Advanced Technology for Large Scale Methanol Plant

Hiroshi Matsumoto[*1] **Haruhito Watanabe**[*1]
Hideaki Nagai[*1] **Kazuhiro Morita**[*1]
Hiroshi Makihara[*2]

Mitsubishi Heavy Industries, Ltd. (MHI) has constructed and operated three large scale methanol plants with the Mitsubishi Gas Chemical Co., Inc. (MGC) basic process using new methanol production technology which was developed through cooperation between MHI and MGC, by our chemical process engineering technology, including the Venezuela plant which was completed in 1994. In accordance with the operation records of the 2 200 t/d Venezuela plant, which involved various advanced technologies, the superiority of the process in regard to high efficiency and less energy consumption has been confirmed. In the new Saudi Arabia 2 500 t/d plant which is under construction, the SUPERCONVERTER (SPC) was implemented, and the scale up and improvement of efficiency by this current process is thought to be reaching the maximum limit. Also, for achieving larger capacities of 5 000 to 10 000 t/d, a national project is underway. MHI is involved in the project to establish new methanol process technology for future increased demand of methanol.

1. Introduction

Because of USA's "Clean Air Act" and the enactment of Environmental Control Laws in various countries, the addition of MTBE (Methyl-Tertiary Butyl Ether) to gasoline for automobiles has increased, showing a conspicuous rise in the demand for methanol, the material conventionally used to produce MTBE as a chemical industrial substance. Furthermore, methanol is drawing attention as an alternative clean energy source for exhaustible petroleum fuel and is considered to be giving rise to a need for future mass production.

Mitsubishi Heavy Industries, Ltd. (MHI) has carried out joint research and development on methanol production technology over a long period of time with Mitsubishi Gas Chemical Co., Inc. (MGC) as the process licenser and has so far successfully designed and constructed three large scale methanol plants. This paper describes the outline and operation records of the latest plant for Venezuela, and also the technical features and the application of new technology to a new plant under construction in Saudi Arabia. Light is also thrown onto new technology development, research themes, the status of progress in this field, and future developments to realize large scale plants for mass production of methanol as a prospective fuel.

2. Outline of Methanol Plant for METOR Venezuela

The plant was completed in January 1994 as the first methanol plant in Venezuela, and production started in March of the same year. It is one of the largest scale methanol plants in the world producing 2 200 t/day chemical grade AA methanol. The plant consists of highly sophisticated technologies, based on MHI's experience over a long period in constructing and operating of large scale methanol processes, including the technical improvements given below. **Fig. 1** shows the overall view of the completed plant.

2.1 Methanol synthesis process and MGC catalyst

The multi-bed quench type methanol synthesis converter, which has an outstanding record in large scale plants, is used in this plant, and the hot quench type converter shown in **Fig. 2** has been employed over the cold quench type converter adopted to improve energy consumption. The synthesis catalyst made by MGC is used, and the distributor has been improved to allow more effective distribution and mixing of quenching gas to ensure load uniformity and long life of the catalyst.

2.2 Steam reformer

The adopted steam reformer is a single-box type with roof burners, and the furnace surface area has been made small to minimize thermal loss. Multitubular heat exchange coils and a plate type combustion air preheater have been installed in the convection section to maximize heat recovery, resulting in a

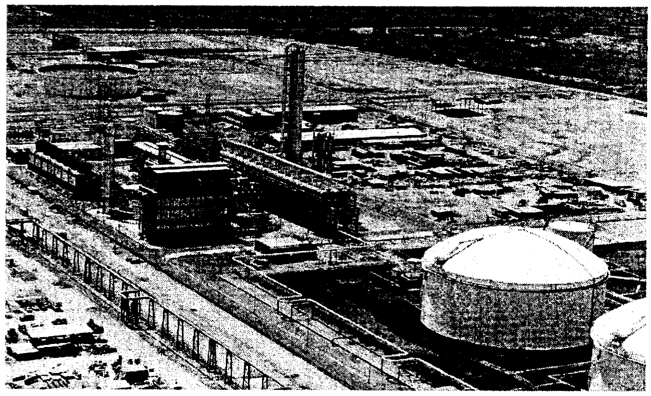

Fig. 1 Methanol plant for METOR Venezuela

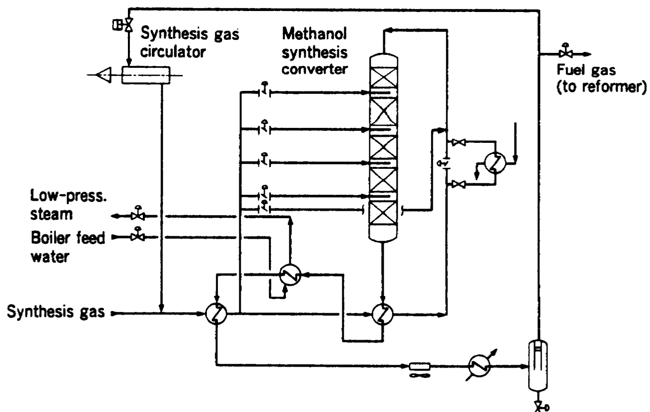

Fig. 2 Process flow of methanol synthesis with quench type converter

*1 Chemical Plant Engineering & Construction Center, Machinery Headquarters
*2 Hiroshima Research & Development Center, Technical Headquarters

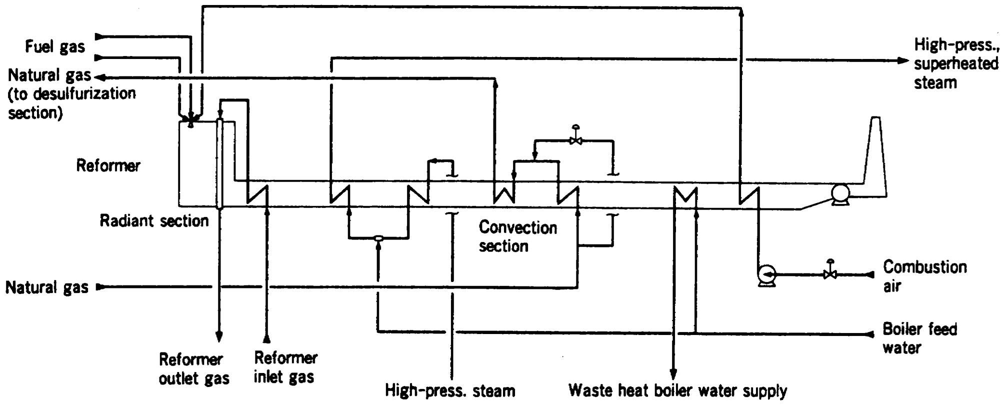

Fig. 3 Process flow of steam reformer

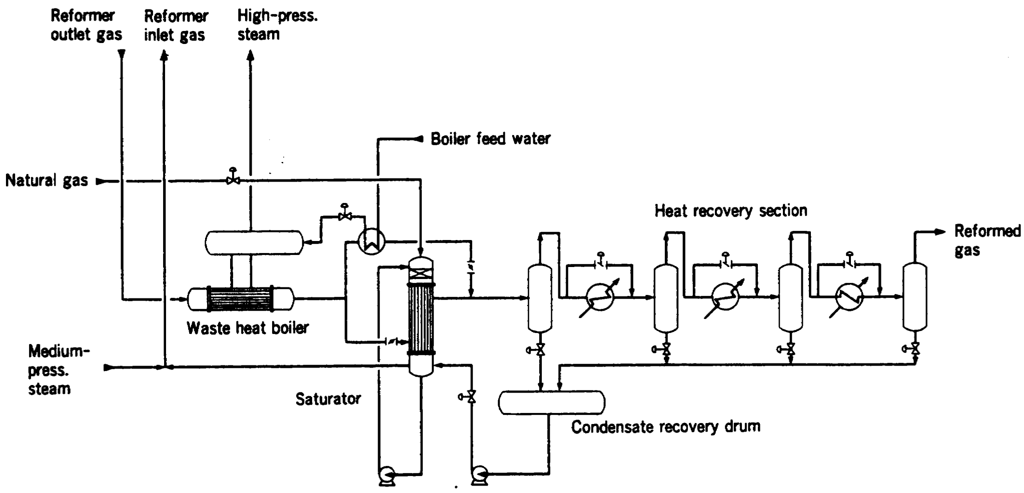

Fig. 4 Process flow of saturator

total furnace efficiency of approximately 93%. **Fig. 3** shows an overview of the process flow of the steam reformer.

2.3 Waste heat recovery section

The reformed gas at the outlet of the reformer reaches temperatures over 870°C and undergoes a heat recovery as the 105 kg/cm^{2}G steam generated in the waste heat boiler. The recovered steam is used for the steam turbine which drives the synthesis gas compressor. Furthermore, a multitubular falling film type gas saturator, developed with MGC, has been installed in the slip stream of the waste heat boiler, and the waste heat is utilized to reevaporate the condensed water with the steam mixed with the gas supplied to the reformer. This enables reutilization of the process drain water, and reduces the load of the boiler feed water treatment unit. An overview of the process flow is given in **Fig. 4**.

2.4 Compressor

There are three compressors (the natural gas booster, synthesis gas compressor and circulator) used in the methanol process. The compressors adopted here are all MAC (Mitsubishi Advanced Compressor) with high efficiencies, ensuring reductions in energy consumption.

2.5 Distillation system

A distillation system composed of three columns, topping, refining and recovery, is used. An air cooler is mainly being used as a condenser in the refining column where the heat load is highest; half of the fans have been provided with variable pitch control functions to control the process temperature. In order that the distillation drain meets environmental regulation, an effluent treatment system with a bio-treatment system has been installed, with the effluent being treated to about 10 ppm in terms of BOD_5 value before being discharged.

2.6 Overall efficiency and comparison with other plants

For assessing design attributes like those described above, a comparison of feed stock unit consumption (the raw gas required per unit of methanol production) is made between other plants designed and constructed by MHI. The results are shown in **Table 1**.

3. Operation records of the Venezuela plant and their significance

The Venezuela plant started production in March, 1994, successfully fulfilling the guarantee operation in June of the same year. **Table 2** shows the operation records in comparison with performance guarantee figures (indexes).

Starting with the 600 t/d (reforming capacity: 800 t/d) plant constructed at MGC, construction and operation records of large scale methanol plants by MHI have reached the levels of the 2 200 t/d plant for Venezuela through the Saudi Arabia/ AR-RAZI I (1 815 t/d) and the AR-RAZI II (1 906 t/d) plants. During this period the scale-up of component due to technical improvements has resulted in higher plant efficiency enabling large-scale production in a single train as shown in Table 1.

Table 1 Comparison of process in overall efficiency

Item of comparison	1st-stage plant in Saudi Arabia	2nd-stage plant in Saudi Arabia	Venezuela plant
Plant production rate	1 815 t/d	1 906 t/d	2 200 t/d
Raw material	Natural gas	Natural gas	Natural gas
Reformer	Two lines	One line	One line
Saturator	None	Installed	Installed
Synthesis compressor	Two lines (MHI/Dresser machine)	One line (MHI/Dresser machine)	One line (MHI/MAC machine)
High-press. steam press.	60 kg/cm²G	60 kg/cm²G	105 kg/cm²G
Synthesis converter type	Cold quench	Hot quench	Hot quench
Design value of feed stock unit consumption (index)	100	86	82*

*: The higher CO_2 content, compared with other plants, is advantageous for methanol production, improving energy consumption.

Table 2 Operation records of Venezuela plant in comparison with performance guarantee figures

Item of guarantee	Performance guarantee (index)	Record at performance guarantee operation
Methanol production rate	100	103
Methanol quality	FEDERAL GRADE"AA"	Acceptable
Raw material natural gas amount*	100	95
Power consumption*	100	55
Process water flow*	100	72

*: Required amount per unit production

Table 3 Comparison of pressurized and atmospheric distillation

Item of comparison	Atmospheric distillation	Pressurized distillation
Required diameter of refining column	100	75
Required heat transfer area of condenser	100	47

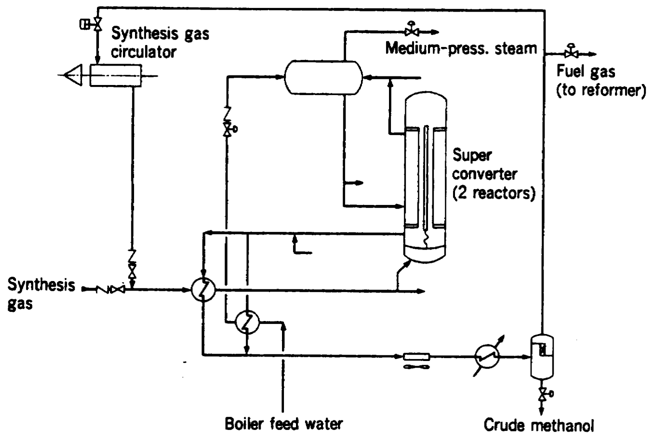

Fig. 5 Process flow of methanol synthesis with super converter (SPC)

The components given below have been a hindrance to production for large-scale plants, which can be designed and constructed for 2 500 t/d class plant.

- Reformer
- Methanol synthesis converter
- Synthesis gas compressor
- Refining column and condenser

Furthermore, it is possible to reduce energy consumption by upgrading the heat recovery system and improving efficiency. The records of the Venezuela plant show that the aforementioned technologies have been proven.

4. Applications to the Saudi Arabia/AR-RAZI plant and new technology

The Saudi Arabia/AR-RAZI plant for which the contract was signed in June, 1995 has a production capacity of 2 500 t per day. The plant is the third unit for AR-RAZI, and its design and construction are under way, with completion targeted for June, 1997. It is the largest scale and latest model plant in the world containing the most sophisticated and latest technologies. Improvements based on the experiences and operation records of the Venezuela plant have been unsparingly made. Moreover, the double pipe catalyst tube type new model synthesis converter (super converter; hereafter called SPC), jointly developed by MHI and MGC, is to be employed for the first time in a large scale commercial plant. The major noteworthy technologies are given below.

4.1 Implementation of SPC

As mentioned in the previous Technical Report[(1)-(3)], in the SPC, the catalyst is loaded in the annular space of the outer and inner tubes and cools off the outer tube circumference with boiler feed water to promote the methanol synthesis reaction. This makes the converter more compact and achieves a heat recovery of more than 10% higher than the conventional process. The high reaction rate and high heat recovery of the SPC lead to a drastic reduction in the synthesis circulating gas flow rate and the generation of high-pressure steam, improving the feed stock unit consumption by approximately 5%. **Fig. 5** shows the synthesis process flow. The converter, currently under manufacturing at MHI Hiroshima Machinery Works, consists of two parallel synthesis converters and has quite a few improvements made based on records of the verification unit (for producing methanol 520 t/d) installed and operated at MGC from 1993.

4.2 Distillation system

The refining column has been changed from conventional atmospheric-pressure type to a pressurized type to reduce the refining column diameter, which has been a limitation in the manufacturing and transportation of the equipment. Furthermore, the rise in condensation temperature causes the temperature difference in the condenser to increase, consequently decreasing the number of condensers (air coolers) and relaxing the plot limit. The comparison of pressurized and atmospheric distillation is shown in **Table 3**. Moreover, the variable pitch control range of the air cooler fan is set to 2/3 of the whole to improve the controllability. Furthermore, a by-product mainly consisting of ethanol is reused as the fuel for the boiler, contributing to the improvement of unit consumption.

4.3 Other technologies and overall efficiency

The overall efficiency of this process plant is improved by 4% over the AR-RAZI plant II (Saudi Arabia/AR-RAZI second stage) because of the drastic reduction in energy consumption due to the SPC; in addition to the application of the outstanding technologies including the MAC, saturator, etc., obtained through the conventional plants.

5. Next-Generation Methanol Production Technology and Future Development

The efficiency of the existing methanol production method, from the viewpoint of the total system, has reached a limit: the production capacity per plant is limited to 2 500 t/d with respect to further scale up of the plant, due to the restriction in the strength and heat transfer of the reaction tube in tubular type steam reformer, while the production capacity per plant with respect to the methanol synthesis converter is also limited to 2 500 t/d because of the limitation in heat removal for preventing the catalyst from getting burned due to overheating caused by exothermal reaction.

Therefore, in order to reduce methanol production costs through new technology and larger-scale production facility, a gas phase fluidized bed methanol reactor development project was planned, and the development program has been launched since 1993 by the New Energy and Industrial Technology Development Organization (NEDO) and the Petroleum Energy Center (PEC).

MHI has been taking part in this project since 1993 as a hardware maker and as an engineering company and, on consignment from NEDO/PEC, has been assiduously working on the project jointly with MGC and three petroleum companies (KASHIMA OIL Co., LTD.; SHOWA SHELL SEKIYU, K. K.; and Mitsubishi Oil Co., Ltd.) An overview of the development program and the role of MHI are introduced below.

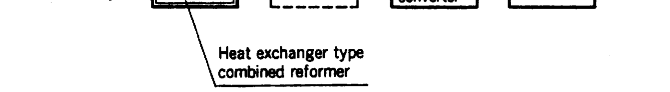

Fig. 6 Comparison of process configuration for conventional and new methanol production

5.1 Outline of new process

(1) Process build-up

The new and conventional methods of methanol production process are compared in **Fig. 6**. The conventional process resorts to the tubular type reformer and the fixed bed methanol synthesis converter as key technologies and has to be operated with the reforming pressure lower than the synthesis pressure due to the thermal strength against the reaction tube. The new process, on the other hand, uses a heat exchanger type combined reformer and fluidized bed methanol synthesis converter as the key technology.

As it will be mentioned later, the new type reformer carries out reforming even at high pressures so that the reformer can be operated with the reforming pressure at the same level as the synthesis pressure, dispensing with the need of a compressor and its power. It further contributes to an improvement in system efficiency since synthesizing gas with compositions more suitable for methanol synthesis will be obtained by compact facility[4].

An overview of the new gas phase fluidized bed process is given in **Fig. 7**.

(2) Heat exchanger type combined reformer

This reformer is a combination of an existing steam reforming method (primary reforming section) and a partial oxidation method (secondary reforming section), with oxygen injected into the secondary reforming section to partially burn the primary reforming section outlet gas. The heat thus generated is used for reforming and then the reaction tube in primary reforming section is heated by the sensible heat of the reformed gas, allowing adjustment of the composition ratio of the reforming and synthesis gases at high pressure.

(3) Fluidized bed synthesis converter

The fluidized bed synthesis converter forms the so-called fluidized bed by injecting raw synthesis gas through the bottom to fluidize the catalyst particle (Cu-Zn type) with an average diameter of 50 to 60 μm, and carries out methanol synthesis while removing the reaction heat by means of the group of cooling tubes. The new method enables recovery of the reaction heat by means of high-pressure steam; and unlike the conventional method, where the operating pressure and temperature had to be changed according to the deterioration of the catalyst, the new method allows replenishment and

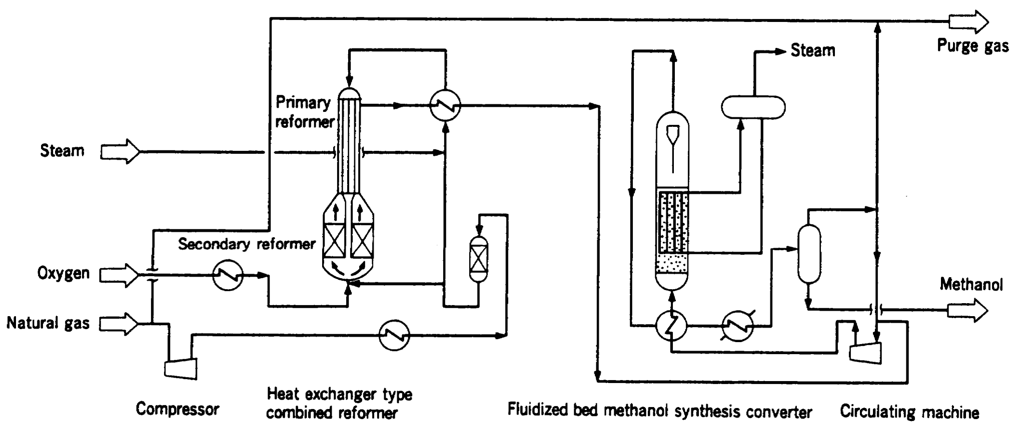

Fig. 7 Gas phase fluidized bed process

exchange of the catalyst even during operation, ensuring steady and stable operation.

5.2 Development project and the status of progress

(1) Development schedule and target

The development of gas phase fluidized bed methanol production technology will be carried out in the following two phases.

① Phase-1: Study and basic research on elementary technology mainly for 10 t/d plant

② Phase-2: Verification research using 100 t/d verification plant

(2) Status of development and future development

Currently continuous operation with intermittent stoppage is repeated at 10 t/d plant to obtain fundamental data, and a study on the design of a 5 000 t/d plant is carried out to evaluate construction cost and process economy. In the future, the process performance and economy are to be reviewed on the basis of the achievements of the development program, and a study is to be made on the limitation of size (scale) of the plant based on the restrictions of construction method/equipment capacity.

6. Conclusion

Methanol is currently mainly used for chemical materials. However, because of its convenience and safety in terms of transportation, storage, and usage, in addition to its outstanding properties in terms of environmental preservation. Methanol is drawing attention and is expected to be as a substitutional fuel for automobiles and power generators. For these reasons, MHI is determined to constantly improve methanol synthesis technology and to develop the technology for producing methanol from natural gas, etc. in large capacities at low cost in order to meet world needs.

References

(1) Takase, I. et al., Mitsubishi (MGC/MHI) Methanol Process, Mitsubishi Juko Giho, Vol.23 No.1 (1986) p.89—94
(2) Makihara, H. et al., Characteristics of a New Methanol Synthesis Reacter, Mitsubishi Heavy Industries Technical Review, Vol.24 No.3 (1987) p.214—219
(3) Makihara, H. and Niwa, K., et al., Characteristics of a New Methanol Synthesis Reacter, Energy Progress, Vol.7 No.1 (1987) p.51—58
(4) NEDO NEWS, No.147 (1995)
(5) Mitsubishi Gas Chemical Co., Inc., Material