Energy Proceedings
Vol 31, 2023
ISSN 2004-2965

Process integration and heat exchanger network synthesis for a methanol-reforming proton exchange membrane fuel cell

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ABSTRACT

The present study focuses on the heat integration of process streams for a methanol-reforming proton exchange membrane fuel cell (PEMFC). A Big-M method-based heat integration-PEMFC-heat exchanger network (HEN) synthesis model is established in the GAMS environment. The optimal operating condition and heat exchange topology structure of the PEMFC system integrated with methanol-reforming are obtained through the developed optimization method. Comparative analysis on two different energy utilization configurations is conducted. The PEMFC system with heat integration performs the reduction of 42.62% in operating cost.

Keywords: heat integration, PEMFC, MSR, mixed-integer non-linear programming, HEN synthesis

NOMENCLATURE

Symbols	
A	Area(m^2)
c	Unit cost ($/W)
$Cost$	Operating cost ($)
E	Voltage (V)
f	Molar flow rate (mol/s)
I	Current (A)
N	Number
p	Pressure (bar)
Q	Heat (W)
r	Reaction rate
T	Temperature (K)
V	Voltage (V)
z	Length (m)
Δh	Enthalpy change (J/mol)
η	Rate
Superscript and subscript	
act	Activation loss
ad	Adsorption process
$cell$	Cell unit
$conc$	Concentration loss
cr	Cross-section
cu	Cold utility
D	Decomposition reaction
de	Desorption process
fc	Fuel cell
hu	Hot utility
MSR	Methanol-steam reforming reaction
$nernst$	Open-circuit
ohm	Ohmic loss
rec	Recovery
WGS	Water-gas shift reaction

1. INTRODUCTION

The combined cooling, heating, and power (CCHP) system has been drawn wide attention with the characteristics of energy-saving, cost-saving, and environmentally friendly. With the continuous development of the CCHP system, the overall energy efficiency is generally 70%-80% [1]. Recently, researchers focus on the proton exchange membrane fuel cell (PEMFC) based CCHP system due to its high energy density and the emission without pollution to the environment. Wang et al. [2] conducted the

thermodynamic analysis of a fuel cell trigeneration system integrated with methanol-reforming driven by solar energy. The results showed that the system energy efficiency is 73.7% at most under the design work condition, while the exergy efficiency is 26.1%. Chen et al. [3] proposed a novel PEMFC-based micro-CCHP system and evaluate the thermodynamic and economic performance. They reported the novel system achieved an energy efficiency of 66.3% and reduced the total annual cost by 20.9%. Previous studies have achieved substantial progress in terms of component and heat source selection, and cycle structure optimization for the PEMFC-based CCHP system. However, less of them pay attention to the heat exchange topology design and process streams integration. A better heat exchanger settlement can not only increase the system's energy efficiency but also reduce the operating cost. Therefore, it is imperative to conduct heat integration for each process stream and optimize the heat exchange topology.

In this study, we present a design method of the PEMFC system integrated with methanol-reforming, including heat integration and heat exchanger network (HEN) synthesis, to achieve the minimum operating cost target. A modeling framework is proposed to handle the heat integration problem with variable streams' data and non-linear process constraints. A simplified case study based on the PEMFC system integrated with methanol-reforming is conducted to verify the effectiveness of the method and evaluate the performances.

2. PROBLEM DESCRIPTION

The PEMFC system integrated with methanol-reforming is shown in Fig. 1. The system consists of a heat integration subsystem, methanol-steam reforming (MSR) subsystem, pressure swing adsorption (PSA) subsystem, fuel cell power generation subsystem, and additional utility (i.e., steam and cooling water).

The heat integration subsystem integrates the streams which possibly exist the heat transfer between each other. Here, the streams that release heat are defined as hot streams, while the streams which absorb heat are identified as cold streams. Thus, the stream comprised of methanol, water, carbon monoxide, carbon dioxide and hydrogen (s7 – s10), and surplus hydrogen stream (s15 – s16) are hot streams. The cold streams are the fuel stream (s3 – s6), the ultra-pure hydrogen stream (s13 – s14), and the air stream (s18 – s19).

The fuel combined with methanol and desalinated water from the fuel tank (s1) is first pressurized through a pump (s2) and mixed with unreacted methanol and desalinated water from the separator (s3). Then, it is heated and vaporized to the target temperature (s6) by the released heat from the hot streams and hot utility. The vaporized reactant carries out chemical reactions driven by hot utility, forming hydrogen, carbon monoxide, and carbon dioxide (s7). The syngas with the unreacted vaporized methanol and steam releases the heat to the cold streams and is further cooled by cold utility (s10). Next, the stream with two-phase gas-liquid enters the separator, the liquid methanol/water mixture is sent back to the mixer (s11), and the syngas is sent to the PSA subsystem (s12) in which ultra-pure hydrogen is generated (s13).

The purified hydrogen is heated to the suitable reaction temperature and fed to the PEMFC to generate electricity (s14), as well as the air (s18) which is also heated to the same temperature (s19). Then, the surplus hydrogen (s15) is sent to purge the PSA to repressurize after dehydration and cooling (s16). The exhaust gas containing carbon monoxide, carbon dioxide, and hydrogen is discharged and recovered

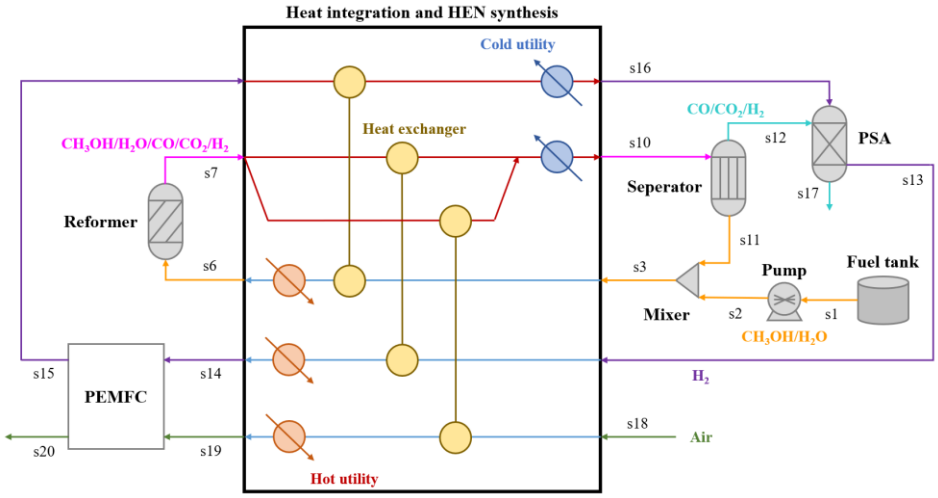

Fig. 1 Schematic of the PEMFC system integrated with methanol-reforming

(s17).

3. MATHEMATICAL MODEL

In this section, the main thermodynamic model including MSR, PEMFC, and PSA is introduced briefly, together with the heat integration method and HEN synthesis approach.

3.1 Methanol-steam reforming subsystem

The MSR is a promising method for hydrogen production. During the MSR procedure, reactants including methanol and water are handled through mixture, vaporization, transfer, separation, purification, etc. Here, the reactor packed with $Cu/ZnO/Al_2O_3$ catalyst particles is selected and the following reactions take place in the reformer:

$$\mathrm{CH_3OH + H_2O \rightarrow CO_2 + 3H_2} \quad (1)$$

$$\mathrm{CH_3OH \rightarrow CO + H_2} \quad (2)$$

$$\mathrm{CO + H_2O \rightarrow CO_2 + H_2} \quad (3)$$

The reactions are the main methanol-steam reforming, methanol decomposition, and the reverse water gas shift reaction, respectively. Correspondingly, kinetic expressions for reaction (1)-(3) developed and corrected by Peppley et al. [4] are well-accepted.

The steady-state model equations for each component are given by the following mole-balance equations. The variation in flow rate of each component can be obtained by the integral of the different segments along the length direction.

$$\frac{df_{\mathrm{CH_3OH}}}{dz} = (-r^{MSR} - r^{D})A^{cr} \quad (4)$$

$$\frac{df_{\mathrm{H_2O}}}{dz} = (-r^{MSR} - r^{WGS})A^{cr} \quad (5)$$

$$\frac{df_{\mathrm{CO}}}{dz} = (r^{D} - r^{WGS})A^{cr} \quad (6)$$

$$\frac{df_{\mathrm{CO_2}}}{dz} = (r^{MSR} + r^{WGS})A^{cr} \quad (7)$$

$$\frac{df_{\mathrm{H_2}}}{dz} = (3r^{MSR} + 2r^{D} + r^{WGS})A^{cr} \quad (8)$$

3.2 Proton exchange membrane fuel cell subsystem

A zero-dimensional PEMFC model is selected in this study. The electrochemical model reveals the mechanisms of cathodic and anodic reactions. The actual voltage of a cell is always lower than the open-circuit voltage due to irreversibilities, such as activation loss, ohmic loss, and concentration loss. The PEMFC stack is comprised of many single cells, thus total power generated by the stack is calculated by Eq. (11).

$$V^{fc} = E^{nernst} - \Delta V^{act} - \Delta V^{ohm} - \Delta V^{conc} \quad (9)$$

$$E^{nernst} = 1.229 - 0.8 \times 10^{-3}\left(T^{fc} - 298.15\right) + 4.3085 \times 10^{-5} T^{fc} \ln\left(p_{\mathrm{H_2}} p_{\mathrm{O_2}}^{0.5}\right) \quad (10)$$

$$W^{fc} = N^{cell} I V^{fc} \quad (11)$$

3.3 Pressure swing adsorption subsystem

For simplicity, the PSA subsystem is recognized as a separator without rigorous dynamic modeling. The performance index we are concerned with is adsorption heat. Table 1 lists the specified adsorption heat of each component of syngas.

Table 1 Heat of adsorption of each component (Unit: J/mol)

Adsorbent	Activated carbon	Zeolite 5A
CO	-20920	-20920
CO_2	-20000	-20000
H_2	-11715	-11715

The total adsorption heat during adsorption process is defined by Eq. (12). Moreover, the absorbed heat during desorb process for the absorbed components should be equal to the released heat during adsorption process considering the PSA operates under steady state.

$$Q^{ad} = \left(1 - \eta_{\mathrm{H_2}}^{rec}\right) f_{\mathrm{H_2}} \cdot \Delta h_{\mathrm{H_2}}^{ad} + f_{\mathrm{CO_2}} \cdot \Delta h_{\mathrm{CO_2}}^{ad} + f_{\mathrm{CO}} \cdot \Delta h_{\mathrm{CO}}^{ad} \quad (12)$$

$$Q^{ad} = Q^{de} \quad (13)$$

3.4 Objective function

The objective function is the minimization of the operating cost of the system, as formulated by Eq. (14). The operating cost is comprised of hot and cold utilities' costs. The hot utility is used to supply the heat to cold streams, desorb process in the PSA subsystem and methanol-steam reforming subsystem, while the cold utility needs to absorb the heat from hot streams and absorption process in the PSA subsystem.

$$Cost = c^{hu}\left(Q^{hu} + Q^{MSR} + Q^{de}\right) + c^{cu}\left(Q^{cu} + Q^{ad}\right) \quad (14)$$

3.5 Heat integration

It is noted that the streams' pressures and temperatures can be optimized. Consequently, the conventional pinch design methods which require fixed stream temperatures or pre-determined temperature intervals are not suitable for this problem. In this study, the optimization method of heat integration proposed by Hui et al. [5] is selected to conduct heat integration with variable streams' data and non-linear process constraints for the minimum utility target. In addition, the Big-M model developed by Grossmann et al. [6] is used to identify the position of a stream relative to the pinch, and thus binary variables are introduced.

The formulated model is a non-convex mixed-integer non-linear programming (MINLP) model. In the present study, the MINLP model is established in GAMS 24.7 on an AMD (R) Ryzen (TM) 7-5800 with 3.4 GHz CPU 16 GB RAM PC, and DICOPT is selected to solve the MINLP model.

3.6 Heat exchanger network synthesis

The HEN synthesis is conducted based on the optimization results of heat integration. Firstly, the temperatures and heat capacity flow rates of streams obtained by heat integration are used as input data to define the inlet and outlet characteristics of streams in the HEN superstructure. Then, it is necessary to determine the number of divided streams for the streams with two-phase gas-liquid due to the significant variation in physical properties of streams, especially heat capacity. The synheat superstructure model presented by Yee et al. [7] has shown good adaptability to the HEN synthesis in our previous work [8, 9]. The necessary modification is conducted to ensure the solution with accuracy and stability.

4. RESULTS AND DISCUSSION

We conduct the heat integration for the PEMFC stack with the nominal power output of 1 MW in this section and evaluate the operating cost compared with the counterpart without heat integration. The basic system parameters and operating condition ranges of each subsystem are given in Table 2 and Table 3, respectively.

Table 2 The basic design parameters

Items	Value
Diameter of reformer (m)	0.07
Isentropic efficiency of pump	0.87
Length of reformer (m)	4.8
Minimum approach temperature (K)	10
Number of cells	13000
Unit cold utility cost ($/W)	0.02
Unit hot utility cost ($/W)	0.08
Void fraction of reformer	0.38

Table 3 The operating condition ranges

Items	Value
Temperature of ambient (K)	293.15-298.15
Temperature of MSR (K)	473.15-573.15
Temperature of PEMFC (K)	333.15-353.15

Table 4 lists the optimal operating condition given by the Big-M model-based heat integration. Aiming at the minimum operating cost target, the optimal temperatures of the MSR and PEMFC are 545.97 K and 342.78 K, respectively. Moreover, the system is suitable to generate the nominal power in the environment of 293.15 K. It is noted that the ambient temperature reached the minimum we set. The phenomena can be explained by Fig. 2.

Table 4 The optimal operating condition

Items	Value
Temperature of ambient (K)	293.15
Temperature of MSR (K)	545.97
Temperature of PEMFC (K)	342.78

Fig. 2 displays the compositive curve of the hot and cold streams. As shown in Fig.2, the heat released from the products generated by the reformer mainly influences the preheating section of the methanol/water mixture. It is necessary to introduce the hot utility to heat the methanol/water mixture further on account of considerable energy demand in the two-phase region. The hot and cold utilities reduce to 629.04 kW and 125.21 kW through heat integration. In addition, we notice that the cold utility increases with the rise in the ambient temperature due to the characteristics of heat capacity flow rate for process streams, and it also explains why the ambient temperature is optimized toward the lower bound.

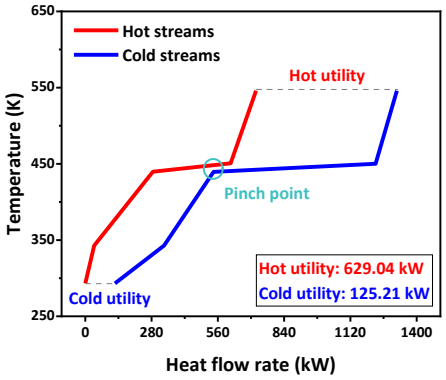

Fig. 2 Compositive curve of process streams

Fig. 3 shows the comparison of operating cost between two configurations of energy demand for the PEMFC system integrated with methanol-reforming. The direct configuration is that the energy demand for all process streams and each component is supplied from the hot and cold utilities. It is obvious that the heat integration configuration wins significant economic benefits. The operating cost of heat integration configuration reduces by 42.62%, especially for hot utility cost. The adoption of heat integration configuration brings two advantages to the system. First, there is a well-deserved economic preponderance.

On the other hand, it achieves a considerable decrease in temperature difference during the heat exchange process, which is beneficial to the design and operation of the heat exchanger.

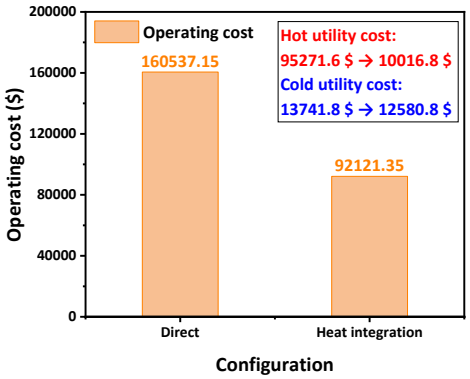

Fig. 3 Operating cost for different configurations of the PEMFC system integrated with methanol-reforming

Fig. 4 provides the HEN configuration of the system with heat integration, which is generated by the modified synheat superstructure model. The system needs 9 heat exchangers for the operating cost target, with the HEN synthesis time of 0.3 s.

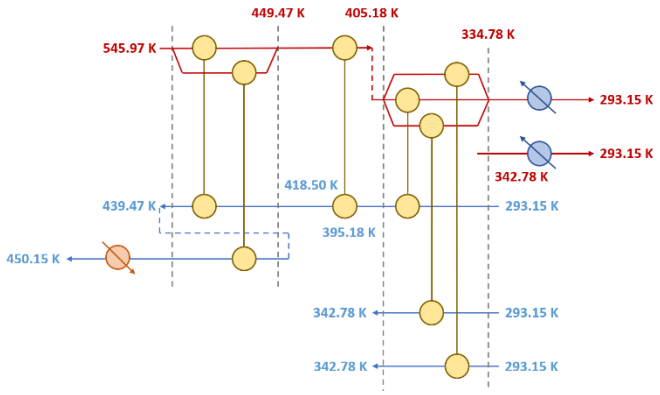

Fig. 4 the HEN of the system with heat integration

5. CONCLUSION

A heat integration concept of process streams for the MSR-PEMFC system is presented and an optimization model with the HEN synthesis is developed, together with the solution algorithm. Following conclusions are drawn.

The heat integration of process streams can significantly reduce the operating cost of the PEMFC system integrated with methanol-reforming by 42.62%. The reduction in hot utility is a dominant contribution in the economic benefit, of which occupies 98.66% in the operating cost benefit. It is necessary to determine the suitable operating scenario according to the physical properties of fuel and expected products during the design stage. A lower ambient temperature is more suitable for the system in this case study. The heat integration and HEN synthesis method presented in this study can give practical guidance to the design of the MSR-PEMFC system with adequate accuracy and moderate solution difficulty.

Finally, a robust techno-economic optimization of the PEMFC system with heat integration should be implemented in order to exploit the potential economic advantages. In addition, other heat recovery systems (i.e., organic Rankine cycle and absorption refrigeration) will be equipped to improve the heat utilization structure of the system further. Relevant work is in progress and the evaluation results will be reported.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support from the Guangdong Science and Technology Department (2021A0505030065).

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