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Development of a high efficiency substitute natural gas production process

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Abstract

We have developed a high efficiency process for producing a substitute natural gas using LPG and naphtha as raw materials. In the process, sulfur poisoning of the steam reforming catalyst is protected and the amount of catalyst used can be reduced applying a high performance desulfurization technology developed. This technology enables the removal of trace amounts of sulfur which cannot be removed by a conventional hydro-desulfurization method. In addition, we have developed a high performance steam reforming catalyst which has a resistance to carbon deposition even under low S/C conditions. The catalyst makes it possible to reduce excessive steam for preventing carbon deposition, and to operate with high thermal efficiency.

Keywords: Steam reforming; Desulfurization; Low S/C

1. Introduction

The substitute natural gas (SNG) production process is a process by which a gas having properties (e.g., composition, heating value, and combustibility) identical to natural gas is produced from various kinds of hydrocarbons, including coal, crude oil, naphtha, or LPG. Japanese city gas companies are pressing ahead with a plan to supply gas intensive and increase the heating value of city gas to improve safety, convenience, and cost efficiency. In Japan, however, local city gas companies have difficulty in introducing natural gas inexpensively of scale and cost, because natural gas is imported as LNG (liquid natural gas) in a large scale. Therefore, they are investigating the way to increase the calorific value of the supply gas by adopting SNG, which requires less investment than that of LNG. We have been developing high efficiency, low environmental impact and compact SNG production process for local city gas companies based on a low temperature steam reforming reaction using LPG and naphtha as raw materials.

Fig. 1 shows the outline of the general SNG production process flow. First, sulfur contained in raw materials such as LPG and naphtha is removed in the desulfurization reactor. Next, the raw material desulfurized is reacted with steam in the steam reformer to degrade the hydrocarbon into methane, H_2, CO and CO_2. Such gas is converted into gas with higher concentrations of methane by reacting with CO, CO_2, and H_2. Then, CO_2 is removed in the decarbonating equipment, and the heating value is finally controlled by adding LPG.

Steam reforming reactions of hydrocarbons are described as follows:

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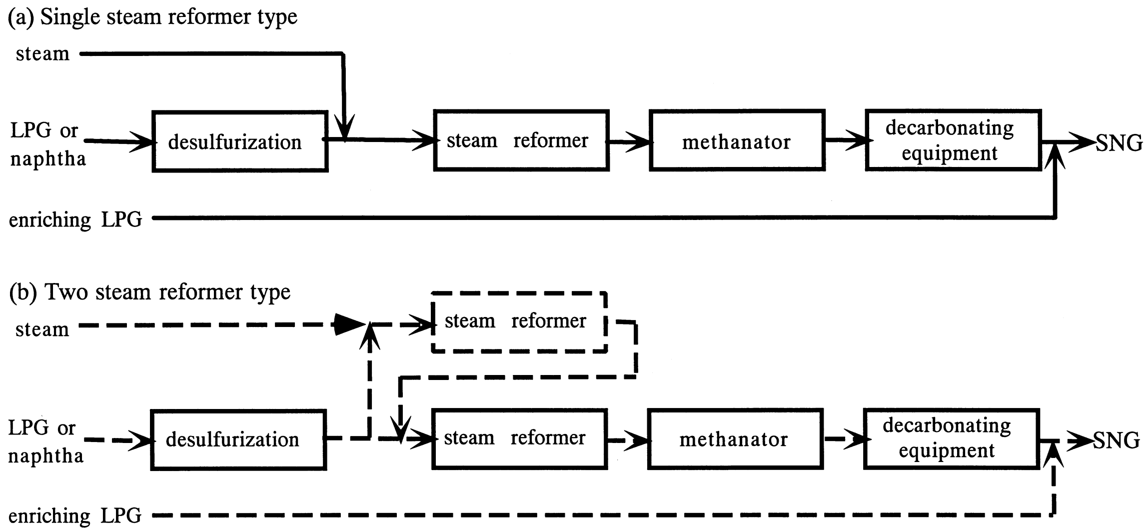

Fig. 1. Flow sheet of substitute natural gas production process.

$$C_nH_m + nH_2O \rightarrow nCO + (n + m/2)H_2 \quad (-\Delta H < 0) \tag{1}$$

$$CO + 3H_2 \Leftrightarrow CH_4 + H_2O \quad (-\Delta H = 206.2\,\mathrm{kJ\,mol^{-1}}) \tag{2}$$

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \quad (-\Delta H = 41.2\,\mathrm{kJ\,mol^{-1}}) \tag{3}$$

The gas composition obtained from chemical formulae (2) and (3) reaches thermodynamic equilibrium when the steam reforming catalyst is sufficiently active. As a result, gas composition is determined if the reaction temperature, pressure, and S/C (mole ratio of steam to carbon in the hydrocarbon in the raw material) are specified. To produce gases with high concentrations of CH_4, it is advantageous to select low reaction temperature, high pressure, and low S/C. In the compact SNG production process, the reaction pressure is usually in the range from 0.7 to 1 MPa to avoid the regulations of high pressure gas. Hence, for high efficiency SNG process operation, it is necessary to have these conditions present for the steam reforming reaction:

1. low reaction temperature, and
2. low S/C.

But we face the following problems to achieve such a high efficiency SNG process.

2. Problems

2.1. Desulfurization

The hydro-desulfurization method is generally used for desulfurization in the steam reforming process. Sulfur concentration after desulfurization is said to be approximately 0.1 ppm, but even about 0.1 ppm of sulfur affects the catalyst used in the post-process. The research by McCarty, SRI, revealed that in equilibrium state, over 80% of the active metal surface of steam reforming catalyst is covered with sulfur due to existence of 0.1 ppm of H_2S under the conditions of SNG process, and it is impossible to avoid deterioration due to sulfur poisoning [1,2]. For this reason, it is necessary to develop a desulfurization method capable of removing very low concentrations of sulfur of 0.1 ppm or less.

2.2. Steam reforming

To improve the efficiency of the SNG process, the steam reforming reaction needs to occur at a low S/C ratio. Reduced S/C may cause the problem of carbon deposition on the catalyst. In a large-scale SNG facility, steam reformer towers are installed to inject the raw material of hydrocarbons evenly between the two towers (Fig. 1(b)) so that S/C can be increased in the first steam reformer to prevent carbon deposition at the inlet of the catalyst layer where carbon deposits easily. On the other hand, a compact SNG process, low S/C operation must be carried out on a single tower reformer due to investment cost requirement. Consequently, we need a steam reforming catalyst having a high resistance to carbon deposition.

3. Features of the OG process

3.1. High performance desulfurization technology

We have developed a high performance desulfurization (HPDS) agent capable of removing sulfur into very low concentrations of 0.1 ppm or below which cannot be removed by the conventional methods, thereby enabling desulfurization to a ppb order or less. An advanced desulfurization process is applied after reducing the sulfur content to 0.1 ppm or less by placing the high performance desulfurization agent downstream of the hydro-desulfurization catalyst (Ni–Mo or Co–Mo) and combined with adsorption agent (ZnO). This makes it, and it is made possible to prevent sulfur from poisoning of the steam reforming catalyst, prolonging the life of catalyst. This high performance desulfurization agent incorporates many merits, as follows:

1. Sulfides in the desulfurization agent are highly stable, resulting in a high sulfur adsorbing ability compared with ZnO.
   - The equilibrium concentration of inorganic sulfur is extremely low.
   - Organic sulfurs such as thiophene can be removed.
2. Side reactions such as methanation scarcely occur when this agent is used, which is possible in the SNG process where the recycled gas for hydrogenation contains much CO and CO_2.
3. The agent has stable strength and structure under operation conditions, and causes no carbon deposition.
4. The agent has sufficient sulfur adsorption capacity.
5. The agent is not expensive.

Fig. 2 shows the profile of the adsorbed sulfur content after a lab-scale experiment of desulfurization of full range naphtha for 1500 h. At the ZnO adsorbent inlet, the sulfur compounds transformed into H_2S by hydro-desulfurization catalyst are adsorbed. Though a large part of ZnO layer has not adsorbed sulfur sufficiently, sulfur is still adsorbed at the inlet of a high performance desulfurization agent installed after the ZnO layer. Measurements by fluorescent X-ray spectrometry revealed that sulfur in steam reforming catalyst was below the detection limit. This result indicates that the high performance desulfurization agent prevents sulfur poisoning by adsorbing sulfur which cannot be removed by the conventional hydro-desulfurization method.

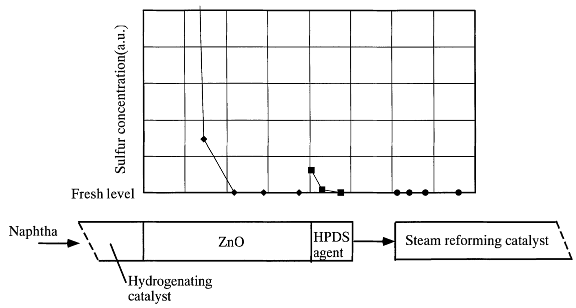

Fig. 2. Sulfur content adsorbed on catalyst layers.

3.2. High performance steam reforming catalyst

The tendency towards carbon deposition of conventional steam reforming catalyst was compared with that of our catalyst as shown in Fig. 3. The conventional catalyst is apt to deposit carbon under S/C=1.5. Therefore, it is difficult to operate the process at an S/C ratio of not more than 1.5 even for a short time. On the other hand, our catalyst enables process operation even when S/C is below 1.5. Fig. 4 shows the results of the evaluation of long term carbon deposition using light naphtha as the raw material at S/C=0.85. The amount of carbon on the catalyst stabilized after increasing at the initial stage, which indicates that the process can be operated at S/C=0.85 without the problems of carbon deposition. Another test was conducted under the same conditions except for using LPG as a raw material, and the results revealed that carbon deposition problem is trivial even at S/C=0.6. As a result, our catalyst enables low S/C operation by which the steam required in a process can be reduced.

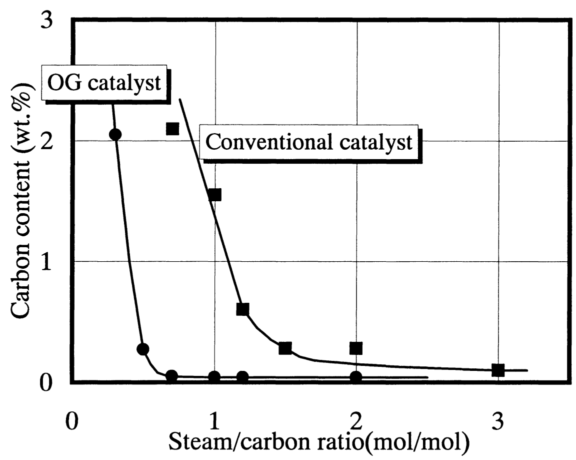

Fig. 3. Coking resistance of steam reforming catalyst. Feed: desulfurized light naphtha, H_2/oil=0.1 (molar ratio), temperature: 490°C, pressure: 0.5 MPa, LHSV: 1.0 h^{-1}, and time: 4 h.

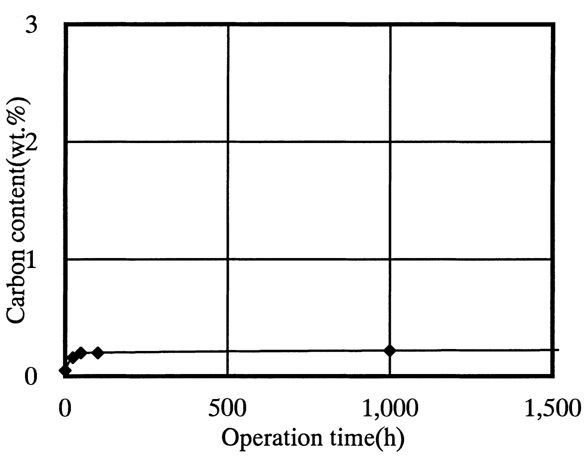

Fig. 4. Coking resistance of steam reforming catalyst. Feed: desulfurized light naphtha ($C_{5.5}H_{12.78}$), S/C=0.85, H_2/oil=0.3 (molar ratio), temperature: 487°C, and pressure: 0.7 MPa.

Consequently, a high heat efficiency SNG production process becomes possible with our catalyst.

In addition, the reactor can be miniaturized because this catalyst has high activity, and the activity remains high without sulfur poisoning by applying to our high performance desulfurization technology.

3.3. Demonstration result

Considering these results, a demonstration test (10 000 Nm^3/day) was conducted using LPG as a

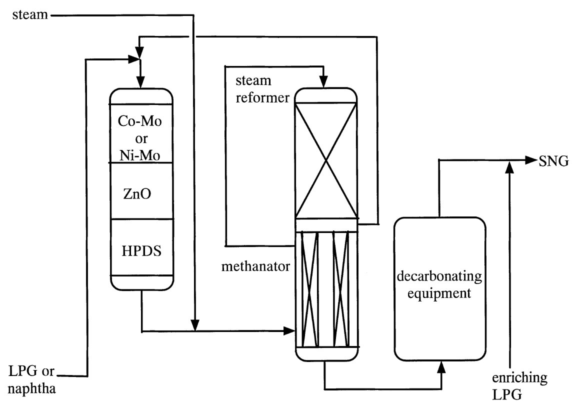

Fig. 5. Flow sheet of OG type compact SNG production process.

raw material. Fig. 5 shows the flow chart of OG type compact SNG production process. Fig. 6 is the temperature profile in the layers of the steam reforming catalyst in the demonstration plant. Any shift in the temperature profile indicating deactivation of the catalytic activities are not seen after 4000 h of operation using LPG as a raw material under the condition of a low S/C ratio of 0.8. At this time, the process has achieved an epoch-making heat efficiency of 97.4%, which is attributed to the low S/C operation without surplus steam. The analytical results of the catalyst after the demonstration test showed no problems.

Based on the results of the demonstration test, our process has already been adopted by local city gas companies. These SNG facilities have satisfactorily been operated for more than two years.

As mentioned in previous sections, it has been proved that light naphtha can also be used as a raw material in the SNG process. Based on these results, it is scheduled to operate an actual plant using light naphtha as raw material.

4. Conclusion

The characteristics of the OG type SNG production process are summarized in Fig. 7. Our high performance desulfurization technology prevents sulfur poisoning of the steam reforming catalyst which is inevitable in the case of the conventional desulfurization method and leads to the reduction of the amount of steam reforming catalyst. In addition, using of our

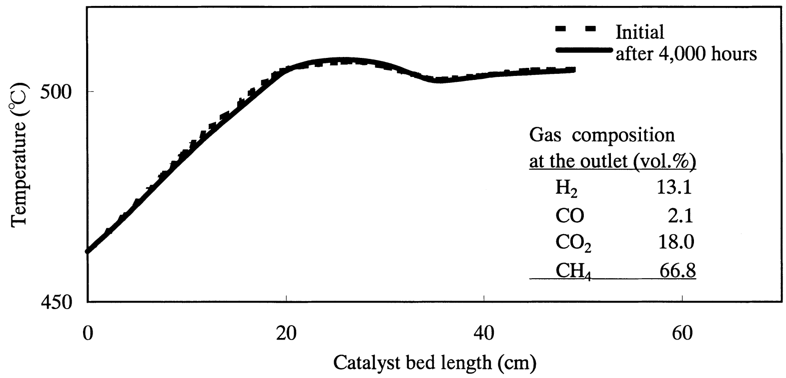

Fig. 6. Temperature profile in the layers of the steam reforming catalyst in the demonstration plant. Law material: butane, S/C=0.8.

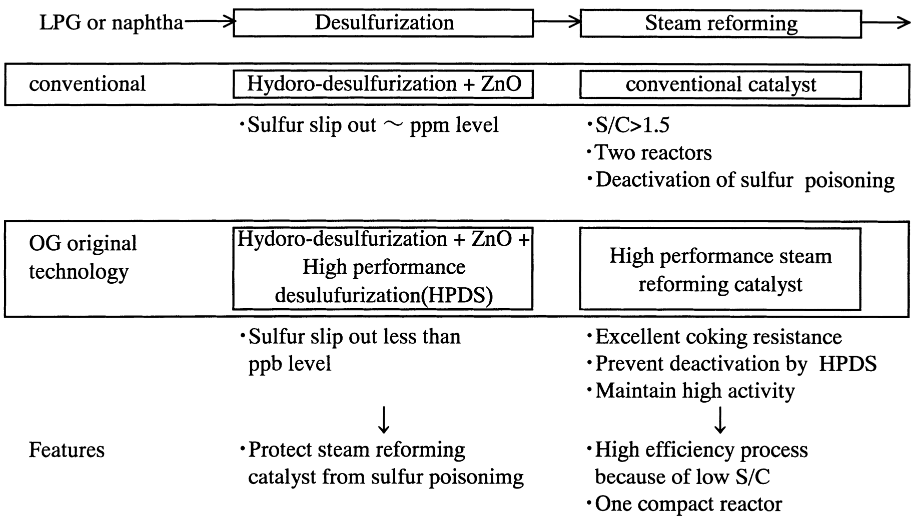

Fig. 7. Features of the OG type compact SNG production process.

high performance steam reforming catalyst made it possible to perform low S/C operation which had been impossible due to carbon deposition, resulting in reducing the use of excessive steam to prevent carbon deposition. This allows a reduction in the number of reactors, and an epoch-making SNG production process with high heat efficiency of 97.4% has been achieved, contributing to reducing environmental impact.

References

[1] J.G. McCarty, H. Wise, J. Chem Phys. 72 (1980) 6332.
[2] J.G. McCarty, H. Wise, J. Chem Phys. 74 (1981) 5877.