

Development of Innovative Methanol Synthesis Process Based on Self-Heat Recuperation

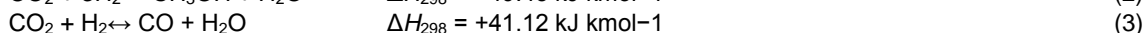
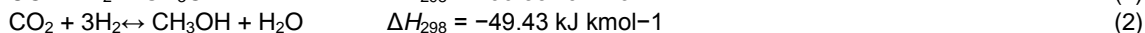
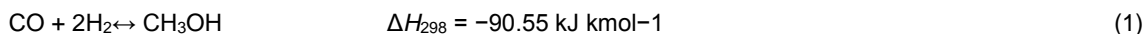
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In recent years, the demand for methanol will continue increasing. As well as other chemical processes, many methanol synthesis processes have reactant recycle system with product separation due to the low conversion ratio of the reactor. For this product separation from reactant recycle stream, a gas-liquid separator or distillation process has often been used. However, this gas-liquid separator and distillation processes are well known as an energy intensive process. Thus, many chemical engineers and investigators have been managing to produce a catalyst which achieves high conversion from reactant to production in the reactor for whole process optimization. In contrast, authors have developed self-heat recuperation technology based on exergy recuperation, in which whole process heat is utilized without any additional heat, leading to the reduction of energy requirement in several chemical processes. In this research, we developed an innovative integrated process design method based on self-heat recuperation for methanol synthesis process from energy saving point of view.

1. Introduction

Recently, the demand for methanol will continue increasing, since methanol is attractive as a fuel for fuel cells, and an intermediate raw material of hydrogen and dimethyl ether (DME) which are categorized a green energy source. Currently, most of methanol is produced from fuel, especially natural gas and coal by steam reforming and gasification reactions. At first, methane from fuel is mixed with steam and reformed to carbon monoxide and hydrogen with catalyst. Then, methanol and water mixture is produced from carbon monoxide and hydrogen. The reactions of methanol synthesis are mainly composed by the following three reactions; CO and CO₂ hydrogenation and the reverse water-gas shift reaction (Farsi and Jahanmiri, 2011)



where ΔH_{298} is the heat of reaction at standard temperature and pressure, i.e. 298 K and 1 atm.

From the thermodynamic equilibrium point of view, it can be seen from above Eqs. (1)-(3) that the suitable condition for this methanol synthesis reaction is low temperature and high pressure.

As well as other chemical processes, many methanol synthesis processes have reactant recycle system with product separation due to the low conversion ratio of the reactor and low product purity. For this product separation from gas reactant recycle stream, the product mixture from reactor is usually fed through a gas-liquid separator to achieve high reaction conversion. However, this process is well known as an energy consuming process because of the condensation latent heat. Thus, many chemical engineers and investigators have been managing to produce a catalyst which achieves high conversion from reactant to production in the reactor for reducing the recycle flow rate owing to increase of operation energy (Fuad et al. 2012).

Authors have developed self-heat recuperation technology, in which the whole process heat is utilized without any additional heat, leading to reduction of energy requirement in several chemical processes.

This self-heat recuperation technology is suitable for thermal and separation processes and is applied to several chemical processes for energy saving as case studies.

In this research, we investigated the feasibility of applying self-heat recuperation technology to the methanol synthesis process. An innovative integrated process design method has been developed from the energy saving point of view. This design method is expected to have an effect to the catalyst selection, reactor and the whole process designs.

2. Self-heat recuperation technology

Self-heat recuperation technology (Kansha et al. 2009a) facilitates recirculation of not only latent heat but also sensible heat in a process, and helps to reduce the energy consumption of the process by using compressors and self-heat exchangers based on exergy recuperation (Matsuda et al. 2010a). In this technology, i) a process unit is divided on the basis of functions to balance the heating and cooling loads by performing enthalpy and exergy analysis and ii) the cooling load is recuperated by compressors and exchanged with the heating load. As a result, the heat of the process stream is perfectly circulated without heat addition, and thus the energy consumption for the process can be greatly reduced (c.f. Figure 1).

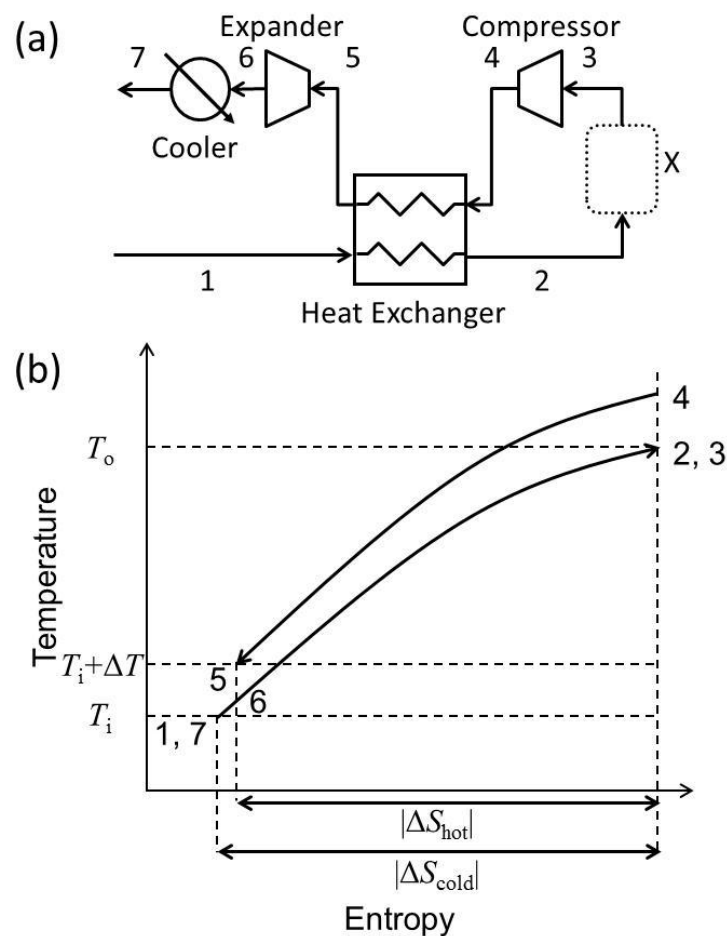


Figure 1: A self-heat recuperative thermal process in the case of a gas fluid: a) flow diagram b) temperature-entropy diagram (Matsuda and Kansha 2012)

In this process, energy for compression is needed to drive the internal heat circulation according to the irreversibility when the adiabatic efficiencies of compressor and expanders are 100 %. Generally, process units consist of several functions such as heating, cooling, reaction, and separation.

Kansha et al. (2013) reported that that this process is inherently designed by accounting for this minimum exergy loss for heat transfer in heat exchangers. Ultimately, the energy required for a thermal process based on self-heat recuperation is equal to the minimum exergy loss during heat transfer when infinite

numbers of compressors and heat exchangers are used alternatively and the compressors work adiabatically.

Expanding the self-heat recuperative thermal process to separation processes such as distillation for azeotropic mixture (Kansha et al. 2009b), for benzene-toluene mixture (Kansha et al. 2010), and for industrial benzene-toluene separation plant (Matsuda et al. 2010b), a system including not only the separation process itself but also the preheating/cooling section, can be divided on the basis of functions, namely the separation module and the heat circulation module, in which the heating and cooling loads are balanced. The enthalpy of inlet stream is equal to the sum of the outlet streams enthalpies in each module. The cooling load in each module is then recuperated by compressors and exchanged by using compression work.

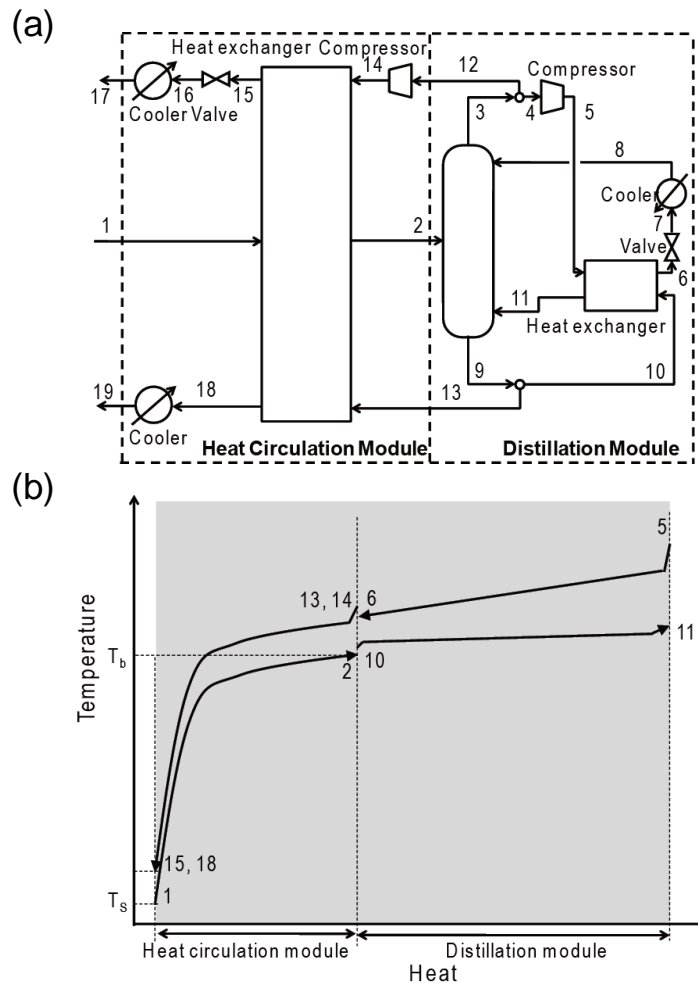


Figure 2: Distillation process with a self-heat recuperation technology: (a) process flow diagram, (b) temperature-heat diagram (Matsuda and Kansha 2012)

3. Methanol synthesis process

Methanol is produced from reformed carbon monoxide and hydrogen from fuel with catalyst. It is well known that the basic material of this catalyst is nickel. After reactions taking place in the reactor, product mixture from reactor contains not only product methanol and water due to sub-reactions represented by Eq.(2) and Eq.(3), but also reactant gases. As well as other many chemical processes, this methanol synthesis processes equip reactant recycle system with product separation. For this product separation from reactant recycle stream, the product mixture from reactor is fed through a gas-liquid separator to achieve a high reaction conversion as shown in Figure 3. Then, the product which contains from methanol and water mixture is fed into distillation processes to purify methanol. However, these gas-liquid separator and distillation processes for reactant recycling and for purification of product methanol are energy

consuming processes (Luyben 2010). Thus, conventionally, many chemical engineers and investigators have been managing to produce a new catalyst which achieves high conversion and selectivity from reactant to production in the reactor for reducing the energy consumption of recycle system by reducing recycle flow rate.

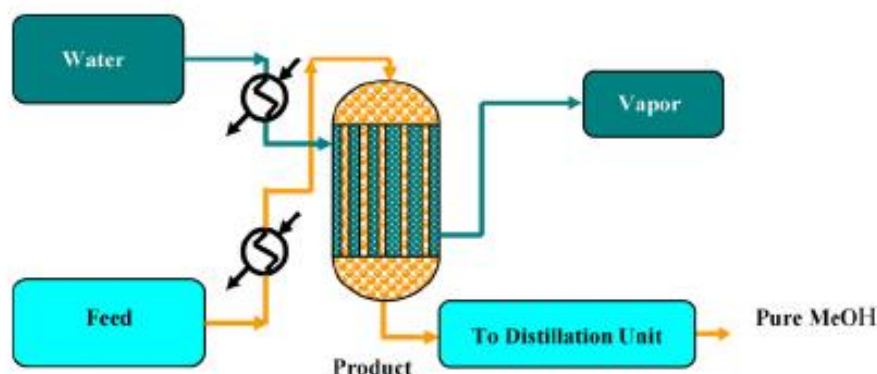


Figure 3: The schematic of a methanol synthesis reactor (Lurgi type: Farsi and Jahanmiri 2011)

4. Simulation results

To investigate the feasibility of the application of the self-heat recuperation technology to the methanol synthesis process, the energy consumption of the methanol production process as compared with the benchmark process was examined by commercial process simulator (PRO/II Ver. 9.0, Invensys). The process simulation conditions such as composition, temperature and pressure of the streams were defined on Table 1. This data is simplified data from the process flow diagram which was calculated for a LPMEOHTM demonstration unit as shown in Figure 4 (Heydorn et al. 2003). By following Table 1 and Figure 4, we designed the benchmark and self-heat recuperative processes on the simulator and examined the energy saving potential of the self-heat recuperation technology. By following the self-heat recuperation technology, benchmark process is divided into three sections; reaction section included into thermal process, reactant recycle section, and product purification section. In this research, we applied the self-heat recuperation technology to each section for minimizing the energy consumption under consideration of keeping state conditions around reactor (Table 1). By simulations the energy consumption of the benchmark process and the process with the self-heat recuperation technology are 6.6 MW (= 3.94 for electricity + 2.66 for heat) and 4.4 MW for electricity. Simulation results show that the self-heat recuperation technology drastically reduces the energy consumption of the gas-liquid separator for recycling system as compared with that of the conventional process.

Table 1: Heat and Material Balance Summary

| Stream No. | 10 | 20 | 30 | 109 | 120 | 149 |
|-----------------|-------|-------|-------|---------|---------|---------|
| Pressure [kPa] | 202.7 | 202.7 | 202.7 | 5067.8 | 5067.8 | 344.5 |
| Temperature [C] | 37.8 | 37.8 | 37.8 | 121.1 | 121.1 | 40.5 |
| Molar Flow Rate | | | | | | |
| H2 [kmol/h] | 1.2 | 35.4 | 730.0 | 1,998.7 | 1,347.4 | 1,231.3 |
| CO [kmol/h] | 58.0 | 5.3 | 298.3 | 825.8 | 509.3 | 464.7 |
| N2 [kmol/h] | 0.60 | 5.7 | 5.4 | 133.5 | 133.5 | 121.7 |
| CO2 [kmol/h] | 0 | 1.4 | 43.1 | 297.3 | 288.4 | 253.1 |
| MEOH [kmol/h] | 0 | 0 | 0 | 19.3 | 338.0 | 19.3 |
| H2O [kmol/h] | 0 | 0 | 0 | 0.20 | 9.83 | 0.20 |

need of consideration to enhance the self-heat recuperation technology to the reactor is the methodology to define how to treat this heat.

6. Conclusions

In this paper, we examined the feasibility of the application of self-heat recuperation technology to the methanol synthesis process. An innovative integrated process design method has been developed for it from energy saving point of view. By installing the self-heat recuperation technology to the methanol synthesis process, the energy consumption of the process is drastically reduced. It can be seen that this phenomenon shows the necessity of a new process design methodology from the perspective of energy saving.

References

- Farsi M., Jahanmiri A., 2011, Methanol production in an optimized dual-membrane fixed-bed reactor, *Chem. Eng. Process.* 50, 1177-1185.
- Fuad M.N.M., Hussain M.A., Zakaria A., 2012, Optimization strategy for long-term catalyst deactivation in a fixed-bed reactor for methanol synthesis process, *Comput. Chem. Eng.*, 44,104-126.
- Heydorn E. C., Diamond B. W., Lilly R. D., 2003, Commercial-scale demonstration of the liquid phase methanol (LPMEOHTM) process, Final Report (Volume 2: Project Performance and Economics) DE-FC22-92PC90543, Department of Energy National Energy Technology Laboratory, Washington DC, USA.
- Kansha Y., Tsuru N., Sato K., Fushimi C., Tsutsumi A., 2009a, Self-heat recuperation technology for energy saving in chemical processes, *Ind. and Eng. Chem. Res.*, 48, 7682-7686.
- Kansha Y., Tsuru, N., Fushimi C., Tsutsumi, A., 2009b, A new design methodology of azeotropic distillation processes based on self-heat recuperation, *Chemical Engineering Transactions*, 18, 51-56.
- Kansha Y., Tsuru, N., Fushimi C., Tsutsumi, A., 2010, Integrated process module for distillation processes based on self-heat recuperation technology, *J. Chem. Eng. Japan*, 41, 446-452.
- Kansha Y., Aziz M., Kishimoto A., Tsutsumi A., 2013, Evaluation of a self-heat recuperative thermal process based on thermodynamic irreversibility and exergy, *J. Chem. Eng. Japan*, 46, 87-91.
- Luyben W.L., 2010, Design and Control of a Methanol Reactor/Column Process, *Ind. Eng. Chem. Res.* 49, 6150–6163
- Matsuda K., Kawazuishi K., Hirochi Y., Sato R., Kansha Y., Fushimi C., Shikatani Y., Kunikiyo H. and Tsutsumi A., 2010a, Advanced energy saving in the reaction section of hydro-desulfurization process with self-heat recuperation technology, *App. Therm. Eng.*, 30, 2300-2306.
- Matsuda K., Kawazuishi K., Kansha Y., Fushimi C., Nagao M., Kunikiyo H., Masuda F. and Tsutsumi A., 2010b, Advanced energy saving in distillation process with self-heat recuperation technology, *Chemical Engineering Transactions*, 21, 31-36.
- Matsuda K., Kansha Y., 2012, Advanced energy saving and its application in industry, Part II Application of Self-Heat Recuperation Technology, Chapter 3 Distillation Section, Eds. Matsuda K., Tsutsumi A., Springer, Berlin, Germany.