Application of chemical heat transformer for co-production system

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1. Introduction

Recently, energy usage has acquired more attention than before. Co-production becomes a key word for energy saving. Especially, in chemical engineering, co-production system means a network system for process heats. A typical example of this co-production system is to transfer reaction heat from exothermic reaction to endothermic reaction. In fact, most of heat from exothermic reaction is not effectively used and discarded into coolers as low exergy heat, and that in endothermic reaction is provided by fuel combustion in industries, leading to enormous energy consumption and exergy loss. Needless to say, co-production system helps energy saving if the exhausted heat from exothermic reaction can be effectively transported to endothermic reaction (including power generation). Possible configurations of the representative co-production system are summarized in Figure 1.
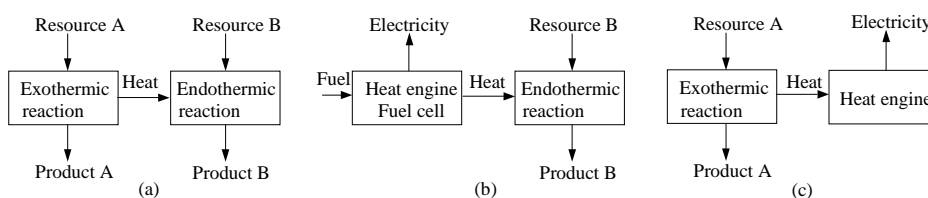

Figure 1: The configuration examples of co-production system

To configure a co-production system (heat network system), development of effective heat transportation among processes is the most important task. For the material of this heat transportation, some of researchers have adopted phase change materials (PCM) (Maruoka et al. 2002, Nomura et al. 2010). PCM are a suitable material for storage of heat, because latent heat of during phase change is quite large. However, the temperature of charging/discharging heat cannot be adjusted by some other parameters. Thus, PCM can be used to transport heat from high temperature heat source to low temperature heat sink as heat cascading utilization. However, the temperature of exhausted heat in industries is not high enough for heat source. Thus, the method such

as heat pump which can transport heat from low temperature heat source to high temperature heat sink is required to design co-production system for various processes, leading to process energy saving. But heat pump is not suitable to supply high temperature heat. Chemical heat pump which transports heat by using heat of reaction has been researched to use for the heat recovery (Dokiya et al. 1996, Saito et al. 1994). However, these chemical heat pumps are only developed for low temperature range (100~350 ℃) and for heat recovery of exhausted heat.

To realize the desired heat transportation among processes in high temperature range (600~900 ℃), we have focused on chemical heat transformer, in which the heat among processes are transported using equilibrium reaction based on exergy recuperation to achieve co-production system, and evaluated the transport performance of this system and the feasibility of co-production system in this study.

2. Chemical heat transformer

Chemical heat transformer is the heat transportation system among processes by using chemical reaction to realize co-production. To be concrete, this chemical heat transformer has two roles, a heat engine and a heat pump, depending on the temperatures of heat sources and sinks. Figure 2 shows the schematic flow diagram in the case (a) of Figure 1 of a chemical heat transformer and chemical reactions as heat source and sinks. In this figure, chemical heat transformer receives the heat from exothermic reaction (R1, heat source) by endothermic reaction (CR1) and provides the heat to the endothermic reaction (R2, heat sinks) by exothermic reaction (CR2). Note that products of CR1 and CR2 are separated into each gas and stored in a holding tank. To use this system, heat can be effectively transported among processes due to the heat of chemical reaction. In the case that the temperature of R1 is higher than that of R2, this chemical heat transformer works as a heat engine as shown in Figure 3. In contrary, in the case that the temperature of R1 is lower than or equal to that of R2, it works as a heat pump as shown in Figure 4. It can be seen from Figure 3 and 4 that a part of the heat of exothermic reaction is transformed to the electric power and that compression works of heat pump is transformed to the product heat of R2. However, the heat difference between CR1 and CR2 is theoretically 0 and this system can effectively transport heat among processes without exergy loss.
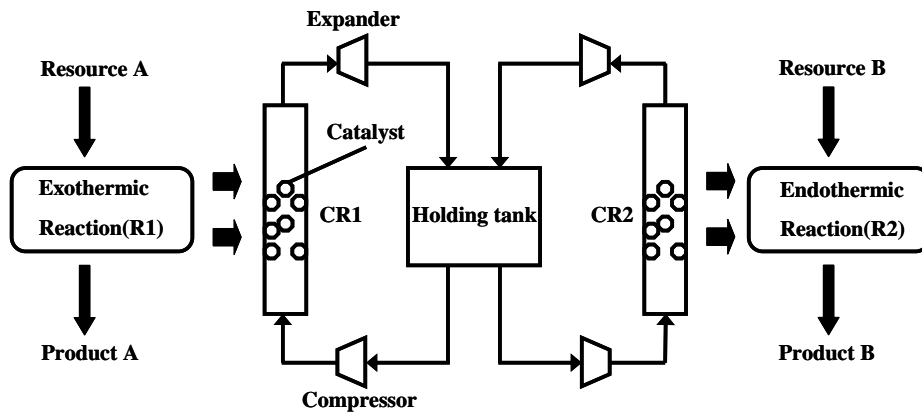

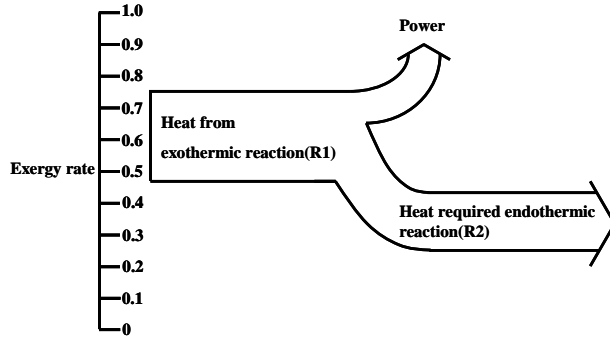Figure 2: The configuration example of chemical heat transformer

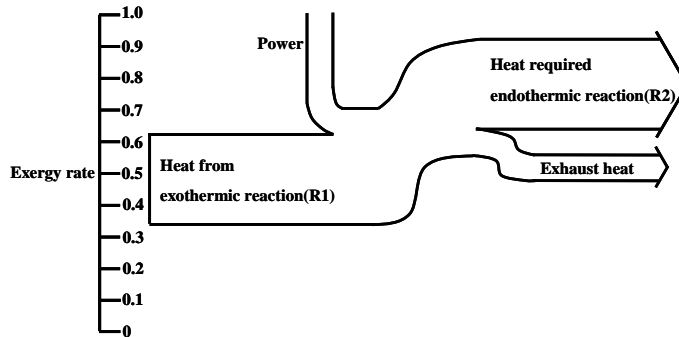Figure 3: Chemical heat transformer work as a heat engine

Figure 4: Chemical heat transformer work as a heat pump

3. Simulation Apparatus

Steam methane reforming was adopted as a reaction of chemical heat transformer because steam methane reforming reaction proceeds at high temperature (700~1100 ℃ in commercial plants) . The process which uses this reaction has been operated for a long time in many commercial plants. Thus, there are so many data and catalysts information about this process. This reaction can be written by the following chemical equations;

$$CH_4(g) + H_2O(g) \Leftrightarrow CO(g) + 3H_2(g), \quad \Delta H = 206 kJ/mol \qquad (1)$$

$$CO(g) + H_2O(g) \Leftrightarrow CO_2(g) + H_2(g), \quad \Delta H = -40 kJ/mol \qquad (2)$$

where Eq. 1 represents the steam methane reforming reaction and Eq. 2 represents the shift reaction from CO to CO_2. The performance of heat transportation was examined by using a commercial process simulator, PRO/II (Invensys, version 8.1), and we adopted Soave-Redlich-Kwong for thermodynamics. We divided the chemical heat transformer into two processes which are steam methane reforming process (SMR) and methanation process (METHANATION). We developed each process based on self-heat recuperation technology as they are shown in Figure 5 and 6. Self-heat recuperation technology is employed to design processes (Kansha et al. 2009). Conversion in each process is determined by thermodynamic equilibrium. We set reaction temperature as a parameter and analyzed the sensitivity of the parameter to find a suitable condition for each process. In both processes, the range of reaction temperature was between 600 and

900 °C, and adiabatic efficiency was 100%. Reaction pressures were 10 and 30 atm in SMR and METHANATION respectively. Furthermore, the minimum temperature differences were kept to be constant at 10 and 50 K in SMR and METHANATION, respectively. Note that generally the pinch points in heat exchangers are located at low temperature zone in SMR and at high temperature zone in METHANATION. Feed ratios of H_2O/CH_4 in SMR and H_2/CO in METHANATION were equal to 3.0. The amount of reaction heat in each process was kept to be constant at 100 kW.

ΔE_{HX} represents the exergy loss which occured in heat exchager due to temperature difference between hot and cold fluids in the countercurrent heat exchanger. Furthermore, $\Delta E_{reaction}$ is the exergy loss which occurred owing to chemical reaction and represents the difference between total exergy change in the reaction and reaction heat exergy. The products of each reaction were separated into each component, hence, the separation energy is required to operate the chemical heat transformer. We calculated the ideal separation energy ($\Delta E_{separation}$) from component of product gas. We considered the total exergy loss as sum of ΔE_{HX}, $\Delta E_{reaction}$ and $\Delta E_{separation}$. We evaluated the performance of each process as *LOX* defined as:

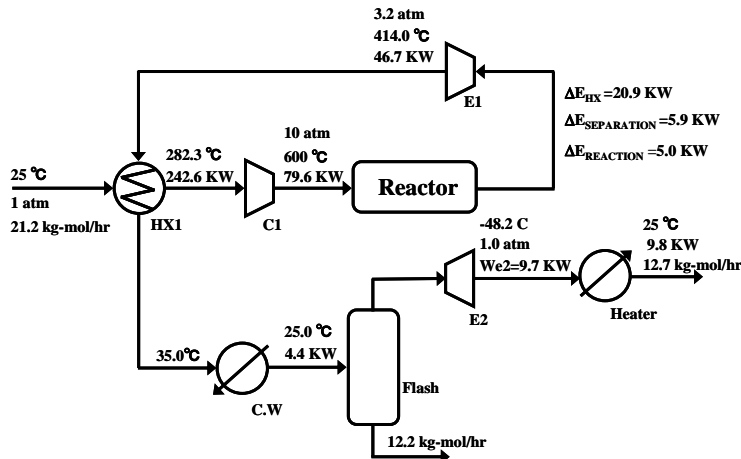$$LOX = \frac{total\ exergy\ loss}{reaction\ heat\ exergy} \tag{3}$$

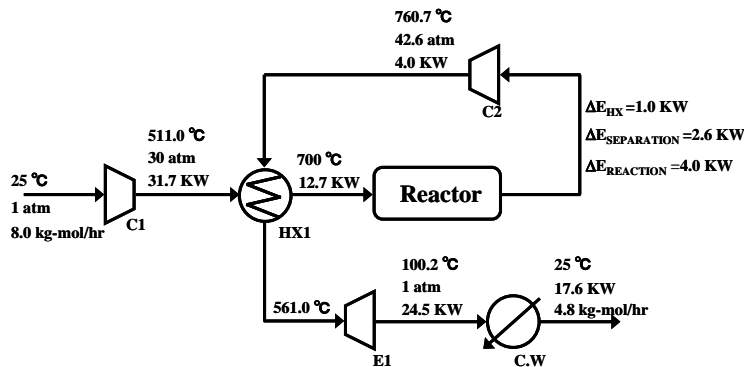*Figure 5: Process module of SMR with self-heat recuperation technology*

Figure 6: Process module of methanation with self-heat recuperation technology

4. Simulation results

In order to estimate the performance of each process, we set reaction temperature as a parameter. The simulation result is shown in Figure 7. Although the performance of SMR was not so high at lower temperature, it is gradually increasing with the reaction temperature rise. As the reaction temperature rises, the conversion ratio increases, leading to that the amount of heat preserved by SMR became larger. ΔE_{HX} is larger than other exergy loss and accounted for more than half of total exergy loss in SMR. $\Delta E_{reaction}$ and $\Delta E_{separation}$ are determined by reaction condition and only ΔE_{HX} can be reduced by arranging the process Thus, SMR has high possibility to improve performance by arranging the process. On the other hand, the performance of METHANATION was high at the entire reaction temperatures and ΔE_{HX} was smaller than other exergy losses. Hence, it is difficult to improve its performance by arranging process. To improve the performance of the chemical heat transformer, the reduction of exergy loss in SMR is required. We considered that an integration of SMR and METHANATION is the most suitable method to reduce exergy loss of the entire process (SMR and METHANTION). In addition, the optimization of entire process is expected to further advance the performance of the developed process.
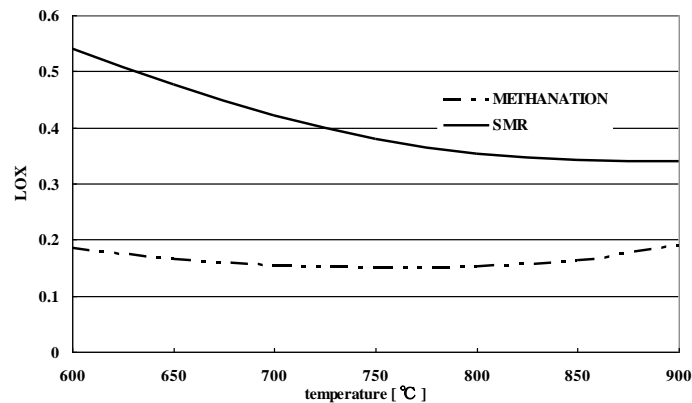

Figure 7: LOX as a function of reaction temperature

5. Conclusion

In this study, we developed a chemical heat transformer to configure co-production system. We adopted steam methane reforming as reaction of chemical heat transformer and proposed the processes of steam methane refoming and methanation based on self-heat recuperation technology. We examined the performance of each process to set reaction temperature as a parameter. Then, we confirmed that the performance of the process of steam methane reforming was especially not high at low temperatures because ΔE_{HX} was large. By arranging process, the exergy loss in the process of steam methane reforming can be reduced. On the other hand, the performance of the process

of methanation was high at entire reaction temperatures. According to these simulation results, we suggested that the integration of the process of steam methane reforming and methanation helps to improve the performance of chemical heat transformer using steam methane reforming and methanation. Thus, this chemical heat transformer is promissng to configure co-production system in the various industries.

Acknowledgement

References

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