

Thermal Analysis of Methanol Reforming Proton Exchange Membrane Fuel Cell System

Jialin Zhao¹, Yongwen Yang¹, Hong Yang², Yanan Li³, Guihai Jiao¹, Lei Zhang¹, Jingjing Xu¹

¹ College of energy and Mechanical Engineering, Shanghai University of Electric Power, China

²China Guodian Yuyuan Power Generation Co., Ltd, China

³China Huaneng Yuhuan Power Generation Co., Ltd, China

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ABSTRACT: Relatively mature methanol reforming PEMFC products have been produced domestically, and power generation efficiency of the whole system can reach 30%, but most of the waste heat is not used. Based on an experiment table of methanol reforming PEMFC system, a large amount of data about the internal temperature, pressure, electric current, voltage of the whole system running under different output power is collected, and the actual waste heat generated by the system at different output power is calculated. Then the theoretical calculation of waste heat is compared with the actual value of waste heat of the system. The direction of waste heat utilization and optimization of the whole system is proposed.

RESEARCH BACKGROUND

Proton exchange membrane fuel cell (PEMFC) is currently the most mature fuel cell, has a wide application in power, mobile power, distributed power and power in the family vehicle[1]. In actual operation, some directly use a hydrogen storage tank to provide hydrogen fuel for the cell stack, some use reformer system to reform natural gas, methanol or other fuels into hydrogen. The way of getting hydrogen by methanol reforming has many features such as better economy, low power consumption, low reforming temperature (about 300°C), easy to store and transport, convenient and safety to charge fuel and so on. Because of these futures, methanol reforming is attracting more and more attention[2].

Barelli et al. [3] simulated and compared kilowatt cogeneration systems with ASPEN, which are based on SOFC and low-temperature PEMFC. The results show that PEMFC cogeneration system working at a state of low temperature and atmospheric pressure is a more efficient system, though the power generation efficiency of SOFC(40%) is slightly higher than the power generation efficiency of low-temperature PEMFC(up to 32%). PEMFC cogeneration system is still the first choice for residents. Borja et al.[4] developed thermodynamics, geometry and economic models, which can be used for multi-unit housing and multi-generation proton exchange membrane fuel cell system. The results obtained by using the above models show that the power generation efficiency in the synthesis/design point reaches 39%, and the efficiency of cogeneration reaches 72%.

China now has more mature methanol reforming proton exchange membrane fuel cell products, the power generation efficiency of these systems are around 30%, but the aspect of the waste heat utilization of system does not attract enough attention, there is a large room for improvement for the overall efficiency of the system. In academic research, there are more simulations about internal

heat conduction of the fuel cell stacks and cooling of systems, but relatively less researches on fuel cell cogeneration systems. There are more literatures about simulating systems by using software, but relatively less researches on the actual operation of systems. There are more researches about fuel cells using direct hydrogen source, but relatively less literatures considering the heat of the fuel reforming part.

RESEARCH OBJECT

The methanol reforming proton exchange membrane fuel cell system test bench in Shanghai university of electric power is shown as Fig.1, DC voltage 48V and rated power 5kW can be outputted together with the external battery on the test bench. The temperature, pressure, voltage, current and other parameters of the methanol fuel cell can be monitored on the test bench, in addition, multiplex numerical values and analog control signals can be outputted on the test bench.



Fig.1. The methanol reforming PEMFC system bench

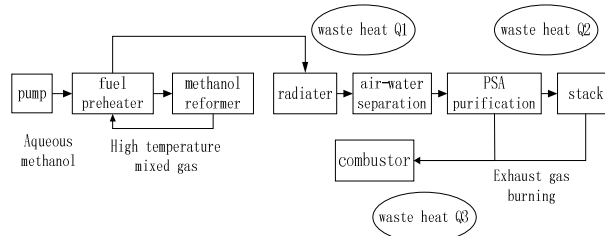


Fig.2. The flow chart of methanol reforming PEMFC system

Flow chart of the methanol reforming PEMFC system is shown as Fig. 2, the fuel in the system is aqueous methanol with the molar ratio of 1:1.5, which is converted to hydrogen mixed gas, and the running temperature in the upper of methanol reformer is 280 ~ 400°C. The mixed gas first preheats the fuel in the fuel preheater, then is cooled in the radiator, after water-gas separation and purification of PSA, high purity hydrogen is separated. At last, electrochemical reaction with the hydrogen is happened in the fuel cell stack, producing the direct current, which is converted into alternating current in the DC-AC converter and is provided to outside users. Surplus combustible gases are mainly produced during the PSA purification process: In order to ensure the activity of molecular sieve adsorbents, hydrogen is needed to rinse molecular sieve for the completion of adsorbent regeneration. The efficiency of hydrogen purification of PSA in the test bench is about 60%. Water-cooled and air-cooled are used in the cooling system, and heat is dissipated to the outside without utilization. In general, the energy efficiency of the system is very low.

As it can be seen from the Fig. 2, there is three major heat loss in the system: heat dissipation in the radiator Q_1 , waste heat generated during the operation of the stack Q_2 and the waste heat produced from the exhaust gas combustion Q_3 . So, the waste heat available in the system can be expressed as Formula 1:

$$Q_w = \sum_{i=1}^3 Q_i \quad (1)$$

The purpose of this paper is to examine the waste heat of the various parts in the system at different output power. Various output power of the system is set from 1000W to 5000W, and keep the equipment operating smoothly for a period of time under different power. Stack current, voltage, methanol fuel flow, inlet and outlet temperature difference and other data are recorded every three seconds. Finally, the data is processed to obtain the waste heat of each part and the waste heat is compared with the theoretical heat.

THERMAL ANALYSIS OF THE SYSTEM

Theoretical Foundation

In order to calculate waste heat of every module in the system during the operation, there is need to use the original data includes generating power of the fuel cell stack, current, voltage, flow of methanol fuel, outflow temperature of reformer, outflow temperature of the preheater, outflow temperature of the radiator and so on. Due to technical reasons, the real-time flow data of hydrogen can't be obtained, so in order to accurately calculate the hydrogen consumption data and other data, the following concepts and formulas will be needed.

(1) The theoretical hydrogen consumption
$$n_{H_2} = \frac{I}{2F} \quad (2)$$

Here, n_{H_2} is the supply of hydrogen fuel per unit time, the unit mol / s. I is the fuel cell stack current, F is Faraday constant, usually, $F=96485.3365$ C/mol.

(2) The waste heat generated by PEMFC

In the case of the known actual voltage and current, according to the difference between the theoretical open circuit voltage and the actual voltage of the stack, heat generated by the proton exchange membrane fuel cell can be calculated as fomular (3):

$$Q_2 = (V_{ocv} - V_{cell}) \cdot I \cdot n_{cell} \cdot 3.6 \quad (3)$$

Here, V_{cell} and I are the output voltage and current of monolithic fuel cell respectively, n_{cell} is the number of pieces in the fuel cell stack. In this paper, V_{ocv} is reversible open circuit voltage of hydrogen fuel cell (volts). $V_{ocv}=1.23$ V, $n_{cell}=80$.

(3) Fuel cell efficiency

$$\eta = \frac{\text{energy released by 1mol fuel}}{-\Delta H} \quad (4)$$

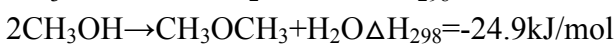
Here, $-\Delta H$ is the high calorific value of Hydrogen combustion, 285.84kJ/mol. It is noteworthy that the fuel cell power generation efficiency here is power generation efficiency of the fuel cell stack itself, not power generation efficiency of the system.

(4) Methanol steam reforming reaction

Primary reaction:



Side reaction:



(5) Heat loss of the hot mixed gas in the radiator is equal to the energy difference between internal energy of the inlet and internal energy of the outlet:

$$Q_1 = E_{out} - E_{in} \quad (6)$$

The total internal energy of per unit mass of the gas mixture can be expressed as fomular(7):

$$E = m_{CO_2} \cdot e_{CO_2} + m_{H_2} \cdot e_{H_2} + m_{H_2O} \cdot e_{H_2O} \quad (7)$$

The actual waste heat condition of system

Waste heat of the radiator Q1

High temperature and high pressure mixture gas was generated when methanol reformer is operating under actual conditions. In addition to the H₂, CO₂ and water vapor, the mixture gas also contains trace amounts of CO, CH₃OCH₃ and CH₄ and other imp-

Table 1. In the methanol reforming module, the temperature of the radiator's inflow and outflow measured under different stack power

Actual average power /W	Methanol aqueous flow /kg·h-1	Radiator inflow temperature /°C	Radiator outflow temperature /°C
1.28	1.81	80.42	26.87
1.70	2.38	84.99	22.25
2.13	2.35	87.31	21.34
2.56	2.66	95.06	25.45
3.10	3.07	103.49	26.1
3.68	3.50	112.01	27.82
3.78	3.62	115.15	28.37
4.31	4.21	116.13	30.91
5.35	5.30	125.81	30.13

urities. These impurities are negligible in the calculation of the mixed gas's internal energy, so mass fraction of each component in the mixed gas is: $\omega(CO_2)=74.58\%$, $\omega(H_2)=10.17\%$, $\omega(H_2O)=15.25\%$.

As shown in Table 1, when experiment runs at different power, in the methanol reforming module, the temperature of the radiator's inflow and outflow is measured by temperature sensor.

Take 1.28kW as an example to calculate the waste heat Q₁ of radiator:the actual average output power of stack is 1281.9W, the measured average mass flow of aqueous methanol solution is

$\dot{m}=1.81\text{kg/h}$. the measured average temperature of the mixture gas out of fuel preheater is 80.42°C,

the measured average temperature of radiator outflow is 26.87 °C.

The waste heat of the mixture gas Q₁ through the radiator can be calculated by combining with Formula (6), (7):

$$\begin{aligned}
Q_1 &= E_{out} - E_{in} \\
&= \dot{m} \cdot \omega_{CO_2} \cdot (e_{CO_2, 80.42^\circ C} - e_{CO_2, 26.87^\circ C}) \\
&+ \dot{m} \cdot \omega_{H_2} \cdot (e_{H_2, 80.42^\circ C} - e_{H_2, 26.87^\circ C}) \\
&+ \dot{m} \cdot \omega_{H_2O} \cdot (e_{H_2O, 80.42^\circ C} - e_{H_2O, 26.87^\circ C}) \\
&= 213.10 \text{ kJ} / \text{h}
\end{aligned}$$

Here, internal energy of the components (H_2 , CO_2 and H_2O) of the mixture gas at different temperature can be obtained by handbook of Chemistry[5].

Other waste heat of radiator Q_1 under other power can be calculated in the same way, and the result is shown in Table 2. In order to see the trend of the waste heat of radiator Q_1 under actual stack generation power, you can see Fig.3.

Table2 The waste heat Q_1 under different stack output power

Actual average power /W	Radiator waste heat Q_1 /kJ·h-1
1281.89	213.10
1697.87	329.12
2125.94	340.90
2556.37	409.42
3099.60	526.15
3684.48	652.51
3781.17	697.42
4314.87	796.99
5350.25	1126.18

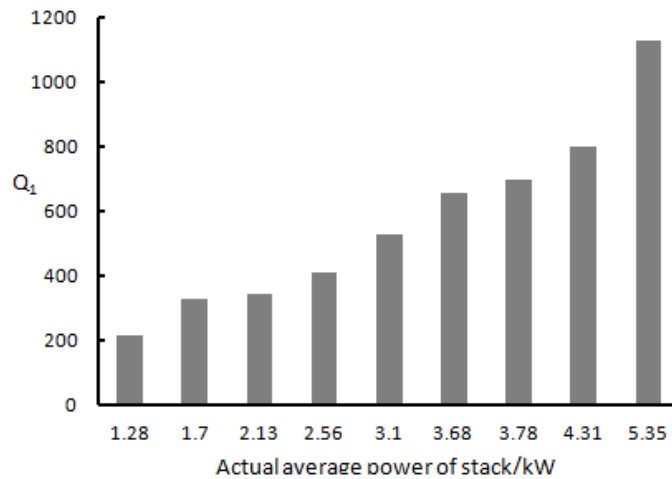


Fig.3. The waste heat of radiator Q_1 under different power

As shown in Fig.3, with the increase of power, the waste heat of radiator Q_1 is increasing regularly.

Waste heat of the fuel cell stack, Q_2

Q_2 generated by PEMFC can be calculated by Formula (3) according to the difference between the theory voltage and actual voltage of stack; Hydrogen consumption in stack was calculated by Formula (2). The power generation efficiency of the stack can be calculated by Formula (4), the specific calculation process as follow. The current, voltage, and other parameters of the stack measured under different output power was shown in Table 3, which was substituted into Formula (3) to calculate the calorific value of stack, Q_2 .

Table 3 The parameters of the stack under different power

Average output power /W	Average output current /A	Average output voltage /V	Monolithic fuel cell voltage/V
1281.89	20.04	63.97	0.800
1697.87	26.98	62.99	0.787
2125.94	35.18	60.44	0.755
2556.37	42.66	59.93	0.749
3099.60	52.21	59.37	0.742
3684.48	61.81	59.62	0.7452
3781.17	63.37	59.66	0.746
4314.87	75.05	57.48	0.719
5350.25	93.81	57.05	0.713

Take 1.28kW as an example, the produced heat under this power running an hour steadily was:

$$\begin{aligned}
 Q_2 &= (V_{ocv} - V_{cell}) \cdot I \cdot n_{cell} \cdot 3600 \\
 &= (1.23V - 0.80V) \times 20.04A \times 80 \times 3600s \\
 &= 2484.3kJ
 \end{aligned}$$

Hydrogen consumption in stack:

$$\begin{aligned}
 n_{H_2} &= I / 2F \\
 &= 20.04A \div (2 \times 96485.3C / mol) \times 3600 \times 80 \\
 &= 29.91mol / h
 \end{aligned}$$

The power generation efficiency of the stack:

$$\begin{aligned}
 \eta &= \frac{\text{Power generation capacity}}{-\Delta H} \\
 &= \frac{1281.89W \times 3600s}{285.84kJ / mol \times 29.91mol} \\
 &= 54.2\%
 \end{aligned}$$

The waste heat of stack Q_2 and power generation efficiency of stack under other power was also calculated as above. The result was shown inTable4.

Table 4 The waste heat of stack Q_2 under different power.

Average output power/W	Hydrogen consumption /(mol·h-1)	Waste heat of stack Q_2 /(kJ·h-1)	Power generation efficiency of stack /%
1281.89	29.91	2484.26	54.20
1697.87	40.23	3436.93	53.36
2125.94	52.50	4807.69	51.20
2556.37	63.66	5907.75	50.77
3099.60	77.92	7336.17	50.30
3684.48	92.25	8629.44	50.51
3781.17	94.58	8837.44	50.55
4314.87	112.01	11054.7	48.71
5350.25	140.00	13962.5	48.32

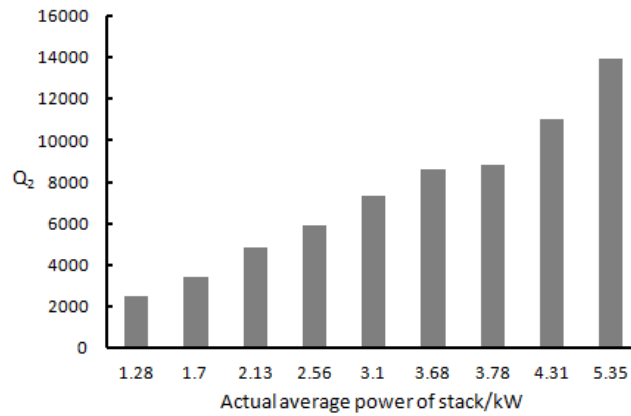


Fig.4 The waste heat of stack Q_2 under different power

The waste heat, Q_2 , under different power was shown in Fig.4. From Fig.4, we can see that Q_2 increases with the increasing of power of the stack.

Waste heat of residual gas combustion, Q_3

In the case of the output power of 1.28 kW, Table4 shows that the amount of hydrogen consumption of the fuel cell stack is 29.91mol/h, and the actually measured flow rate of methanol consumption is 30.65mol/h. The fully capable of producing hydrogen reaction is 91.95mol/h by methanol reforming expression. The waste heat Q_3 generated from the burning of residual gas burning is equal to the heat of hydrogen combustion minus the heat absorption of remaining methanol reforming reaction. Here, the combustion heat of hydrogen is low calorific value:

$$\begin{aligned}
 Q_3 &= (91.95 - 29.91) \text{mol} \times 241.83 \text{kJ/mol} \\
 &\quad - 30.65 \text{mol} \times 49.4 \text{kJ/mol} \\
 &= 13489.02 \text{kJ}
 \end{aligned}$$

The purification efficiency of PSA: $\eta_{PSA} = 29.91 \div 91.95 = 32.53\%$

The waste heat Q_3 and the purification efficiency of PSA under different output power will be respectively calculated as shown in Table 5.

Table 5 Waste heat Q_3 under different output power

Power of stack/W	Flow rate of methanol / $(\text{mol} \cdot \text{h}^{-1})$	H ₂ production of methanol / $(\text{mol} \cdot \text{h}^{-1})$	H ₂ consumption of stack / $(\text{mol} \cdot \text{h}^{-1})$	Purification efficiency of PSA /%	Waste heat of remaining gas Q_3 /kJ
1281.89	30.65	91.95	29.91	32.53	13489.85
1697.87	40.38	121.15	40.23	33.21	17573.66
2125.94	39.78	119.35	52.50	43.99	14201.91
2556.37	45.16	135.49	63.66	46.99	15137.76
3099.60	52.10	156.29	77.92	49.86	16378.04
3684.48	59.29	177.88	92.25	51.86	17780.38
3781.17	61.40	184.21	94.58	51.35	18640.07
4314.87	71.41	214.22	112.01	52.29	21190.02
5350.25	89.75	269.24	140.00	52.00	26819.07

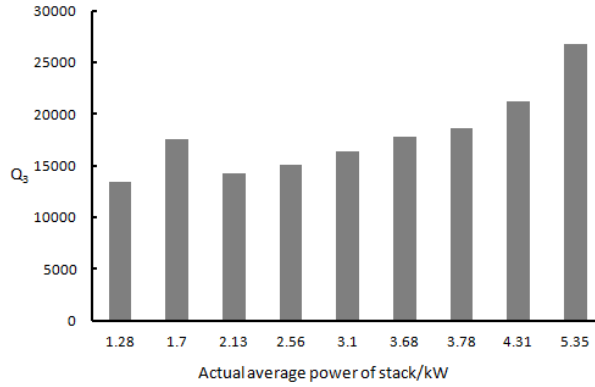


Fig.5. Waste heat of remaining gas Q_3 under different power

As shown in Fig.5, the waste heat Q_3 increases with the increase of the output power of electric stack. Q_3 will reach 26819 kJ/h when output power of electric stack reaches 5.35 kW, which causes wastage of system energy.

Analysis of waste heat of the system

Still in the case of the output power of 1.28 kW, the equipment consumes 30.65 mol methanol for running an hour, as we all know, low calorific value of methanol is 724.738 kJ/mol, so the chemical energy entering the whole system is 22268.34 kJ.

Power generation efficiency of the system:

$$\eta_{\text{sys}} = \frac{\text{Power generation of the system}}{\text{The chemical energy entering the system}}$$

$$= \frac{1282.89 \text{ W} \times 3.6}{30.65 \text{ mol} \times 724.738 \text{ kJ/mol}} \times 100\%$$

$$= 20.72\%$$

Q_1 、 Q_2 and Q_3 add up to the total waste heat, Q_w , its value is 16187.21 kJ, which accounts for 72.87% of total chemical energy of the system.

As shown in Table 6, power generation efficiency of the system under different output power of stack is calculated. In addition, the overall power generation efficiency of the system (η_{sys}) and the waste heat efficiency of the system (η_w) are calculated in Table 6.

The percentage of the three parts of waste heat under different power system of total waste heat situation is shown in Fig. 6, the waste heat Q_3 from the burning of the remaining gas occupy a large part, which is due to low purification efficiency of the process of PSA purification. And the waste heat Q_1 from radiator accounts for a small proportion of total waste heat, because the high temperature and high pressure gas out of the reformer first preheats the fuel in the preheater, when the gas arrives in radiator, its temperature has dropped to 80 ~ 120°C and it has a low heat quality.

Table 6 Waste heat under different output power of stack

Average output power of stack /W	Q_1/kJ	Q_2/kJ	Q_3/kJ	Q_w/kJ	The chemical energy entering the system /kJ	$\eta_{\text{sys}}/\%$	$\eta_w/\%$	Waste heat efficiency of theory/%
1281.89	213.1	2484.26	13489.85	16187.21	22212.74	20.72	72.87	69.6
1697.87	329.12	3436.93	17573.66	21339.71	29266.41	20.84	72.92	
2125.94	340.9	4807.69	14201.91	19350.50	28831.91	26.48	67.11	
2556.37	409.42	5907.75	15137.76	21454.93	32728.78	28.05	65.55	
3099.60	526.15	7336.17	16378.04	24240.36	37754.48	29.48	64.21	
3684.48	652.51	8629.44	17780.38	27062.33	42970.44	30.79	62.98	
3781.17	697.42	8837.44	18640.07	28174.93	44498.03	30.52	63.32	
4314.87	796.99	11054.7	21190.02	33041.71	51747.44	29.94	63.85	
5350.25	1126.18	13962.5	26819.07	41907.75	65038.29	29.54	64.44	

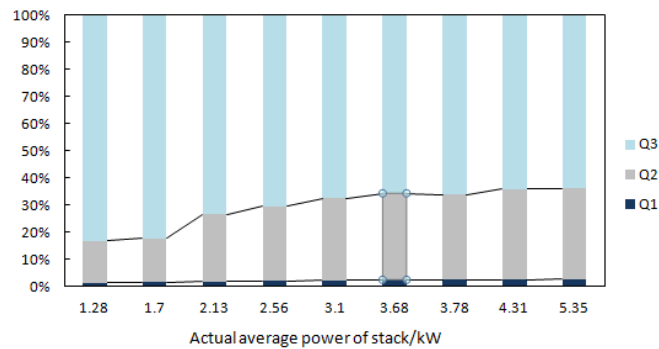


Fig.6. The percentage bar charts of system's waste heat

CONCLUSION

- 1) The results show that with the increase of cell stack output power, waste heat of system increases significantly, but its proportion accounting for chemical energy of the entire system decreased from 72.87% to 64.44%.
- 2) To ensure the purity of hydrogen, a certain amount of hydrogen is needed to rinse molecular sieve in the process of PSA purification, the efficiency of PSA purification increases with the increasing flow of methanol determined by cell stack power. PSA purification efficiency is only 32.53% in the case of 1kW power, while it can reach 52% in the case of 5kW power.
- 3) The waste heat Q_3 from the residual gas combustion accounts for the largest proportion of the overall system, it reaches more than 64% of the total waste heat and more than 30% of chemical energy. The main reason is related to the efficiency of molecular sieve. In the optimizing the efficiency of the system, higher purification efficiency of PSA systems should be considered, in addition, attention should be focused on the use of waste heat Q_3 generated by the residual gas combustion.
- 4) These three part waste heat are not all the waste heat, in addition, a little waste heat lost in the air through the surface of the device.

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