

Description

Title of Invention

METHOD FOR PRODUCTION OF METHANOL WITH HIGH EFFICIENCY, AND METHOD FOR PRODUCTION OF ACETIC ACID RAW MATERIAL OR MMA RAW MATERIAL UTILIZING THE SAME

Technical Field

[0001]

The present invention relates to a method and an apparatus for efficiently producing methanol from a lower hydrocarbon such as natural gas, and further relates to a method and an apparatus for efficiently producing an acetic acid raw material or an MMA raw material by utilizing the method and apparatus.

Background Art

[0002]

Methanol can be used as a raw material for basic chemicals such as acetic acid and MMA (methyl methacrylate), and can be used as a raw material for DME (dimethyl ether) that is gaining attention as a next generation fuel. In addition, methanol is considered to be used as an energy source for fuel cells. Accordingly, demand for methanol is expected to increase more and more in the future. In order to industrially produce methanol, a conventional method has been used in which syngas (also referred to as synthesis gas) mainly including hydrogen and carbon monoxide is formed from a lower hydrocarbon such as natural gas, and the obtained syngas is subject to reaction based on a vapor-phase synthesis process

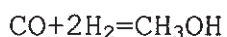
in the presence of a catalyst to obtain crude methanol (Patent Literature 1).

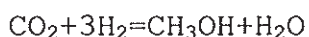
[0003]

When acetic acid is to be produced, the methanol obtained is subject to carbonylation with carbon monoxide in the presence of a rhodium catalyst, which allows efficient production of acetic acid (Non-Patent Literature 1). On the other hand, when MMA is to be produced, the methanol obtained is subject to reaction together with ethylene and carbon monoxide in the presence of a catalyst including Group VIII metal to produce methyl propionate, and then the methyl propionate is condensed with formaldehyde, which allows efficient production of MMA (Patent Literatures 2, 3, 4 and 5). The formaldehyde used for the condensation can be obtained by oxidative dehydrogenation reaction of methanol in the presence of a catalyst.

[0004]

Meanwhile, with respect to the production of methanol as a raw material for acetic acid and MMA, Patent Literature 1 describes a technique of methanol synthesis where steam reforming of a hydrocarbon gas containing steam added thereto is performed by heating the hydrocarbon gas to 800 to 1,000°C in the presence of a Ni-based catalyst to obtain syngas, and then the obtained syngas is subject to reaction under the conditions of 50 to 150 atm and 200 to 300°C in the presence of a Cu-based catalyst. It is known that the following two reaction formulas are involved in to synthesize methanol from the syngas.





[0005]

As is understood from the stoichiometric relationship between these two reaction formulas, the methanol synthesis enjoys the highest efficiency when the stoichiometric formula $[\text{H}_2] = 2[\text{CO}] + 3[\text{CO}_2]$ is established, where $[\text{X}]$ denotes molar concentration of compound X in syngas as a raw material for methanol. Further, defining an R value as shown in a formula below, the methanol synthesis enjoys the highest efficiency when $R=2$ is established, which is derived from the stoichiometric formulas.

$$([\text{H}_2] - [\text{CO}_2]) / ([\text{CO}] + [\text{CO}_2]) = R$$

[0006]

However, when steam reforming is performed in accordance with the method shown in Patent Literature 1, methanol cannot be synthesized efficiently because hydrogen is generated excessively as compared with carbon monoxide and thus R becomes larger than 2. Therefore, as shown in Non-Patent Literature 2, there is proposed a technique for achieving $R=2$ by feeding a predetermined amount of carbon dioxide from outside of the system to syngas obtained by steam reforming, or by adding steam and carbon dioxide to a lower hydrocarbon gas as a raw material so as to perform CO_2 reforming together with steam reforming.

Citation List

Patent Literatures

[0007]

Patent Literature 1: Japanese Patent Application Laid-Open

No. 01-180841

Patent Literature 2: United States Patent No. 6476255

Patent Literature 3: United States Patent No. 6478929

Patent Literature 4: United States Patent No. 6489506

Patent Literature 5: United States Patent No. 6544924

Non-Patent Literatures

[0008]

Non-Patent Literature 1: "Industrial Organic Chemistry - Major Raw Materials and Intermediates - (4th edition)", Tokyo Kagaku Dojin, p.194-195

Non-Patent Literature 2: H. Holm-Larsen, "CO₂ reforming for large scale methanol plants-an actual case", Studies in Surface Science and Catalysis, 2001, p.441-446

Summary of Invention

Technical Problem

[0009]

However, adjustment of R to be R=2 in accordance with the above-mentioned method needs to adjust a steam/carbon ratio (a value obtained by dividing the molar number of H₂O molecules by the molar number of carbon atoms included in hydrocarbon gas, which is also referred to as an S/C ratio) as high as approximately 2.5 by excessively adding steam to the raw material gas so as to suppress deposition of carbon. As a result, there may be a case where heat duty of a reformer is increased which leads to a high production cost.

[0010]

In view of such circumstances, it is an object of the present invention to provide a method and an apparatus for efficiently producing methanol from a lower hydrocarbon such as natural gas.

Solution to Problem

[0011]

In order to achieve the above object, the method for production of methanol according to the present invention includes a reforming step for reforming a lower hydrocarbon gas containing steam and carbon dioxide added thereto in the presence of a catalyst to generate syngas mainly including hydrogen and carbon monoxide, a methanol synthesis step for synthesizing methanol by reaction of the syngas obtained in the reforming step in the presence of a catalyst, a recycling step by separating the methanol synthesized in the methanol synthesis step from a residual gas containing unreacted gas and merging the residual gas as a recycle gas with the syngas, and a hydrogen separating step by separating hydrogen gas from at least a part of the recycle gas and merging the hydrogen gas with the syngas.

Advantageous Effects of Invention

[0012]

According to the present invention, it becomes possible to efficiently produce methanol from a lower hydrocarbon such as natural gas, and it also becomes possible to efficiently produce an acetic acid raw material and an MMA raw material from the obtained methanol.

Brief Description of Drawings

[0013]

FIG. 1 is a schematic flow diagram showing a specific example of the methanol production apparatus according to the present invention.

FIG. 2 is a graph showing the relationship between the S/C ratio of the raw material gas and the feed rate of the raw material gas when a predetermined amount of syngas is generated by reforming natural gas.

FIG. 3 is a graph showing the relationship between the S/C ratio of the raw material gas and the carbon activity at the reaction outlet when syngas is generated by reforming natural gas.

FIG. 4 is a schematic flow diagram showing a conventional apparatus for the production of methanol.

FIG. 5 is a schematic flow diagram showing a plant for the production of an MMA raw material including the methanol production apparatus of a specific example of the present invention.

FIG. 6 is a schematic flow diagram showing a conventional plant for the production of an MMA raw material.

FIG. 7 is a schematic flow diagram showing a plant for the production of an acetic acid raw material including the methanol production apparatus of a specific example of the present invention.

FIG. 8 is a schematic flow diagram showing a conventional plant for the production of an acetic acid raw material.

FIG. 9 is a schematic flow diagram showing a methanol plant including a conventional steam reformer.

Description of Embodiments

[0014]

First, a specific example of the methanol production apparatus according to the present invention will be described with reference to the schematic flow diagram of FIG. 1. This methanol production apparatus includes a reformer 1 for reforming a lower hydrocarbon gas containing steam and carbon dioxide added thereto in the presence of a catalyst to generate syngas mainly including hydrogen and carbon monoxide, a methanol reactor 3 for synthesizing methanol in the presence of a catalyst by reaction of the syngas obtained in the reformer 1, a recycle unit 4 for separating methanol synthesized in the methanol reactor 3 from a residual gas containing unreacted gas, and for merging the residual gas as a recycle gas with the syngas, and a hydrogen separation unit 6 for separating a hydrogen gas from at least a part of the recycle gas, and for merging the hydrogen gas with the syngas.

[0015]

More specifically, a feed line L1 for a lower hydrocarbon gas used as a raw material is connected to an inlet of the reformer 1. The lower hydrocarbon gas feed line L1 is provided with a branched line L4 for extracting part of the lower hydrocarbon gas that is used as a fuel for a heating furnace 2 mentioned below.

[0016]

The lower hydrocarbon gas used as a raw material may contain sulfur compounds such as mercaptan that acts as catalyst poisons for a reforming catalyst mentioned below. In order to remove the sulfur compounds, it is preferable to provide a sulfur removing means (not shown) on the upstream side of the reformer 1. The sulfur removing means may include, for example, a Co-Mo-based catalyst or a Ni-Mo-based catalyst that hydrocracks the sulfur compounds, and an adsorbent of zinc oxide for removing the obtained hydrogen sulfide by adsorption.

[0017]

The lower hydrocarbon gas feed line L1 is merged with a CO₂ feed line L2 for feeding carbon dioxide for CO₂ reforming and a steam feed line L3 for feeding steam for steam reforming. It is preferable to provide a flow rate controlling means (not shown) such as a flowmeter and a valve on each of the CO₂ and the steam feed lines L2 and L3 so as to be able to individually control the flow rates of the carbon dioxide and the steam.

[0018]

The reformer 1 includes, for example, a tubular-type reactor which is filled with a reforming catalyst. The reactor is set in a heating furnace 2 so that the central axis of the reactor is directed vertically. The inside of the reformer 1 is heated by radiation heat which is generated by fuel combustion using a burner of the heating furnace 2.

[0019]

For the fuel for the burner, several fluids can be used in addition to natural gas supplied via the branched line L4 mentioned

above, that is, a fluid ejected via a column top line L10 from a methanol separator 5 mentioned below, a fluid ejected via a purge line L11 for purging the recycle loop of the methanol synthesis step, and a fluid ejected via a line L12 from a hydrogen separation unit 6. Flue gas generated after combustion of these fuels is discharged from the heating furnace 2 via a flue gas line L5.

[0020]

For a reforming catalyst used in this reformer 1, it is preferable to use a CO₂ reforming catalyst including ruthenium (Ru) and/or rhodium (Rh) loaded on magnesia (MgO) as a carrier. The amount of the ruthenium (Ru) and/or rhodium (Rh) to be loaded is preferably 200 wtppm or more but 2,000 wtppm or less, more preferably 200 wtppm or more but 700 wtppm or less based on the magnesia support. This is because the deposition of carbon becomes less likely to occur on the catalyst when the specified amount of Ru and/or Rh are/is loaded on the MgO carrier. Accordingly, reforming reaction can be performed under more efficient conditions beyond the limitation that is imposed when a conventional Ni-based catalyst is used (in general, an operation is carried out at an S/C ratio of 2.0 or more so as to avoid carbon deposition).

[0021]

Furthermore, it is preferable to fill the reformer 1 with the reforming catalyst so that GHSV (gas hourly space velocity) becomes 2,000 hr⁻¹ or more but 10,000 hr⁻¹ or less. This is because the number of catalyst tubes required becomes too much when this value is less than 2,000 hr⁻¹, and the amount of methane remaining

in the syngas increases significantly when the value exceeds 10,000 hr⁻¹.

[0022]

A commercially available metal oxide may be used for the magnesia support, or a magnesia obtained by calcining a commercially available metal hydroxide may be used. In either case, the purity of the magnesia is preferably 98% by mass or more, more preferably 99% by mass or more. Specifically, it is desirable that the support be free from impurities such as iron, nickel and silicon dioxide (SiO₂) since these impurities increase the deposition activity of carbon and are decomposed at a high temperature under a reduced gas atmosphere. When these impurities are nevertheless included, their overall content of 1% by mass or less is preferable, and 0.1% by mass or less is more preferable.

[0023]

Furthermore, it is preferable that the magnesia support has a specific surface area of 0.1 m²/g or less. In general, a support having a broader specific surface area is more preferable from a kinetic viewpoint since reaction sites increase as the specific surface area increases, whereas the CO₂ reforming catalyst used in the present invention does not require a broad specific surface area since it has a quite high activity against a reforming reaction, and it is rather not preferable to broaden the specific surface area since a deposition reaction of carbon is more promoted if the area is broadened. Therefore, the specific surface area of the support is preferably set to 0.1 m²/g or less. Although the lower limit of the specific surface area of the support is not

specifically defined, it is considered that the specific surface area becomes the minimum when the support is supposed to be a complete sphere with no pore. The specific surface area of the support as used herein is measured based on a BET method at a temperature of 15°C.

[0024]

The catalyst can be prepared by calcining the magnesia support at 1,000°C or more but 1,500°C or less and loading Ru and/or Rh by, for example, an impregnation process. The impregnation process refers to a process including dispersing a support in water, and adding a metal salt of Ru or Rh or an aqueous solution thereof thereto for mixing so as to impregnate the support with a catalyst metal. It is preferable to use a water-soluble salt for the metal salt. For example, it is preferable to use an inorganic acid salt such as nitrate and chloride, or an organic acid salt such as acetate and oxalate. Alternatively, it is possible to dissolve an acetylacetonato salt or the like of Ru or Rh instead of the water-soluble salt in an organic solvent such as acetone and impregnate the support with the solution.

[0025]

After the support is impregnated by the above method, the support is separated from the aqueous solution, and dried at a temperature of 100 to 200°C, preferably 100 to 150°C, in the case of the water-soluble salt. On the other hand, when the impregnation is conducted by using an organic solvent, drying is conducted at a temperature 50 to 100°C higher than the boiling point of the solvent. After the drying, calcination is conducted.

The temperature and the time for the calcination are suitably selected depending on the desired specific surface area of the support, but the calcination is generally conducted at a temperature of 300 to 1,300°C for 1 to 5 hours.

[0026]

As for the process for loading Ru and/or Rh, instead of the impregnation process, an incipient-wetness process may be used where a support is degassed, and a metal salt solution of a volume corresponding to the volume of pores of the support is added in small quantities to uniformly wet the surface of the support, and then the support is dried and calcined. Alternatively, a Spray process may be used where the support is sprayed with a metal salt solution in the form of mist and then the support is dried and calcined. The shape of the reforming catalyst is not specifically limited, and various forms can be used such as a powder form, a granular form, a spherical form, a columnar form and a cylindrical form. Generally, suitable form is selected depending on the type of a catalyst bed to be filled.

[0027]

The methanol reactor 3 is located downstream of the reformer 1. A conventional reactor used in the methanol synthesis may be used for this methanol reactor 3. For example, a reactor of a shell-and-tube heat exchanger type having tubes filled with a copper-based catalyst can be used. The reaction conditions in the tube side are also not specifically limited, and reaction for the synthesis of methanol can be performed under the conditions of about 5 to 15 MPaG and about 200 to 300°C that are usual conditions

for the methanol synthesis. In this case, the reaction heat of the methanol synthesis reaction can be recovered as steam by feeding boiler water to the shell side.

[0028]

It is to be noted that the reaction is carried out at a lower temperature and a higher pressure in the methanol synthesis step as compared to those in the upstream reforming step, and therefore a cooling means (not shown) for cooling the syngas to a predetermined temperature and a compressor (not shown) for pressurizing the syngas to a predetermined pressure are provided between the reformer 1 and the methanol reactor 3. A line connecting the reformer 1 outlet and running toward the methanol reactor 3 merges with a hydrogen gas line L6 from a hydrogen separation unit 6 mentioned below to form a line L7. Namely, the line L7 is provided for a mixed gas that is a mixture of the syngas discharged from the reformer 1 and a high-purity hydrogen gas separated in the hydrogen separation unit 6.

[0029]

The line connecting the reformer 1 outlet and running toward the methanol reactor 3 further merges with a line for the recycle gas in the methanol synthesis step to form a line L8. Namely, the line L8 is provided for a mixed gas that is a mixture of the gas flowing through the line L7 and the recycle gas. The gas flowing through the line L8 is then fed to the methanol reactor 3.

[0030]

The recycle unit 4 is located downstream of the methanol

reactor 3. The recycle unit 4 includes a cooler for cooling the reaction gas discharged from the methanol reactor 3, and a vapor-liquid separation vessel for separating the crude methanol, which is condensed by the cooling in the cooler, from a residual gas containing unreacted gas. The residual gas containing unreacted gas is fed to the upstream side of the methanol reactor 3 as a recycle gas while the pressure thereof being kept at a high pressure, and merges with the gas flowing through the line L7.

[0031]

A methanol separator 5, located downstream of the recycle unit 4, purifies the crude methanol that has been ejected from the above-mentioned vapor-liquid separation vessel and produces high purity methanol. For the purification of the crude methanol, a distillation column, for example, can be used which includes a reboiler and a condenser, and methanol with a high purity can be obtained from the bottom of the column or the middle stage of the column by distilling the crude methanol in the column. Furthermore, the fluid that has been ejected from the top of the column through a column top line L10 is subjected to a combustion treatment by the burner of the heating furnace 2 together with the gas that flows through the branched line L4.

[0032]

Meanwhile, the residual gas containing unreacted gas contains a lower hydrocarbon component mainly including methane. Since this lower hydrocarbon component is inactive for the methanol synthesis reaction, it gradually accumulates in the recycle loop. In order to suppress this built-up concentration

of the lower hydrocarbon component to a certain level or less, the recycle loop is provided with a purge line L11 for extracting a part of the recycle gas. The gas that has been extracted via the purge line L11 is subjected to a combustion treatment by the burner of the heating furnace 2 together with the above-mentioned gas that flows through the branched line L4 and the fluid that is ejected via the column top line L10.

[0033]

The methanol production apparatus of FIG. 1 is provided with a collection line for collecting at least a part of the gas that is extracted via this purge line L11. Furthermore, this collection line is connected to the hydrogen separation unit 6. In the hydrogen separation unit 6, the gas that has been collected from the recycle loop via the purge line L11 and collection line is subjected to a fractionation operation to separate high-purity hydrogen gas. As mentioned above, the high-purity hydrogen gas flows through the hydrogen gas line L6 and merges with the syngas that is ejected from the reformer 1. The above-mentioned collection line may be branched directly from the recycle loop without using the purge line L11.

[0034]

For the hydrogen separation unit 6, for example, a PSA (Pressure Swing Adsorption) unit or a hydrogen separation membrane can be used. The PSA unit includes a plurality of packed columns filled with an adsorbent, which is configured to repeatedly pressurize and depressurize each of the packed columns by switching the packed column receiving a feed gas at certain time

intervals, which allows adsorption and desorption of a specific gas component. With this arrangement, high-purity hydrogen gas can be obtained. On the other hand, the hydrogen separation membrane produces high-purity hydrogen gas by selectively transporting only hydrogen molecules through a membrane formed by palladium or a polymer based on the principle of a molecular sieve.

[0035]

As described above, the methanol synthesis reaction can be performed under the condition of $R=2$ that is the most efficient condition for methanol synthesis, by extracting a part of the gas of the recycle loop and merging the hydrogen gas separated from the extracted gas with the syngas. It is to be noted that provision of a flow rate controlling means (not shown) that includes a flowmeter, a valve and the like on the hydrogen gas line L6 is preferable, which enables easy control of the R value of the gas that flows through the line L7 after the hydrogen gas is merged. The gas flowing through the line L12 that remains after separation of the high-purity hydrogen gas is subjected to a combustion treatment by the burner in the heating furnace 2 together with the gas through the branched line L4, the fluid through the column top line L10 and the gas through the purge line L11 mentioned above.

[0036]

Next, a specific example of the method for the production of methanol of the present invention will be described with reference to the methanol production apparatus of FIG. 1 described above. The method for the production of methanol of a specific

example of the present invention includes a reforming step for reforming a lower hydrocarbon gas containing steam and carbon dioxide added thereto in the presence of a catalyst to generate syngas mainly including hydrogen and carbon monoxide, a methanol synthesis step for synthesizing methanol by reaction of the syngas obtained in the reforming step in the presence of a catalyst, a recycling step for separating methanol synthesized in the methanol synthesis step from a residual gas containing unreacted gas, and merging the residual gas as a recycle gas with the syngas, and a hydrogen separating step for separating hydrogen gas from at least a part of the recycle gas and for merging the hydrogen gas with the syngas.

[0037]

To be described more specifically, at first, a part of the gas for the fuel to be sent to the heating furnace 2 is extracted from a lower hydrocarbon gas feedstock that has been sent from the outside of the system via the lower hydrocarbon gas feed line L1. Thereafter, carbon dioxide for CO₂ reforming and steam for steam reforming are added to the lower hydrocarbon gas feedstock to form a raw material gas.

[0038]

It is preferable that the addition amount of the carbon dioxide is controlled so that the CO₂/carbon ratio in this raw material gas becomes 0.1 or more but 0.6 or less. As used herein, the CO₂/carbon ratio is a value obtained by dividing the molar number of the CO₂ molecules in the raw material gas by the molar number of the carbon atoms included in the hydrocarbon gas in the

raw material gas. By setting the CO_2 /carbon ratio to 0.1 or more, CO_2 can be utilized efficiently as a raw material for methanol. On the other hand, by setting the ratio to 0.6 or less, the duty of the reformer 1 can be prevented from being excessive.

[0039]

On the other hand, the addition amount of the steam is controlled so that the steam/carbon ratio (S/C ratio) in the above-mentioned raw material gas becomes preferably 0.7 or more but 1.7 or less, more preferably 0.8 or more but 1.5 or less. The reason is that, as is understood from the graph in FIG. 2 showing the relationship between the S/C ratio of the raw material gas and the feed rate of the raw material gas when a predetermined amount of syngas is generated by reforming natural gas, the increase in the required amount of the raw material gas can be suppressed to about 10 percent of the optimum value by setting the upper limit of the S/C ratio to 1.7 or less, and thus the duty of the reformer 1 can be prevented from being excessive.

[0040]

With respect to the lower limit of the S/C ratio, as is understood from the graph in FIG. 3 showing the relationship between the S/C ratio of the raw material gas and the carbon activity at the reaction outlet when syngas is generated by reforming reaction of natural gas, the carbon activity can be suppressed to be not more than 1.0 that is the threshold value at which carbon deposit, by setting the steam/carbon ratio to 0.7 or more. Namely, carbon deposition at the outlet of the reactor can be prevented by adjusting the steam/carbon ratio to 0.7 or

more. The carbon activity will be described later in more detail.

[0041]

The raw material gas including the lower hydrocarbon gas, carbon dioxide and steam is fed into the tube of the reformer 1, where the tube is filled with a reforming catalyst. The reformer 1 is heated from outside by the radiation heat in the heating furnace 2. With this arrangement, the raw material gas fed to the reformer 1 is heated to a predetermined temperature and catalyzed by the reforming catalyst while the raw material gas flows through the tube of the reformer 1, and thus the raw material gas is reformed into syngas mainly including hydrogen and carbon monoxide.

[0042]

It is preferable to control the inside of the tube of the reformer 1 so that the reaction temperature at the outlet becomes 850°C or more but 950°C or less, and the reaction pressure becomes 1.0 MPaG or more but 3.0 MPaG or less. By controlling the reaction conditions to be within these ranges and controlling the composition of the raw material gas to be within the above-mentioned ranges of the steam/carbon ratio and CO₂/carbon ratio, the raw material gas can be reformed efficiently without having carbon deposition.

[0043]

Furthermore, it is preferable that the syngas at the outlet of the reformer 1 have a carbon activity of 0.36 or more but 1.0 or less. This is because when the carbon activity is less than 0.36, the S/C ratio becomes larger than 1.7 as is apparent from

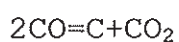
FIG. 3, and thus the duty of the reformer 1 becomes excessive. On the other hand, the higher the carbon activity is, the better the energy efficiency in the reformer 1 is; however, when the carbon activity exceeds 1.0, carbon is likely to deposit at the outlet of the reactor. The carbon activity as used herein refers to an index showing likelihood of carbon generation, and when the carbon activity is 1.0 or less, carbon generation does not occur thermodynamically, whereas when the carbon activity exceeds 1.0, the potential for carbon generation increases.

[0044]

The carbon activity can be obtained from a ratio of the partial pressures of product gases at certain temperature and pressure and the equilibrium constant of a carbon generation reaction. For example, with respect to a carbon deposition reaction (Boundouard reaction) from carbon monoxide represented by the following formula 1, a carbon activity (A_c) can be obtained by the following formula 2 using the ratio of the partial pressures of carbon dioxide and carbon monoxide and the equilibrium constant of this reaction. In the following formula 2, K is the equilibrium constant of the Boundouard reaction, and P_{CO} and P_{CO_2} are the partial pressures of CO and CO₂ under operating conditions, respectively.

[0045]

[Formula 1]



[Formula 2]

$$A_c = K \cdot (P_{CO})^2 / P_{CO_2}$$

[0046]

As described above, the carbon activity (A_c) can be obtained by calculation of the balance of the products if the composition of the raw material gas to the reformer 1 and reaction conditions (temperature and pressure) are determined. Therefore, it becomes possible to control the carbon activity A_c at the outlet of the reformer 1 to a desired value by suitably adjusting these parameters. The relationship between the equilibrium constant and temperature in the above-mentioned formula 2 can be obtained with reference to, for example, D. R. Stull et. al., The Chemical Thermodynamics of Organic Compounds, John Wiley (1969).

[0047]

The syngas that has come out from the reformer 1 is cooled to a predetermined temperature by a cooling means (not shown), and then the syngas is pressurized to a predetermined pressure by a compressor (not shown). The high-purity hydrogen gas that has been separated by the hydrogen separation unit 6 is merged with the syngas. In this merging of the hydrogen gas, the flow rate of the hydrogen gas is adjusted so that the R value of the gas that flows through the line L7 after the merging becomes preferably within the range from 1.8 to 2.2, more preferably 2.0. By doing so, it becomes possible to conduct methanol synthesis with a high efficiency. Furthermore, the recycle gas in the methanol synthesis step is merged with the gas that flows through the line L7. The gas that flows through the line L8 after the merging is then fed to the methanol reactor 3.

[0048]

The gas that has come out from the methanol reactor 3 is then fed to the recycle unit 4, and cooled therein by a cooler such as a heat exchanger. Thereafter the liquid fraction that has generated by the condensation by the cooling is separated from the residual gas containing unreacted gas. The liquid fraction obtained here is crude methanol including methanol and water, and the crude methanol is fed to the subsequent methanol separator 5 and purified therein by, for example, a distillation column. By doing so, high purity methanol can be obtained.

[0049]

On the other hand, the residual gas containing unreacted gas is fed as recycle gas to the upstream side of the methanol reactor 3 for recycle, and is merged with the syngas that has been generated in the reformer 1 as mentioned above.

[0050]

In order to prevent gradual accumulation of components that are inert for methanol synthesis such as methane in the recycle loop, a part of the recycle gas is extracted out of the system and subjected to a combustion treatment by the burner of the heating furnace 2. In the present invention, at least a part of this extracted gas is fed to the hydrogen separation unit 6, and high-purity hydrogen gas is separated in the hydrogen separation unit 6. The obtained high-purity hydrogen gas is then merged with the syngas generated in the reformer 1.

[0051]

By doing so, it becomes possible to control the R value of the gas that flows through the line L7 to a desired value. Namely,

it becomes possible to adjust the R value of the gas that flows through the line L7 to about $R=2$, which is the most efficient for methanol synthesis as mentioned above, by suitably adjusting the flow rate of the high-purity hydrogen gas that is introduced via the line L6. In addition, since the R value of the product gas at the outlet of the reformer 1 before addition of the high-purity hydrogen gas can be set to be lower than 2, the steam/carbon ratio of the raw material gas of the reformer 1 can be decreased. As a result, it becomes possible to decrease the heat duty of the reformer 1.

[0052]

The lower the steam/carbon ratio of the raw material gas of the reformer 1 is, the lower the heat duty of the reformer 1 can be. Therefore, a lower steam/carbon ratio is preferable from the viewpoint of reduction of energy consumption. However, decrease of the steam/carbon ratio increases the carbon activity A_c thereby increasing the likelihood of carbon deposition. In such case, carbon deposition can be suppressed by using a CO_2 reforming catalyst including a MgO support and a predetermined amount of Ru and/or Rh loaded thereon mentioned above.

[0053]

Next, a production plant of an acetic acid raw material or an MMA raw material including the methanol production apparatus of a specific example of the present invention will be described. The production plant of an acetic acid raw material or an MMA raw material includes a reforming means for reforming lower hydrocarbon gas that is introduced together with carbon dioxide

and steam in the presence of a CO₂ reforming catalyst, a carbon monoxide separation means for extracting a part of the syngas obtained in the reforming means and separate carbon monoxide from the part of the syngas, and a methanol generating means for treating the residual syngas after extraction of the part of the syngas and generating methanol. Since the production plant of an acetic acid raw material and the production plant of an MMA raw material are constituted by the same elements in essence, the respective means mentioned above will be described specifically in the following with reference to the production plant of an MMA raw material shown in FIG. 5.

[0054]

In the production plant shown in FIG. 5, reformer 101 is used as a reforming means. The reformer 101 is approximately the same as the reformer 1 shown in FIG. 1 and has a structure in which a catalyst tube filled with a CO₂ reforming catalyst is disposed in a heating furnace 102, and lower hydrocarbon gas such as natural gas is introduced into the catalyst tube via raw material feed line L101. A CO₂ feed line L102 and a steam feed line L103 which respectively feed carbon dioxide and steam are connected to the raw material feed line L101.

[0055]

For the fuel of the burner of the heating furnace 102, the lower hydrocarbon gas is used, which is fed via a branched line L104 that is branched at the upstream side of the above-mentioned raw material feed line L101. Further, various gases that are ejected from a carbon monoxide separation means and a methanol

generation means are used. The flue gases after combustion of these various fuels are discharged to an outside via a flue gas line L105.

[0056]

A part of the syngas that has been generated in the reformer 101 is extracted and fed to the carbon monoxide separation means via a line L121, and the residue is fed to the methanol generation means via a line L106. First, the carbon monoxide separation means will be described. The carbon monoxide separation means includes CO₂ removal unit 103 for removing carbon dioxide from the above-mentioned extracted part of the syngas, and cryogenic separation unit 104 for treating the gas that has been CO₂-removed in the CO₂ removal unit 103 to separate the gas into carbon monoxide gas and other gases.

[0057]

The CO₂ removal unit 103 may use, for example, a chemical absorption process using an absorbent such as an alkanolamine solution and an alkali solution. This process allows absorption of the carbon dioxide included in the syngas by means of countercurrent-contacting of the syngas with an absorbent in an absorption column. The CO₂ removed gas is discharged from the top of the absorption column, and fed to the subsequent cryogenic separation unit 104. On the other hand, the absorbent that has absorbed the carbon dioxide is discharged from the bottom of the absorption column, fed to a regeneration column, and regenerated therein by heating. The carbon dioxide stripped from the absorbent during the regeneration is discharged from the top of

the regeneration column, and returned as a recycle gas to the upstream side of the reformer 101 via a line L122.

[0058]

In the cryogenic separation unit 104, the CO₂ removed gas is liquefied by cooling, and then it is separated into hydrogen, lower hydrocarbon and carbon monoxide by rectification. A part of the separated hydrogen is returned to the upstream side of the methanol generation means via a line L123. The separated hydrogen is further fed as a purge gas to a sulfur removing means (not shown) that is disposed upstream of the reformer 101 via a line L124. Furthermore, the separated lower hydrocarbon is fed to the burner of the above-mentioned heating furnace 102 via a line L125. On the other hand, the carbon monoxide is fed to subsequent MMA production unit 109 via a line L126 and used therein as a raw material for MMA.

[0059]

Next, the methanol generation unit will be described. The methanol generation unit is constituted by a methanol reactor 105 for synthesizing methanol by reaction of the syngas obtained in the reformer 101 in the presence of a catalyst, a recycle unit 106 for separating the methanol synthesized in the methanol reactor 105 as a crude methanol from a residual gas containing unreacted gas, and for merging the residual gas as a recycle gas with the syngas, and a hydrogen separation unit 108 for separating hydrogen gas from at least a part of the recycle gas and for merging the hydrogen gas with the syngas.

[0060]

A methanol separator 107 for producing high purity methanol by purifying the crude methanol obtained by the recycle unit 106 is located downstream of the recycle unit 106. Since those constitutional elements are approximately the same as the methanol reactor 3, recycle unit 4, hydrogen separation unit 6 and methanol separator 5 shown in FIG. 1, respectively, the detailed descriptions thereof are omitted.

[0061]

A connection line L106 that comes out from the reformer 101 and runs toward the methanol reactor 105 further merges with the a line of hydrogen gas that has been separated in the above-mentioned cryogenic separation unit 104 and a line of the high-purity hydrogen gas that has been separated in the hydrogen separation unit 108 to form line L107. Namely, the line L106 for the residual syngas that remains after a part is extracted for the carbon monoxide separation means merges with a line L112 and a line L123 to form the line L107.

[0062]

The line L107 further merges with a line for the recycle gas in the methanol synthesis step to form a line L108. Namely, the residual gas containing unreacted gas that remains after separation of the crude methanol in the recycle unit 106 is fed to the upstream side of the methanol reactor 105 for recycle while the pressure thereof being kept at a high pressure, and merges with the gas that flows through the line L107. The gas flowing through the line L108 after the merging is then fed to the methanol reactor 105. It is to be noted that a purge line L111 for

extracting a part of the recycle gas is disposed on the recycle line. The gas that has been extracted via the purge line L111 is subjected to a combustion treatment by the above-mentioned burner of the heating furnace 102 together with a fluid that is ejected from methanol separator 107 via the line L110 and the gas in the branched line 104.

[0063]

Furthermore, a collection line for collecting at least a part of the gas extracted from the recycle line is disposed on the purge line 111. This collection line is connected to the hydrogen separation unit 108. In the hydrogen separation unit 108, the gas that has been collected is subjected to a fractionation operation to separate high-purity hydrogen gas. The high-purity hydrogen gas that has been separated merges with the above-mentioned line L106 via a line 112. On the other hand, the gas that remains after separation of the high-purity hydrogen gas is fed to the above-mentioned burner of the heating furnace 102 via a line L113 and subjected to a combustion treatment therein.

[0064]

By the above-mentioned processes, an MMA raw material can be produced while producing methanol as a product. Namely, a part of the product methanol obtained in the methanol separator 107 is extracted via the line L120, and this methanol is fed to the MMA production unit 109 as an MMA raw material, together with the carbon monoxide that is fed from the carbon monoxide separation means via a line L126 and ethylene that is fed from the outside of the system via a line L127. By doing so, it becomes possible

to extract the product MMA from a line L128 while extracting the product methanol from a line L109.

[0065]

Next, the method for the production of the MMA raw material will be described, which is conducted by using the production plant of FIG. 5 described above. This method includes a reforming step by introducing lower hydrocarbon gas together with carbon dioxide and steam into a reformer filled with a CO₂ reforming catalyst, a carbon monoxide separation step by extracting a part of the syngas obtained in the reforming step and separating carbon monoxide from the part of the syngas, and a methanol generating step by treating the residual syngas after the extraction of the part of the syngas to generate methanol.

[0066]

To be described more specifically, at first, a part of the gas for the fuel of the heating furnace 102 is extracted from the lower hydrocarbon gas that has been fed from the outside of the system, thereafter the carbon dioxide from the CO₂ removal unit 103 and the carbon dioxide from the outside of the system are added to the lower hydrocarbon gas for CO₂ reforming, and steam for steam reforming is further added thereto. This mixed gas is introduced as raw material gas into the reformer 101. It is to be noted that the lower hydrocarbon gas may be subjected to a treatment for removing sulfur components as necessary, and in this case, the hydrogen gas from the cryogenic separation unit 104 may be added as a purge gas.

[0067]

As already described in the production method of the apparatus shown in FIG. 1, the amount of the carbon dioxide that is added from the outside of the system is preferably controlled so that the CO_2 /carbon ratio in the raw material gas introduced to the reformer 101 is within the range of from 0.1 to 0.6, and is more preferably controlled so that the ratio is within the range of from 0.3 to 0.5. Furthermore, the amount of the steam that is added from the outside of the system is preferably controlled so that the steam/carbon ratio in the raw material gas introduced to the reformer 101 is within the range of from 0.7 to 1.7, and is more preferably controlled so that the ratio is within the range of from 1.0 to 1.4.

[0068]

In addition, as mentioned above, it is preferable to control the inside of the catalyst tube of the reformer 101 so that the reaction temperature at the outlet is within the range of from 800°C to 950°C and the reaction pressure is within the range of from 1.0 MPaG to 3.0 MPaG. Furthermore, it is preferable that the syngas at the outlet of the reformer 101 has a carbon activity of from 0.36 to 1.0. By controlling the reaction conditions to be within these ranges and controlling the composition of the raw material gas to keep the steam/carbon ratio and CO_2 /carbon ratio within the above-mentioned ranges, the raw material gas can be reformed efficiently without causing carbon deposition.

[0069]

A part of the syngas that has come out from the reformer 101 is extracted and fed to the carbon monoxide separation means,

and the residual syngas is fed to the methanol synthesis means. In the carbon monoxide separation means, as mentioned above, carbon monoxide as an MMA raw material is generated by the CO₂ removal unit 103 and cryogenic separation unit 104. On the other hand, in the methanol synthesis means, the residual syngas is cooled and pressurized, and thereafter the syngas is merged with the hydrogen gas from the cryogenic separation unit 104 and the high-purity hydrogen gas that has been separated in the hydrogen separation unit 108.

[0070]

The gas after the merging is further merged into recycle gas mentioned below, and the resulted gas is fed to the methanol reactor 105. Since the following method is similar to the method that has been already described in the production method of the apparatus shown in FIG. 1, the description thereof is omitted. The gas that flows through the line L107 in which the above-mentioned R value is adjusted is obtained by merging the residual syngas after extracting the part of the syngas with the hydrogen gas from the cryogenic separation unit 104 and the high-purity hydrogen gas from the hydrogen separation unit 108.

[0071]

As described above, by controlling the R value of the raw material gas in the methanol generation step to be within a desired range by using the high-purity hydrogen gas that is introduced from the hydrogen separation unit 108, the R value of the generated gas at the outlet of the reformer 101 before adding hydrogen gas can be decreased to lower than 2 while keeping the raw material

gas to the methanol generation step at an optimal stoichiometric ratio for methanol synthesis. By doing so, it becomes possible to produce an acetic acid raw material and an MMA raw material efficiently. Furthermore, since the steam/carbon ratio of the raw material gas to the reformer 101 can be decreased, the heat duty of the reformer 101 can also be decreased.

Examples

[0072]

Example 1

In line with the block flow diagram in FIG. 1, a process calculation was conducted supposing the case where methanol is produced from natural gas. As the operating conditions of reformer 1, an outlet temperature was 875°C, an outlet pressure was 2.0 MPaG, a steam/carbon ratio of the raw material gas at the inlet was 1.5, and a CO₂/carbon ratio thereof was 0.25.

Furthermore, the Heat Duty of the reformer 1 was 288 Gcal/h, and the flow rate of the fluid flowing through the line L8 was 2,500,000 Nm³/h. Furthermore, 25,000 Nm³/h of hydrogen gas was separated from a part of the gas that was extracted from a recycle loop for purging and added to syngas so that the R value of the fluid flowing through the line L7 became 2.0. The result of this process calculation is shown in the following Table 1.

[0073]

[Table 1]

Line number	1	2	3	4	5	6	7	8	9	10	11	12
Fluid name	Natural gas	CO ₂	Steam	Natural gas	Flue gas	H ₂ gas	Syngas	Syngas	MeOH	MeOH removed	Purge	H ₂ Removed gas
Flow rate (Nm ³ /h)	116,000	26,000	-	5,400	640,000	25,000	450,000	2,500,000	-	6,000	35,000	39,000
Flow rate (ton/h)	-	-	160	-	-	-	-	-	152	-	-	-
Composition (mol%)												
H ₂	-	-	-	-		100	63	49	-			
CO	-	-	-	-		-	21	9	-			
CO ₂	-	100	-	-		-	7	8	-			
N ₂	0.1	-	-	0.1		-	-	-	-			
CH ₄	91.5	-	-	91.5		-	9	33	-			
C2	4.2	-	-	4.2		-	-	-	-			
C3	2.5	-	-	2.5		-	-	-	-			
C4	1.3	-	-	1.3		-	-	-	-			
C5	0.4	-	-	0.4		-	-	-	-			
C6	0.1	-	-	0.1		-	-	-	-			
MeOH/H ₂ O	-	-	-/100	-		-	-	-	100/0			

[0074]

As is understood from the result of the Table 1, since the R value of the outlet gas of the reformer 1 can be suppressed to be a value lower than 2 while keeping optimal R=2 in the methanol synthesis step, the addition amount of carbon dioxide that is used as raw material gas for methanol can be increased, and the concentration of the methane in the recycle loop can be decreased. As a result, it became possible to obtain the production amount of methanol of 3,640 t/d (152 t/h). In addition, under the above-mentioned reforming reaction conditions, the carbon activity (Ac) of the syngas at the outlet of the reformer 1 is 0.43. Although carbon is likely to deposit under this condition, use of a reforming catalyst including a MgO support and Ru and/or Rh loaded thereon in an amount of 200 wtppm and more and 2,000 wtppm or less makes it possible to perform a good reforming reaction without causing carbon deposition.

[0075]

Comparative Example 1

For the comparison with Example 1, a process calculation was conducted under the same conditions to those in the above-mentioned Example 1, except that the hydrogen separation step was not used as shown in the block flow diagram in FIG. 4. The result of the process calculation is shown in the following Table 2.

[0076]

[Table 2]

Line number	1	2	3	4	5	7	8	9	10	11
Fluid name	Natural gas	CO ₂	Steam	Natural gas	Flue gas	Syngas	Syngas	MeOH	MeOH removed	Purge
Flow rate (Nm ³ /h) (ton/h)	116,000	26,000	-	5,400	740,000	430,000	2,500,000	-	7,000	93,000
Composition (mol%)	-	-	160	-	-	-	-	144	-	-
H ₂	-	-	-	-	-	61	42	-	-	-
CO	-	-	-	-	-	22	11	-	-	-
CO ₂	-	100	-	-	-	7	11	-	-	-
N ₂	0.1	-	-	0.1	-	-	-	-	-	-
CH ₄	91.5	-	-	91.5	-	9	35	-	-	-
C2	4.2	-	-	4.2	-	-	-	-	-	-
C3	2.5	-	-	2.5	-	-	-	-	-	-
C4	1.3	-	-	1.3	-	-	-	-	-	-
C5	0.4	-	-	0.4	-	-	-	-	-	-
C6	0.1	-	-	0.1	-	-	-	-	-	-
MeOH/H ₂ O	-	-	-/100	-	-	-	-	100/0	-	-

[0077]

As is understood from the result of the Table 2, since the R value of the fluid flowing through the line L7 was 1.8 which was lower than that in Example 1, and the concentration of the methane in the recycle loop was higher than that in Example 1,

the production amount of methanol was 3,450 t/d (144 t/h), which was about 5% lower than that in Example 1.

[0078]

Example 2

A process calculation was conducted under the same conditions to those in the above-mentioned Example 1, except that the steam/carbon ratio of the raw material gas at the inlet of the reformer 1 was 1.35, and the CO₂/carbon ratio thereof was 0.29, and 42,000 Nm³/h of hydrogen gas was separated from a part of the gas that had been extracted from the recycle loop for purging, and added to the syngas. The result of the process calculation is shown in the following Table 3.

[0079]

[Table 3]

Line number	1	2	3	4	5	6	7	8	9	10	11	12
Fluid name	Natural gas	CO ₂	Steam	Natural gas	Flue gas	H ₂ gas	Syngas	Syngas	MeOH	MeOH -removed	Purge	H ₂ - Removed gas
Flow rate (Nm ³ /h) (ton/h)	118, 000	39, 000	-	5, 400	650, 000	42, 000	470, 000	2, 500, 000	-	6, 100	890	65, 000
Composition (mol%)												
H ₂	-	-	-	-		100	62	49	-			
CO	-	-	-	-		-	21	9	-			
CO ₂	-	100	-	-		-	7	8	-			
N ₂	0.1	-	-	0.1		-	-	-	-			
CH ₄	91.5	-	-	91.5		-	9	33	-			
C2	4.2	-	-	4.2		-	-	-	-			
C3	2.5	-	-	2.5		-	-	-	-			
C4	1.3	-	-	1.3		-	-	-	-			
C5	0.4	-	-	0.4		-	-	-	-			
C6	0.1	-	-	0.1		-	-	-	-			
MeOH/H ₂ O	-	-	-/100	-		-	-	-	100/0			

[0080]

As is apparent from the result in the Table 3, since a larger amount of hydrogen gas than that in Example 1 was added to the syngas, the reformer can be operated at a lower steam/carbon ratio than that in Example 1. As a result, the addition amount of the carbon dioxide can be increased more than that in Example 1, and thus the production amount of methanol was 3,740 t/d (156 t/h), which was about 3% higher than that in Example 1.

[0081]

It is to be noted that under these conditions for reforming reaction in Example 2, the carbon activity (A_c) of the syngas at the outlet of the reformer 1 is 0.49. Although carbon is likely to deposit under this condition, use of a reforming catalyst including a MgO support and Ru and/or Rh loaded thereon in an amount of 200 wtppm or more but 2,000 wtppm or less makes it possible to perform a good reforming reaction without causing carbon deposition.

[0082]

Comparative Example 2

For the comparison with Example 2, a process calculation was conducted under the same conditions to those in the above-mentioned Example 2, except that the hydrogen separation step is not used as shown in the block flow diagram in FIG. 4. The result of the process calculation is shown in the following Table 4.

[0083]

[Table 4]

Line number	1	2	3	4	5	7	8	9	10	11
Fluid name	Natural gas	CO ₂	Steam	Natural gas	Flue gas	Syngas	Syngas	MeOH	MeOH removed	Purge
Flow rate (Nm ³ /h)	120,000	39,000	-	5,400	750,000	430,000	2,500,000	-	7,700	100,000
(ton/h)	-	-	150	-	-	-	-	144	-	-
Composition (mol%)										
H ₂	-	-	-	-		59	38	-		
CO	-	-	-	-		23	13	-		
CO ₂	-	100	-	-		7	13	-		
N ₂	0.1	-	-	0.1		-	-	-		
CH ₄	91.5	-	-	91.5		10	36	-		
C2	4.2	-	-	4.2		-	-	-		
C3	2.5	-	-	2.5		-	-	-		
C4	1.3	-	-	1.3		-	-	-		
C5	0.4	-	-	0.4		-	-	-		
C6	0.1	-	-	0.1		-	-	-		
MeOH/H ₂ O	-	-	-/100	-		-	-	100/0		

[0084]

As is understood from the result of the Table 4, since the R value of the fluid flowing through the line L7 was 1.68 and was lower than that in Example 2, and the concentration of the methane in the recycle loop was higher than that in Example 2, the

production amount of methanol was 3,450 t/d (144 t/h), which was about 8% lower than that in Example 2.

[0085]

Comparative Example 3

A process calculation was conducted according to a conventional flow shown in FIG. 4, supposing the case when the R value of the fluid flowing through the line L7 is set to 2.0 by adjusting the addition amount of the carbon dioxide instead of the addition of the hydrogen gas. Namely, in this Comparative Example 3, the process calculation was conducted under the same conditions to those in the above-mentioned Example 2, except that the hydrogen separation step was not used and the R value of the fluid flowing through the line L7 was set to 2.0 by controlling the flow rate of the fluid flowing through the line L2. Under these reaction conditions, the steam/carbon ratio of the raw material gas at the inlet of the reformer 1 was 1.75, and the CO₂/carbon ratio thereof was 0.20. The result of the process calculation is shown in the following Table 5.

[0086]

[Table 5]

Line number	1	2	3	4	5	7	8	9	10	11
Fluid name	Natural gas	CO ₂	Steam	Natural gas	Flue gas	Syngas	Syngas	MeOH	MeOH removed	Purge
Flow rate (Nm ³ /h)	111,000	25,000	-	5,400	630,000	430,000	2,500,000	-	5,700	84,000
(ton/h)	-	-	180	-	-	-	-	145	-	-
Composition (mol%)										
H ₂	-	-	-	-		63	49	-		
CO	-	-	-	-		20	8	-		
CO ₂	-	100	-	-		8	8	-		
N ₂	0.1	-	-	0.1		-	-	-		
CH ₄	91.5	-	-	91.5		8	33	-		
C2	4.2	-	-	4.2		-	-	-		
C3	2.5	-	-	2.5		-	-	-		
C4	1.3	-	-	1.3		-	-	-		
C5	0.4	-	-	0.4		-	-	-		
C6	0.1	-	-	0.1		-	-	-		
MeOH/H ₂ O	-	-	-/100	-		-	-	100/0		

[0087]

As is apparent from the result in the Table 5, since hydrogen was not added to the syngas, it was necessary to increase the steam/carbon ratio at the inlet of the reformer to 1.75, which was higher than that in Example 2, so as to set the R value to

2 at the outlet of the reformer 1, and thus the amount of the carbon dioxide that could be added was lower than that in Example 2. As a result, the production amount of methanol was 3,480 t/d (145 t/h), which was about 7% lower than that in Example 2. It is to be noted that under these conditions for a reforming reaction, the carbon activity A_c of the syngas at the outlet of the reformer 1 was 0.35.

[0088]

Comparative Example 4

A process calculation was conducted according to a conventional flow shown in FIG. 4, supposing the case when reforming is conducted by conventional steam reforming. Namely, in this Comparative Example 4, the process calculation was conducted under the same conditions to those in the above-mentioned Example 2, except that the hydrogen separation step was not used, and the flow rate of the fluid flowing through the line L2 was set to zero. Under these reaction conditions, the steam/carbon ratio of the raw material gas at the inlet of the reformer 1 was 3.00, and the CO_2 /carbon ratio thereof was 0.00. The result of the process calculation is shown in the following Table 6.

[0089]

[Table 6]

Line number	1	2	3	4	5	7	8	9	10	11
Fluid name	Natural gas	CO ₂	Steam	Natural gas	Flue gas	Syngas	Syngas	MeOH	MeOH removed	Purge
Flow rate (Nm ³ /h) (ton/h)	96,000	-	-	7,900	590,000	410,000	2,500,000	-	1,600	110,000
Composition (mol%)	-	-	260	-	-	-	-	125	-	-
H ₂	-	-	-	-	-	73	80	-	-	-
CO	-	-	-	-	-	15	4	-	-	-
CO ₂	-	-	-	-	-	8	3	-	-	-
N ₂	0.1	-	-	0.1	-	-	-	-	-	-
CH ₄	91.5	-	-	91.5	-	4	13	-	-	-
C2	4.2	-	-	4.2	-	-	-	-	-	-
C3	2.5	-	-	2.5	-	-	-	-	-	-
C4	1.3	-	-	1.3	-	-	-	-	-	-
C5	0.4	-	-	0.4	-	-	-	-	-	-
C6	0.1	-	-	0.1	-	-	-	-	-	-
MeOH/H ₂ O	-	-	-/100	-	-	-	-	100/0	-	-

[0090]

As is understood from the result of the Table 6, since carbon dioxide was not added, the amount of carbon as a raw material for methanol was decreased and the R value of the fluid flowing through the line L7 was 2.85, the production amount of methanol was 3,000

t/d (125 t/h), which was about 19% lower than that in Example 2. It is to be noted that under these conditions for a reforming reaction, the carbon activity A_c of the syngas at the outlet of the reformer 1 was 0.15.

[0091]

Reference Example

As a reference example, a process calculation in the case where 125 t/h of a product methanol is produced was conducted supposing a conventional methanol plant including a steam reformer shown in FIG. 9. As the conditions for the process calculation, the outlet temperature of the catalyst tube of the reformer 101 was 875°C, and the outlet pressure was 2.0 MPaG. Furthermore, the steam/carbon ratio of the raw material gas fed to the reformer 101 was 3.0. The result of this process calculation is shown in the following Table 7.

[0092]

[Table 7]

Line number	101	103	104	105	106	108	109	110	111	115
Fluid name	Feed NG	Steam	Fuel NG	Flue Gas	SG for MeOH	MeOH Reac Inlet	Product MeOH	Separator OVHD	MeOH Reac Purge Gas	H ₂ to Desul
Volume flow rate (×10 ³ Nm ³ /h)	96	-	7.9	591	411	2503	-	1.6	109	5.3
Mass flow rate (ton/h)	-	265	-	-	-	-	125	-	-	-
Composition (mol%)										
H ₂	0.0	0.0	0.0	0.0	72.7	80.2	0.0	20.9	81.6	72.7
O ₂	0.0	0.0	0.0	1.7	0.0	0.0	0.0	0.0	0.0	0.0
N ₂	0.1	0.0	0.1	68.3	0.0	0.1	0.0	0.1	0.1	0.0
CO	0.0	0.0	0.0	0.0	14.7	3.7	0.0	2.2	1.5	14.7
CO ₂	0.0	0.0	0.0	5.1	8.0	2.7	0.0	30.5	1.6	8.0
H ₂ O	0.0	100.0	0.0	24.9	0.5	0.1	0.0	0.0	0.1	0.5
CH ₄	91.5	0.0	91.5	0.0	4.0	12.8	0.0	46.4	14.5	4.0
C ₂ H ₆	4.2	0.0	4.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₃ H ₈	2.5	0.0	2.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₄ H ₁₀	1.3	0.0	1.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₅ H ₁₂	0.4	0.0	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₆ +	0.1	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH ₃ OH	0.0	0.0	0.0	0.0	0.0	0.5	100.0	0.0	0.6	0.0
C ₂ H ₄	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

[0093]

As is apparent from the result in the Table 7, the volume flow rate of the natural gas fed to the reformer 101 was 96×10³ Nm³/h. Furthermore, the R value of the syngas generated in the

reformer 101 was 2.85.

[0094]

Example 3

Next, the methanol plant including the reformer with the steam reforming catalyst filled therein, which was supposed in the above-mentioned Reference Example, was remodeled by replacing the steam reforming catalyst with a CO₂ reforming catalyst and disposing a facility for separating carbon monoxide from a part of syngas obtained by reforming in the presence of the CO₂ reforming catalyst. With this arrangement, a process calculation was conducted supposing the case that MMA is produced by using raw materials of methanol and carbon monoxide that are generated by the remodeled plant and ethylene that is introduced from the outside of the system.

[0095]

Namely, as shown in the flow diagram in FIG. 5, the above-mentioned plant after remodeling produces a product methanol by adding carbon dioxide and steam to natural gas, and reforming the natural gas in the presence of the CO₂ reforming catalyst, and then extracting a part of the obtained syngas for the separation of carbon monoxide mentioned below followed by treating the remaining syngas in the methanol generation step. Furthermore, the extracted part of the syngas was treated in the CO₂ removal unit 103 and cryogenic separation unit 104, thereby separating a carbon monoxide from the extracted part of the syngas. A part of the thus-obtained methanol and carbon monoxide are fed to the MMA production unit 109 together with ethylene introduced

from the outside of the system to produce MMA.

[0096]

As the conditions for the above-mentioned process calculation, the outlet temperature and the outlet pressure of the catalyst tube of the reformer 101 was 875°C and 1.85 MPaG, respectively. Furthermore, the steam/carbon ratio of the raw material gas that was fed to the reformer 101 was 1.22, and the CO₂/carbon ratio thereof was 0.34. Furthermore, a part of the purge gas from the recycle loop of the methanol generation step was collected and subjected to a separation treatment to obtain high-purity hydrogen. This high-purity hydrogen and hydrogen from the cryogenic separation unit 104 were merged into the syngas to be fed to the methanol generation step so as to adjust the R value of the merged gas flowing through the line L107 to 2.0. The result of the process calculation around the methanol plant including the reforming step is shown in the following Table 8, and the result of the process calculation around others, mainly the carbon monoxide separation step, is shown in the following Table 9.

[0097]

[Table 8]

Line number	101	102	103	104	105	106	107	108	109	110	111	112	113
Fluid name	Feed NG	CO ₂	Steam	Fuel NG	Flue Gas	SG for MeOH	Recycle H ₂ -SG	MeOH Reac Inlet	Product MeOH	Separator OVHD	MeOH Reac Purge Gas	PSA H ₂	PSA Off Gas
Volume flow rate (×10 ³ Nm ³ /h)	119	43	-	5.0	649	392	450	2304	-	5.9	4.1	38	58
Mass flow rate (ton/h)	-	-	134	-	-	-	-	-	125	-	-	-	-
Composition (mol%)													
H ₂	0.0	0.0	0.0	0.0	0.0	57.3	62.5	49.5	0.0	5.1	46.4	100.0	11.5
O ₂	0.0	0.0	0.0	0.0	1.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N ₂	0.1	0.0	0.0	0.1	69.7	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.1
CO	0.0	0.0	0.0	0.0	0.0	24.7	21.8	9.5	0.0	3.5	6.5	0.0	10.8
CO ₂	0.0	100.0	0.0	0.0	10.6	7.2	6.3	7.9	0.0	47.9	8.3	0.0	13.7
H ₂ O	0.0	0.0	100.0	0.0	18.0	0.5	0.5	0.1	0.0	0.0	0.1	0.0	0.1
CH ₄	91.5	0.0	0.0	91.5	0.0	10.3	8.9	32.2	0.0	43.5	37.8	0.0	62.3
C ₂ H ₆	4.2	0.0	0.0	4.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₃ H ₈	2.5	0.0	0.0	2.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₄ H ₁₀	1.3	0.0	0.0	1.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₅ H ₁₂	0.4	0.0	0.0	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₆ ⁺	0.1	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH ₃ OH	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.7	100.0	0.0	0.9	0.0	1.5
C ₂ H ₄	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
MMA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

[0098]

[Table 9]

Line number	120	121	122	123	124	125	126	127	128
Fluid name	MeOH for Chemical	SG for CO	Recycle CO ₂	H ₂ to MeOH Reac	H ₂ to Desul	CH ₄ Rich Gas	CO for Chemical	C ₂ H ₄	MMA
Volume flow rate ($\times 10^3 \text{Nm}^3/\text{h}$)	-	41	3.1	20	5.1	4.3	8.5	9.4	-
Mass flow rate (ton/h)	27	-	-	-	-	-	-	-	34
Composition (mol%)									
H ₂	0.0	57.3	0.0	93.4	93.4	1.9	0.0	0.0	0.0
O ₂	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N ₂	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0
CO	0.0	24.7	0.0	6.6	6.6	0.0	99.8	0.0	0.0
CO ₂	0.0	7.2	99.6	0.0	0.0	0.0	0.0	0.0	0.0
H ₂ O	0.0	0.5	0.4	0.0	0.0	0.0	0.0	0.0	0.0
CH ₄	0.0	10.3	0.0	0.0	0.0	98.1	0.1	0.0	0.0
C ₂ H ₆	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₃ H ₈	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₄ H ₁₀	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₅ H ₁₂	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₆ +	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH ₃ OH	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₂ H ₄	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.0	0.0
MMA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

[0099]

As is understood from the results of the Tables 8 to 9, since the R value of the outlet gas of the reformer 101 can be suppressed

to a value lower than 2 while the R value of the gas flowing through the line L107 is set to 2.0, the addition amount of carbon dioxide that is used as raw material gas for methanol can be increased, and the concentration of the methane in the recycle loop can be decreased. As a result, it became possible to produce 34 t/h of MMA while keeping the production amount of the product methanol of 125 t/h, which was the same as that in Reference Example.

[0100]

It is to be noted that under these conditions for a reforming reaction, the carbon activity (A_c) of the syngas at the outlet of the reformer 101 was 0.53. Although the value is a condition under which carbon is likely to deposit, use of a CO₂ reforming catalyst including a MgO support and Ru and/or Rh loaded thereon in an amount ranging from 200 wtppm to 2,000 wtppm makes it possible to perform a good reforming reaction without causing carbon deposition.

[0101]

Comparative Example 5

For the comparison with Example 3, the methanol plant including the reformer with the steam reforming catalyst filled therein, which was supposed in the above-mentioned Reference Example, was used as it was, and a process calculation was conducted supposing the case that natural gas is partially oxidized (POX) to produce carbon monoxide as a raw material for MMA while extracting a part of a product methanol that can be obtained by the plant.

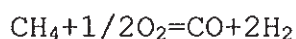
[0102]

Namely, in this process, as shown in the flow diagram in FIG. 6, the product methanol was produced from natural gas in a similar manner to that in Reference Example in FIG. 9. In a parallel way, steam that is fed via the line L143 and oxygen that is fed via the line L144 are added to the natural gas that has been extracted via the line L142, and thereafter the natural gas was fed to a sulfur removing unit (not shown) to remove sulfur components.

[0103]

Furthermore, the sulfur-removed gas is fed to POX unit 112, and is subject to partial oxidation reaction therein represented by the following chemical formula to generate a gas containing carbon monoxide. Furthermore, this gas was treated in the CO₂ removal unit 113 and cryogenic separation unit 114 in a similar manner to that in Example 3 to separate the carbon monoxide gas.

[Formula 3]



[0104]

As the conditions for the above-mentioned process calculation, the outlet temperature of the catalyst tube of the reformer 101 was 875°C, and the outlet pressure was 2.0 MPaG. Furthermore, the steam/carbon ratio of the raw material gas fed to the reformer 101 was 3.0. The result of the process calculation around the methanol plant is shown in the following Table 10, and the result of the process calculation around other steps, mainly the partial oxidation step, is shown in the following Table 11.

[0105]

[Table 10]

Line number	101	102	103	104	105	106	108	109	110	111	115
Fluid name	Feed NG	CO ₂	Steam	Fuel NG	Flue Gas	SG for MeOH	MeOH Reac Inlet	Product MeOH	Separator O/H/D	MeOH Reac Purge Gas	H ₂ to Desul
Volume flow rate (×10 ³ Nm ³ /h)	96	-	-	7.9	591	411	2503	-	1.6	109	5.3
Mass flow rate (ton/h)	-	-	265	-	-	-	-	98	-	-	-
Composition (mol%)											
H ₂	0.0	-	0.0	0.0	0.0	72.7	80.2	0.0	20.9	81.6	72.7
O ₂	0.0	-	0.0	0.0	1.7	0.0	0.0	0.0	0.0	0.0	0.0
N ₂	0.1	-	0.0	0.1	68.3	0.0	0.1	0.0	0.1	0.1	0.0
CO	0.0	-	0.0	0.0	0.0	14.7	3.7	0.0	2.2	1.5	14.7
CO ₂	0.0	-	0.0	0.0	5.1	8.0	2.7	0.0	30.5	1.6	8.0
H ₂ O	0.0	-	100.0	0.0	24.9	0.5	0.1	0.0	0.0	0.1	0.5
CH ₄	91.5	-	0.0	91.5	0.0	4.0	12.8	0.0	46.4	14.5	4.0
C ₂ H ₆	4.2	-	0.0	4.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₃ H ₈	2.5	-	0.0	2.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₄ H ₁₀	1.3	-	0.0	1.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₅ H ₁₂	0.4	-	0.0	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₆ ⁺	0.1	-	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH ₃ OH	0.0	-	0.0	0.0	0.0	0.0	0.5	100.0	0.0	0.6	0.0
C ₂ H ₄	0.0	-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
MMA	0.0	-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total	100.0	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

[0106]

[Table 11]

Line number	140	141	142	143	144	145	146	147	148	149	150
Fluid name	MeOH for Chemical	C ₂ H ₄	NG to POX	Steam	O ₂	POX Outlet	CO ₂	H ₂	CH ₄ Rich Gas	CO for Chemical	MMA
Volume flow rate (×10 ³ Nm ³ /h)	-	9.4	11	-	8.3	34	2.2	23	0.4	8.6	-
Mass flow rate (ton/h)	27	-	-	4.9	-	-	-	-	-	-	34
Composition (mol%)											
H ₂	0.0	0.0	0.0	0.0	0.0	62.7	0.0	92.8	16.9	0.0	0.0
O ₂	0.0	0.0	0.0	0.0	99.5	0.0	0.0	0.0	0.0	0.0	0.0
N ₂	0.0	0.0	0.1	0.0	0.5	0.1	0.0	0.0	0.0	0.6	0.0
CO	0.0	0.0	0.0	0.0	0.0	29.8	0.0	7.2	0.0	99.3	0.0
CO ₂	0.0	0.0	0.0	0.0	0.0	6.1	94.5	0.0	0.0	0.0	0.0
H ₂ O	0.0	0.0	0.0	100.0	0.0	0.2	5.5	0.0	0.0	0.0	0.0
CH ₄	0.0	0.0	91.5	0.0	0.0	1.1	0.0	0.0	83.1	0.1	0.0
C ₂ H ₆	0.0	0.0	4.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₃ H ₈	0.0	0.0	2.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₄ H ₁₀	0.0	0.0	1.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₅ H ₁₂	0.0	0.0	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₆ +	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH ₃ OH	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₂ H ₄	0.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
MMA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

[0107]

As is understood from the results of the Tables 10 to 11, since the syngas as a methanol raw material was produced by steam reforming that is inferior to CO₂ reforming in energy efficiency, the production amount of the product methanol was 98 t/h, which was about 20% lower than that in Example 3.

[0108]

Example 4

As shown in FIG. 7, a process calculation was conducted supposing the case when acetic acid is produced by using raw materials of methanol and carbon monoxide that are generated by a plant that is remodeled in a similar manner to that in Example 3. In this process calculation, as the conditions, the outlet temperature and the outlet pressure of the catalyst tube of the reformer 101 was 875°C and 1.85 MPaG, respectively. Furthermore, the steam/carbon ratio of the raw material gas that was fed to the reformer 101 was 1.20, and the CO₂/carbon ratio thereof was 0.39. Furthermore, the R value at the line L107 after merging of the syngas and hydrogen was set to 2.0. The result of the process calculation around the methanol plant is shown in the following Table 12, and the result of the process calculation around other steps, mainly the carbon monoxide separation step, is shown in the following Table 13.

[0109]

[Table 12]

Line number	101	102	103	104	105	106	107	108	109	110	111	112	113
Fluid name	Feed NG	CO ₂	Steam	Fuel NG	Flue Gas	SG for MeOH	Recycle H ₂ +SG	MeOH Reac Inlet	Product MeOH	Separator OPH	MeOH Reac Purge Gas	PSA H ₂	PSA Off Gas
Volume flow rate (×10 ³ Nm ³ /h)	117	46	-	6.2	647	357	429	2217	-	5.7	7.5	33	49
Mass flow rate (ton/h)	-	-	130	-	-	-	-	-	125	-	-	-	-
Composition (mol%)													
H ₂	0.0	0.0	0.0	0.0	0.0	56.2	62.9	50.1	0.0	5.2	47.0	100.0	11.7
O ₂	0.0	0.0	0.0	0.0	1.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N ₂	0.1	0.0	0.0	0.1	69.8	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.1
CO	0.0	0.0	0.0	0.0	0.0	25.6	21.9	9.4	0.0	3.5	6.4	0.0	10.7
CO ₂	0.0	100.0	0.0	0.0	10.4	7.7	6.4	7.9	0.0	48.3	8.3	0.0	13.8
H ₂ O	0.0	0.0	100.0	0.0	18.1	0.5	0.4	0.1	0.0	0.0	0.1	0.0	0.1
CH ₄	91.5	0.0	0.0	91.5	0.0	10.0	8.3	31.7	0.0	43.0	37.3	0.0	62.0
C ₂ H ₆	4.2	0.0	0.0	4.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₃ H ₈	2.5	0.0	0.0	2.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₄ H ₁₀	1.3	0.0	0.0	1.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₅ H ₁₂	0.4	0.0	0.0	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₆ +	0.1	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH ₃ OH	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.7	100.0	0.0	0.9	0.0	1.5
C ₂ H ₄	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH ₃ COOH	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

[0110]

[Table 13]

Line number	120	121	122	123	124	125	126	129
Fluid name	MeOH for Chemical	SG for CO	Recycle CO ₂	H ₂ to MeOH Reac	H ₂ to Desul.	CH ₄ Rich Gas	CO for Chemical	CH ₃ COOH
Volume flow rate (×10 ³ Nm ³ /h)	-	75	6.0	40	5.1	7.6	16	-
Mass flow rate (ton/h)	22	-	-	-	-	-	-	40
Composition (mol%)								
H ₂	0.0	56.2	0.0	93.1	93.1	1.9	0.0	0.0
O ₂	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
N ₂	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0
CO	0.0	25.6	0.0	6.9	6.9	0.0	99.8	0.0
CO ₂	0.0	7.7	99.4	0.0	0.0	0.0	0.0	0.0
H ₂ O	0.0	0.5	0.6	0.0	0.0	0.0	0.0	0.0
CH ₄	0.0	10.0	0.0	0.0	0.0	98.1	0.1	0.0
C ₂ H ₆	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₃ H ₈	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₄ H ₁₀	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₅ H ₁₂	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₆ +	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH ₃ OH	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₂ H ₄	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH ₃ COOH	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

[0111]

As is understood from the comparison of the results of the Tables 12 to 13, it became possible to produce 40 t/h of acetic acid while keeping the production amount of the product methanol of 125 t/h, which was the same as that in Reference Example and

Example 3.

[0112]

It is to be noted that under these conditions for a reforming reaction, the carbon activity (A_c) of the syngas at the outlet of the reformer 101 was 0.54. Although the values is a condition under which carbon is likely to deposit, use of a CO_2 reforming catalyst including a MgO support and Ru and/or Rh loaded thereon in an amount ranging from 200 wtpm to 2,000 wtpm makes it possible to perform a good reforming reaction without causing carbon deposition.

[0113]

Comparative Example 6

For comparison with Example 4, the methanol plant including the reformer with the steam reforming catalyst filled therein, which was supposed in the above-mentioned Reference Example, was used as it was, and a process calculation was conducted supposing the case that natural gas is partially oxidized (POX) to produce carbon monoxide as an acetic acid raw material while extracting a part of a product methanol that can be obtained by the plant. As shown in the flow diagram of FIG. 8, the process supposed herein is equivalent to the process of FIG. 6 that was supposed in Comparative Example 5 except for the acetic acid production unit 110.

[0114]

As the conditions for the above-mentioned process calculation, the outlet temperature and the outlet pressure of the catalyst tube of the reformer 101 was 875°C and 2.0 MPaG,

respectively. Furthermore, the steam/carbon ratio of the raw material gas fed to the reformer 101 was 3.0. The result of the process calculation around the methanol plant is shown in the following Table 14, and the result of the process calculation around others, mainly the partial oxidation step, is shown in the following Table 15.

[0115]

[Table 14]

Line number	101	102	103	104	105	106	108	109	110	111	115
Fluid name	Feed NG	CO ₂	Steam	Fuel NG	Flue Gas	SG for MeOH	MeOH Reac Inlet	Product MeOH	Separator OVHD	MeOH Reac Purge Gas	H ₂ to Desul
Volume flow rate (×10 ³ Nm ³ /h)	96	-	-	7.9	591	411	2503	-	1.6	109	5.3
Mass flow rate (ton/h)	-	-	265	-	-	-	-	103	-	-	-
Composition (mol%)											
H ₂	0.0	-	0.0	0.0	0.0	72.7	80.2	0.0	20.9	81.6	72.7
O ₂	0.0	-	0.0	0.0	1.7	0.0	0.0	0.0	0.0	0.0	0.0
N ₂	0.1	-	0.0	0.1	68.3	0.0	0.1	0.0	0.1	0.1	0.0
CO	0.0	-	0.0	0.0	0.0	14.7	3.7	0.0	2.2	1.5	14.7
CO ₂	0.0	-	0.0	0.0	5.1	8.0	2.7	0.0	30.5	1.6	8.0
H ₂ O	0.0	-	100.0	0.0	24.9	0.5	0.1	0.0	0.0	0.1	0.5
CH ₄	91.5	-	0.0	91.5	0.0	4.0	12.8	0.0	46.4	14.5	4.0
C ₂ H ₆	4.2	-	0.0	4.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₃ H ₈	2.5	-	0.0	2.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₄ H ₁₀	1.3	-	0.0	1.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₆ H ₁₂	0.4	-	0.0	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₆ +	0.1	-	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH ₃ OH	0.0	-	0.0	0.0	0.0	0.0	0.5	100.0	0.0	0.6	0.0
C ₂ H ₄	0.0	-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH ₃ COOH	0.0	-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total	100.0	-	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

[0116]

[Table 15]

Line number	140	142	143	144	145	146	147	148	149	151
Fluid name	MeOH for Chemical	NG to POX	Steam	O ₂	POX Outlet	CO ₂	H ₂	CH ₄ Rich Gas	CO for Chemical	CH ₃ COOH
Volume flow rate (×10 ³ Nm ³ /h)	-	21	-	16	64	4.1	43	0.8	16	-
Mass flow rate (ton/h)	22	-	9.2	-	-	-	-	-	-	40
Composition (mol%)										
H ₂	0.0	0.0	0.0	0.0	62.7	0.0	92.8	16.9	0.0	0.0
O ₂	0.0	0.0	0.0	99.5	0.0	0.0	0.0	0.0	0.0	0.0
N ₂	0.0	0.1	0.0	0.5	0.1	0.0	0.0	0.0	0.6	0.0
CO	0.0	0.0	0.0	0.0	29.8	0.0	7.2	0.0	99.3	0.0
CO ₂	0.0	0.0	0.0	0.0	6.1	94.5	0.0	0.0	0.0	0.0
H ₂ O	0.0	0.0	100.0	0.0	0.2	5.5	0.0	0.0	0.0	0.0
CH ₄	0.0	91.5	0.0	0.0	1.1	0.0	0.0	83.1	0.1	0.0
C ₂ H ₆	0.0	4.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₃ H ₈	0.0	2.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₄ H ₁₀	0.0	1.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₅ H ₁₂	0.0	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₆ +	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH ₃ OH	100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₂ H ₄	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH ₃ COOH	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

[0117]

As is understood from the result of the Tables 14 to 15, since the syngas as a methanol raw material was produced by steam reforming that is inferior to CO₂ reforming in energy efficiency,

the production amount of the product methanol was 103 t/h, which was about 20% lower than that in Example 4.

Reference Signs List

[0118]

- | | |
|----------|------------------------------|
| 1, 101 | Reformer |
| 2, 102 | Heating furnace |
| 3, 105 | Methanol reactor |
| 4, 106 | Recycle unit |
| 5, 107 | Methanol separator |
| 6, 108 | Hydrogen separation unit |
| 103, 113 | CO ₂ removal unit |
| 104, 114 | Cryogenic separation unit |
| 109 | MMA production unit |
| 110 | Acetic acid production unit |
| 112 | POX unit |

Claims

1. A method for production of methanol comprising the steps of: reforming a lower hydrocarbon gas containing steam and carbon dioxide added thereto in the presence of a catalyst to generate syngas mainly including hydrogen and carbon monoxide; synthesizing methanol by reaction of the syngas obtained in the reforming step in the presence of a catalyst; recycling by separating the methanol synthesized in the methanol synthesis step from a residual gas containing unreacted gas and merging the residual gas as a recycle gas with the syngas; and separating hydrogen by separating hydrogen gas from at least a part of the recycle gas and merging the hydrogen gas with the syngas.

2. The method for production of methanol according to claim 1, wherein a PSA unit is used for the separation of the hydrogen gas.

3. The method for production of methanol according to claim 1 or 2, wherein a raw material gas in the reforming step has a steam/carbon ratio of 0.7 or more but 1.7 or less.

4. The method for production of methanol according to any of claims 1 to 3, wherein the syngas obtained in the reforming step has a carbon activity of 0.36 or more but 1.0 or less.

5. The method for production of methanol according to any of claims 1 to 4, wherein the catalyst used in the reforming step has a MgO calcined at 1,000°C or more but 1,500°C or less and Ru and/or Rh loaded thereon in an amount of 200 wtppm or more but 2,000 wtppm or less.

6. The method for production of methanol according to

any of claims 1 to 5, wherein the catalyst used in the reforming step has a support having a specific surface area of $0.1 \text{ m}^2/\text{g}$ or less.

7. The method for production of methanol according to any of claims 1 to 6, wherein the reaction conditions in the reforming step are an outlet reaction temperature of 850°C or more but 950°C or less, a reaction pressure of 1.0 MPaG or more but 3.0 MPaG or less, the GHSV thereof of $2,000 \text{ hr}^{-1}$ or more but $10,000 \text{ hr}^{-1}$ or less, and the $\text{CO}_2/\text{carbon}$ ratio of the raw material gas thereof of 0.1 or more but 0.6 or less.

8. The method for production of methanol according to any of claims 1 to 7, wherein the gas after merging the hydrogen gas with the syngas has an R value of from 1.8 to 2.2, and the residual gas after separating the hydrogen gas in the hydrogen separation step is utilized as a heat source for the reformer.

9. A method for production of an acetic acid raw material or an MMA raw material, which comprises the method for the production of methanol according to any of claims 1 to 8, further comprising the step of separating carbon monoxide by extracting a part of the syngas obtained in the reforming step and separating carbon monoxide from the part of the syngas, and a residual syngas after the extraction of the part of the syngas is fed to the methanol synthesis.

10. The method for production of an acetic acid raw material or an MMA raw material according to claim 9, wherein the carbon monoxide separation step comprises the steps of: removing CO_2 gas from the part of the syngas; and cryogenically separating

carbon monoxide from a CO₂-removed gas by a cryogenic separation process.

11. The method for production of an acetic acid raw material or an MMA raw material according to claim 10, wherein the CO₂ gas removed in the CO₂ removing step is fed to an upstream side of the reforming step for recycle.

12. A methanol production apparatus comprising: a reformer for reforming a lower hydrocarbon gas containing steam and carbon dioxide added thereto in the presence of a catalyst to generate syngas mainly including hydrogen and carbon monoxide; a methanol reactor for synthesizing methanol by reaction of the syngas obtained in the reformer in the presence of a catalyst; a recycle unit for separating the methanol synthesized in the methanol reactor from a residual gas containing unreacted gas and merging the residual gas as a recycle gas with the syngas; and a hydrogen separation unit for separating hydrogen gas from at least a part of the recycle gas and merging the hydrogen gas with the syngas.

13. A plant for production of an acetic acid raw material or an MMA raw material, which comprises the methanol production apparatus according to claim 12, further comprising a carbon monoxide separation unit for extracting a part of the syngas obtained in the reformer and separating carbon monoxide from the part of the syngas, and supplying a residual syngas after the extraction of the part of the syngas to the methanol reactor.

14. A method for remodeling a methanol plant including a reformer, which is filled with a steam reforming catalyst, for

producing an acetic acid raw material or an MMA raw material in addition to methanol, the method comprising replacing the steam reforming catalyst in the reformer with a CO₂ reforming catalyst so as to reform lower hydrocarbon gas with carbon dioxide and steam, and providing a facility for separating carbon monoxide from a part of syngas obtained by the reforming.