

ELEMENTARY TECHNOLOGY DEVELOPMENT :

DEVELOPMENT OF VARIOUS REFORMERS

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1. FOREWORD

For development of fuel processors for fuel cell power plants, Fuji Electric has put much effort into the methanol reformer for smaller fuel cells, on-site methanol reformer, and on-site natural gas fuel reforming units. The results up to now are introduced here for the reference of those concerned with fuel cell power plants.

The fuel cell power plant reformer development process is summarized in Fig. 1.

This paper classifies reformers into four groups, by

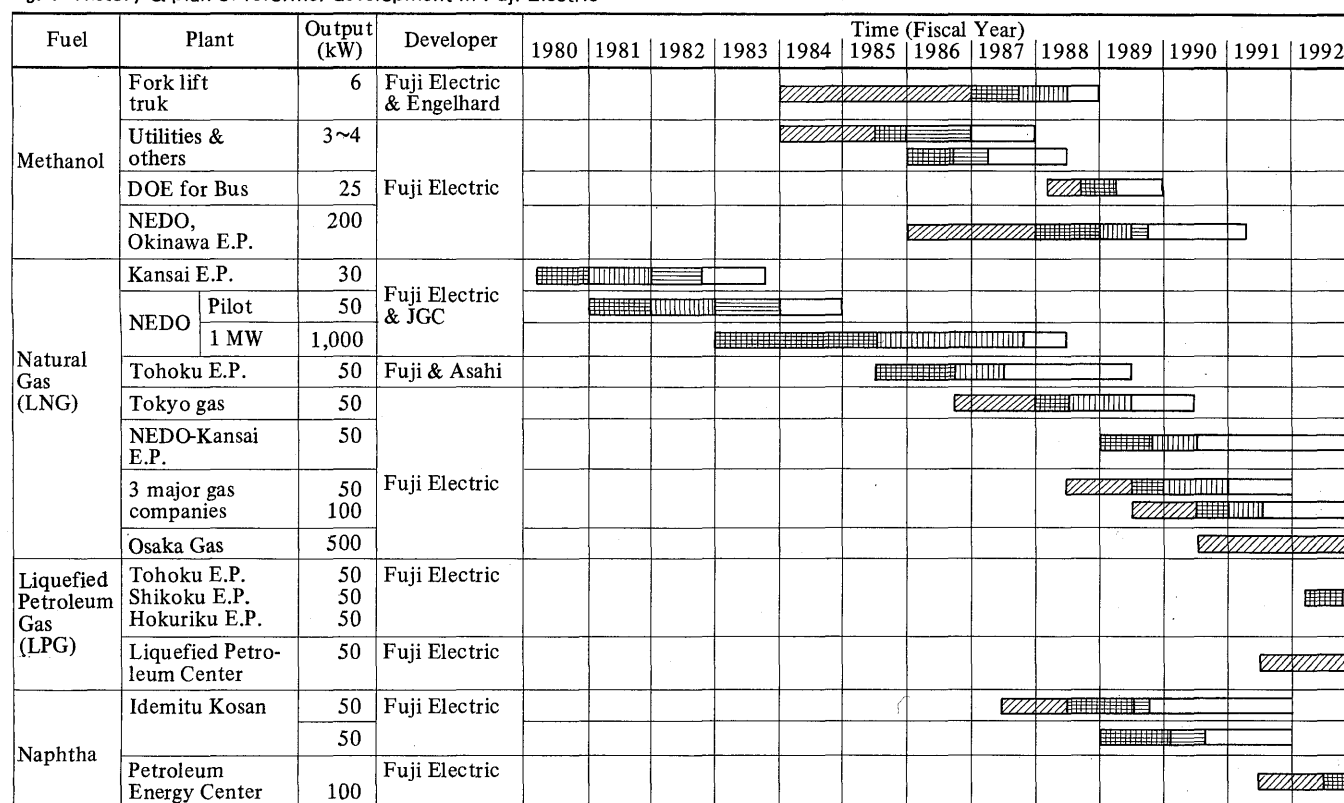
type of raw material: methanol, natural gas (town gas, LNG), LPG, and naphtha.

2. DEVELOPMENT OF VARIOUS REFORMERS


2.1 Methanol reformer


The reaction which converts methanol with steam is shown below. This reaction uses a Cu compound catalyst and is performed under a temperature of approximately 200 to 300°C and a low pressure of 10 kg/cm² or less.


Fig. 1 History & plan of reformer development in Fuji Electric




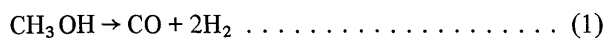
Development 

Design & Manufacturing 

Test in Factory 

Installation on Site 

Operation 



Because methanol is a clean liquid raw material which does not require special preprocessing, it is considered to be suitable for transportation and vehicle power sources and when other raw materials are difficult to transport or otherwise difficult to handle.

2.1.1 Methanol reformer for low capacity and vehicles

The methanol reformer, whose development was started independently in 1984, is a 3 to 6 kW low capacity reformer for use with systems for small power plants.

In 1985, this reformer was delivered to the customer as a system and certification operation commenced. At almost the same time, development of methanol reformer technology for fork-lift (FLT) was conducted cooperatively with the Englehard Co. and technology of fuel cell power system for vehicles was accumulated and in 1987 to 1988, the system was installed in an actual vehicle and test operated. Based on the technology accumulated through these developments, development of 25 kW and 50 kW reformers for systems which are mounted in buses was initiated for the United States Department of Energy (DOE). Demonstration operation of the 25 kW reformer was started in the United States in October 1989 and received favorable comment. A 50 kW reformer is currently under development.

Compared to large reformers, the development points of these reformers are (1) small size and light weight, (2) ability to withstand frequent starting and stopping and short starting and stopping time, and (3) excellent resistant to vibration, dust, and other environmental conditions.

2.1.2 On-site methanol reformer

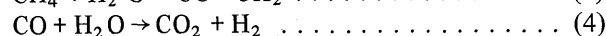
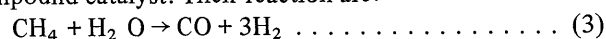
The reformer for fuel cell power generating system for detached islands whose development was started in 1986 upon receipt of an order from the New Energy and Industrial Technology Development Organization (NEDO) is a tubular heat exchanger type reformer that uses an indirect heating system with a heating medium. Design of an actual unit was started after reforming tests with actual size tubes filled with catalyst and development of a catalyst combustion system for heating the catalyst. This reformer was delivered to Tokashiki Island, Okinawa in September 1989. In 1990, certification operation was completed through approximately 8,500 hours of operation up to the end of research. Since it is an on-site system, the reformer performs pressurized operation at 3 kg/cm² and as a result of increasing the load track-ability, an momentary load change of 20% is possible.

2.2 Natural gas reforming unit

Currently the large town gas companies of Japan supply town gas with liquefied natural gas (LNG) as the raw material. A large part of this town gas is methane (approximately 90%) and the remaining part is ethane, propane, and butane. The town gas reforming unit which converts such town gas into hydrogen enriched gas which can be used in the fuel cell stack allows continuous system operation without accompanying raw material storage operation

in areas with town gas lines. Areas with town gas lines are mainly large cities. The power demand in these areas is also large. Therefore, the features of the fuel cell power plant are displayed and the possibility of it becoming widely popular is large.

Hydrogen generators for fuel cells using steam reformation of hydrocarbon represented by methane usually perform generation under a temperature of 650 to 800°C and a pressure of 1 to 10 kg/cm² using an Ni compound or Ru compound catalyst. Their reaction are:



However, natural gas generally contains organic sulfur compounds (odorants) which block the activity of the reformer catalyst. The content of this organic sulfur compound is small, but since it is accumulated by long term operation and degrades the reformer catalyst considerably, desulfurization is necessary as raw material preprocessing. Although it depends on the operating conditions, since a high temperature is necessary to reform the methane, which is the main component, the reform gas contains a large amount of carbon monoxide (CO) which causes catalyst poisoning in the phosphoric acid fuel cell stack. Therefore, postprocessing which reduces this CO is necessary. Because of the above, the natural gas reforming unit is basically made up of three catalytic reactors with desulfurizing, reforming, and shift converting functions, respectively.

2.2.1 Desulfurizer

Since the life of the reformer catalyst varies substantially with the sulfur density, the desulfurizing operation is an important factor which has an affect all the way up to the reformer design specifications.

From the beginning of development in 1986 to the present, the hydrogenating desulfurizing method and adsorption desulfurizing method were selected and evaluated as desulfurizing methods to amply remove the comparatively low density sulfur compounds of 10 ppm or less included in natural gas and town gas.

The hydrogenating desulfurizing method is a method which causes dimethylsulfide (DMS), tertiary-butylmercaptan (TBM), and other organic sulfur compounds to react with hydrogen at a temperature of 300 to 350°C under a cobalt molybdenum (Co-Mo) or nickel molybdenum (Ni-Mo) catalyst and turns them into hydrogen sulfide (H₂S) and chemically absorbs by zinc oxide (ZnO) and is comparatively compact. The chemical adsorption desulfurizing method attempts adsorption removal at a temperature ranging from normal room temperature to about 250°C with a Cu compound catalyst. It is a desulfurizing method aimed at simplification of the system. Its features include no need for recycled hydrogen and wide range of catalyst bed temperature.

The actual unit uses one of these methods. For an on-site fuel cell power plant, in particular, independent temperature control in the desulfurizing part is omitted and the result is that the temperature of the desulfurizing catalyst bed changes with the change of the flow rate of raw material

accompanying load changes.

Since the reformed hydrogen is recycled for hydrogenation in the system itself, hydrogenation hydrogen is not supplied at startup. In such various cases, measures must be taken so that desulfurizing performance does not drop.

2.2.2 Reformer

During the period from 1980 to 1985 when development of the phosphoric acid fuel cell power generating system as a test plant started, development of reformer was mainly conducted cooperatively with engineering firms with a record of achievements with large reforms for conventional chemical plants. From 1986, a development contract for an on-site fuel cell power plant of about 50 to 100 kW was concluded with a major gas manufacturer and independent development aimed at small size and cost reduction was started. Especially, the development point was made maximum utilization of the performance of the catalyst while considering the supply of thermal energy for reaction.

2.2.3 CO shift converter

Full-scale development of a CO shift converter was started in 1986 together with the desulfurizer and reformer. The reformer catalyst bed is controlled so that the catalyst bed is maintained at a temperature high enough to raise the reaction rate of (3) of the reactions previously mentioned. On the other-hand, the reaction of (4) is a heat generating reaction and from the standpoint of chemical reaction balance, a higher reaction rate is obtained at low temperature as long as the reaction speed is not limited by catalyst activity. Therefore, the reformer outlet gas contains 10 to 20% of CO. To reduce this CO, in the past a process consisting of a reactor filled with an Fe compound catalyst or a Cu compound catalyst and a heat exchanger which removes the reaction heat was used.

The functions of this process were simplified here by using only a Cu compound catalyst reactor with built-in heat exchanger. The reformed gas is sent to mono tube shift cooled by pressurized water and the CO concentration is reduced to 1% or less which is allowable to be supplied to the fuel cell stack.

less which is allowable to concentration be supplied to the fuel cell stack.

2.3 LPG reforming unit

Whereas the main component of town gas (LNG) is methane, the main component of liquefied petroleum gas

(LPG) is propane or butane. The basic configuration of the reforming unit is the same as for town gas, but careful attention must be given to such points as (1) desulfurization of the large sulfur content is important, (2) a large steam/carbon (S/C) ratio must be taken at reforming at which the carbon/hydrogen atoms ratio in the raw material is large, and (3) when a large amount of unsaturated hydrocarbons is included, hydrogenation to saturated hydrocarbons is necessary.

For combustibility by burner also, while luminous flame occurs easier than natural gas, the high calorific value per unit volume must be taken into account.

2.4 Naphtha reforming unit

Development of an on-site fuel cell with naphtha as the raw material is being conducted by oil companies under the Petroleum Energy Center. Fuji Electric has developed a naphtha reformer cooperatively with Idemitsu Kosan Co., Ltd. The capacity was a hydrogen generation amount for 50 kW and a catalyst developed by Idemitsu Kosan Co., Ltd. was used. First, one unit was installed at the Idemitsu Kosan Co., Ltd. Central Research Laboratory in Anegasaki as an independent hydrogen generating unit. Later a 20 kW fuel cell stack was installed and independent operation or operation combined with the fuel cell was made possible. Innovations suitable for naphtha reforming, such as operation by changing the steam/carbon ratio substantially or stable evaporation of the naphtha, were made. This unit has already been operated for more than 5,200 hours.

A 50 kW fuel cell power plant was designed and manufactured, utilizing the results above. This system is currently operating in the Idemitsu Kosan Co., Ltd. Central Research Laboratory. The reforming unit in this system is almost the same as the unit previously described, but we want to plan development of a new reformer that utilizes the results to be obtained so far.

3. CONCLUSION

Development process of the reforming unit for fuel cell was introduced above. In the future, we want to develop a reformer for fuel cell power plant with still better performance based on the result of actual operation.

Finally, the authors wish to thank the concerned parties for their guidance and encouragement regarding this reforming unit development.