reformer is introduced through the pipe 23 into the containing solution regenerator 3. The "containing solution" supplied through the pipe 21 to the containing solution regenerator is contacted counter-currently with these raw materials of the steam reformer and regenerated, and a part of the water in the "containing solution" is simultaneously vaporized. The absorbent solution regenerated is taken out through the pipe 25 from the containing solution regenerator 3 at 175°C, cooled in the heat-exchanger 7, reduced in pressure, cooled further in the absorbent solution cooler 9, and recycled to the first carbon dioxide absorber 1 to be used. A gas of 212100 Nm³/H under the pressure of 23.8 Kg/cm² G and temperature of 213°C with the following composition is discharged through the pipe 24 from the containing solution regenerator 3.

	CO_2	6.33 mol%	
	N_2	0.21 mol%	
35	CH_4	24.00 mol%	35
	C_2H_6	1.36 mol%	
	C_3H_8	0.09 mol%	
	C_4H_{10}	28 ppm (mole basis)	
	H_2O	68.02 mol%	

This gas is introduced to the steam reformer 4 to be steam-reformed and cooled in the synthesis gas cooler 5 to turn into a synthesis gas with the following composition.

	CO_2	8.80 mol%
	CO	19.47 mol%
	H_2	68.17 mol%

CH ₄	3.27 mol%
N ₂	0.20 mol%
H ₂ O	0.08 mol%

The aforementioned value R of the synthesis gas is 2.1.

- 5 CLAIMS 5
1. A process for producing a synthesis gas having a high content of hydrogen and carbon oxides in which gaseous raw materials containing a large amount of hydrocarbons with steam added are subjected to a steam reforming reaction, wherein, for producing a synthesis gas enriched by carbon oxides, a carbon dioxide containing solution prepared by the contact of an aqueous carbon dioxide
- 10 absorbent solution with a carbon dioxide containing gas is allowed to contact at elevated temperature a 10 diluent gas selected from said gaseous raw materials, said steam, a mixture of said gaseous raw materials and said steam, each of which is flowing into said reforming reaction, and said synthesis gas which is flowing out of said reforming reaction to strip carbon dioxide out of said carbon dioxide
- 15 stripped is allowed again to contact said carbon dioxide containing gas to prepare said carbon dioxide 15 containing solution which is recycled to be used in the process.
2. A process as claimed in claim 1 wherein the partial pressure of carbon dioxide in said carbon dioxide containing gas which contacts said absorbent solution is 0.005 atmosphere in absolute
- 20 3. A process as claimed in claim 1 and substantially as hereinbefore described with reference to 20 the accompanying drawing.
4. A process as claimed in claim 1 and substantially as hereinbefore described with reference to the Example.