

## Feasibility Study of Integrating Absorption Heat Pump into Methanol Steam Reforming Process for Hydrogen Production

Willy Yanto Wijaya<sup>1)</sup>, Ken Okazaki<sup>2)</sup>, Kazuyoshi Fushinobu<sup>2)</sup>, Abdul Waris<sup>1)</sup>

<sup>1)</sup>Nuclear Physics and Biophysics Research Division,  
Faculty of Mathematics and Natural Sciences  
Institut Teknologi Bandung, Bandung

<sup>2)</sup>Department of Mechanical and Control Engineering  
Tokyo Institute of Technology, Tokyo, Japan

e-mail: willy\_yanto\_wijaya@yahoo.com, awaris@fi.itb.ac.id

### Abstract

Theoretically, Methanol Steam Reforming (MSR) process to produce hydrogen only requires endothermic heat with temperature lower than 100 °C. Meanwhile, waste heat in the temperature level of 100-150 °C is disposed in huge amount by various industrial sectors every year. If this abundant waste heat can be recovered and stored into hydrogen energy through the MSR, a potential gain and high-efficient energy system could be achieved. However, empirically, temperature level  $\geq 200$  °C is required for the MSR process to have high conversion from the methanol to hydrogen. Therefore, Absorption Heat Pump (AHP) system is then utilized to enhance the temperature level of the waste heat. Nevertheless, AHP system certainly requires additional input energy. This research was to investigate the feasibility of integrating the AHP system into MSR process to produce hydrogen. Further consideration on hydrogen to electricity conversion using Fuel Cell (FC) would also be provided. The feasibility study was conducted through the efficiency calculations, either for energy or exergy terms, for several theoretical as well as actual-approximation cases.

**Keywords :** methanol steam reforming, absorption heat pump, fuel cell, exergy.

### 1. Introduction

Depleting fossil fuel and various environmental problems have pushed the world to achieve more efficient and sustainable energy systems<sup>1-6)</sup>. Attempts have been made by increasing the power plants efficiency, finding alternative renewable energy sources as well as introducing various energy-conversion technologies.

In any system comprising of energy conversion processes, the concept of exergy, besides energy, is very important. It shows us how the potential useful work can be extracted. Combustion processes are naturally quite irreversible and thus much exergy is destroyed. Therefore, there should be a less-irreversible way to convert the chemical energy of the fuel to the useful work (electricity). It was this idea that gave birth to the concept of Fuel Cell (FC).

Another important point to realize a total high-efficient system is the principle of material/energy recycling. Endothermic reactions that can make use of the low-quality energy (*i.e.* the waste heat) and convert it to high-quality chemical energy will go along with this recycling principle<sup>7)</sup>. Methanol Steam Reforming (MSR) is then one of them to answer, where this process theoretically only requires less than 100°C temperature to proceed and currently, extremely abundant heat in the temperature of 100-150°C is being wasted. Even for the case of Japan only, more than 400 PJ heat in that temperature level is being wasted every year from various industrial sectors<sup>8)</sup>.

However, in the actual processes, MSR requires temperature level about 200°C<sup>8)</sup>. Since then, many efforts have been made to decrease this reforming process reaction temperature whether by utilizing membrane/catalyst technology or investigating other MSR parameters' influence<sup>8-13)</sup>.

Another possibility is to increase the temperature level of the waste heat. For this reason, Absorption Heat Pump (AHP) system is then utilized to increase the waste heat temperature level. AHP is a highly efficient system in the term of exergy and recycling principle since the main energy-source input is heat and only a little amount of pump work is required. It has been widely used in the application of space heating and big-scale industrial processes<sup>14-17)</sup>.

Therefore, integrating these AHP, MSR and FC systems will suggest a hint that a total high-efficient energy system can be realized. However, how feasible this integrated system will be, still need to be verified. This paper will investigate the feasibility of this integrated system by means of energy/exergy efficiency calculation and analysis for several theoretical as well as actual-approximation cases.

Besides, a special consideration will be given in particular for the hydrogen production efficiency. The main reason is due to the development of various technologies using hydrogen energy, in which one of them is fuel cell. Therefore, knowing the hydrogen production efficiency will also give us more vivid understanding of how MSR and AHP can play role in the exergy enhancement of the low quality waste heat.

## 2. System Description

### 2.1 Absorption heat pump (AHP)

Our investigation on the AHP system will be based on the heat pump system constructed by Ebara Corporation<sup>18,19</sup>. Figure 1 shows the simplified diagram of the actual system. Here, the heat input to the AHP system is  $Q_G$  (in Generator) and  $Q_E$  (in Evaporator). On the other hand, the heat output from the AHP system is  $Q_A$  (in Absorber) and  $Q_C$  (in Condenser). However, only  $Q_A$  is the desired output which will be transmitted as the heated steam input to the MSR process. The heat input to this AHP system itself is the waste heat contained in the warm water in temperature of 90 °C. The temperature of both Generator and Evaporator ( $T_G$  and  $T_E$ ) is about 80°C, and 37°C for Condenser ( $T_C$ ). For the case of Absorber, the temperature ( $T_A$ ) will be adjusted to three cases: 120°C, 160°C and 200°C by increasing the number of heat-up step. Besides the waste heat input, another energy input source to the AHP is the electricity to drive the pumps. This amount of electricity is relatively small since the pump only work on the liquid/refrigerant solution.

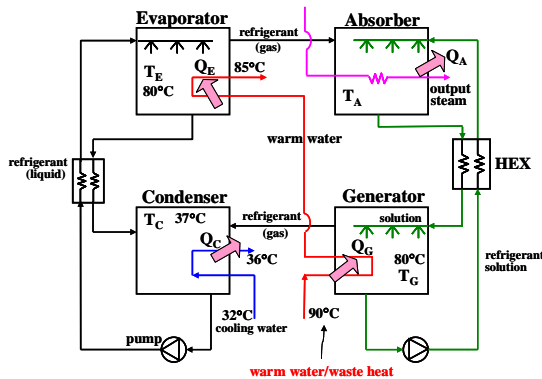


Figure 1. Absorption Heat Pump Diagram

Then, from the thermodynamics point of view, we have Heat Balance equation:

$$Q_E + Q_G = Q_A + Q_C, \quad (1)$$

and Entropy Balance equation:

$$\frac{Q_C}{T_C} + \frac{Q_A}{T_A} = \frac{Q_G + Q_E}{T_D}, \quad (2)$$

where  $T_E = T_G = T_D$ . Combining Eq. (1) and (2), we can get Coefficient of Performance (COP) of the AHP as follow:

$$COP = \frac{Q_A}{Q_G + Q_E} = \left( \frac{T_A}{T_A - T_C} \right) \left( \frac{T_D - T_C}{T_D} \right). \quad (3)$$

Substituting the values of  $T_D$  and  $T_C$  to Eq. (3) with  $T_A$  as the changing variable, the values of COP will be gained as shown in the Figure 2.

COP is an important parameter in refrigeration/heat pump systems that can be viewed

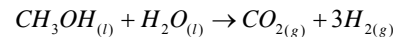
“equivalent” to efficiency. It shows the ratio between the desired output (in this case  $Q_A$ ) and the required input ( $Q_G + Q_E$ ). In Figure 2, for the desired  $T_A$  120°C (393K), 160°C (433K) and 200°C (473K), the AHP will have the theoretical COP of 0.57, 0.42, and 0.35 respectively. However, for the case of actual system, the AHP will only reach COP of 0.45, 0.3, and 0.225. Consequently, if the desired generated steam energy in Absorber ( $Q_A$ ) is 130.97 kJ, the heat input energy required ( $Q_G + Q_E$ ) will be 229.77 kJ, 311.83 kJ and 374.2 kJ respectively for the theoretical COP value. For the actual COP, it will be 291.04 kJ, 436.56 kJ and 582.08 kJ. For convenience, these AHP system data were summarized in Table 1.

Table 1. Detailed Data of the Absorption Heat Pump System

| Number of Heat Up Step                              | 1      | 2      | 3      |
|---|--------|--------|--------|
| Source of Thermal Energy                            |        |        |        |
| Warm H <sub>2</sub> O (entrance) (°C)               | 90     | 90     | 90     |
| Warm H <sub>2</sub> O (exit) (°C)                   | 85     | 85     | 85     |
| (Solution in Generator) (°C)                        | 80     | 80     | 80     |
| Refrigerant in Evaporator °C                        | 80     | 80     | 80     |
| Source of Cooling                                   |        |        |        |
| Cooling H <sub>2</sub> O (entrance) (°C)            | 32     | 32     | 32     |
| Cooling H <sub>2</sub> O (exit) (°C)                | 36     | 36     | 36     |
| Refrigerant in Condenser °C                         | 37     | 37     | 37     |
| Generated Steam Temperature in Absorber (exit) (°C) | 120    | 160    | 200    |
| Theoretical COP                                     | 0.57   | 0.42   | 0.35   |
| Actual COP  | 0.45   | 0.3    | 0.225  |
| Generated Steam Energy (in Absorber) (exit) (kJ)    | 130.97 | 130.97 | 130.97 |
| Warm Water Energy Required (Theoretical) (kJ)       | 229.77 | 311.83 | 374.20 |
| Warm Water Energy Required (Actual) (kJ)            | 291.04 | 436.56 | 582.08 |

### 2.2 Methanol steam reforming (MSR)

MSR is an endothermic reaction with chemical reaction formula:



$$\Delta H^\circ_{MSR} = 130.97 \text{ kJ/mol } CH_3OH$$

$$\Delta G^\circ_{MSR} = 9.18 \text{ kJ/mol } CH_3OH. \quad (4)$$

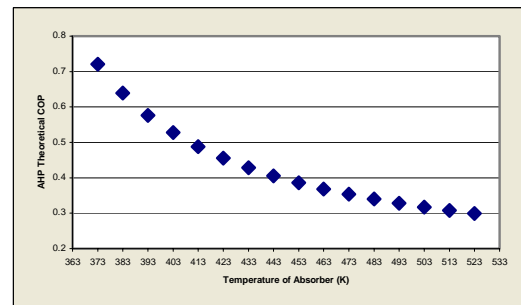


Figure 2. Graph of Absorption Heat Pump Theoretical COP

These enthalpy and Gibbs-energy changes can be calculated from the enthalpy of formation difference ( $\Delta H_f^\circ$ ) between the product and reactant sides of the reaction. The initial state of the reactants and final state of the products are considered in Standard Reference State (25°C, 1 atm) with the ambient temperature and pressure in that state as well (denoted by superscript °). This  $\Delta H_{MSR}^\circ$ , in fact, can also be calculated from the difference of enthalpy of combustion ( $\Delta H_C^\circ$ ) between 1 mole of methanol and 3 moles of hydrogen. The same case could be applied to  $\Delta G_{MSR}^\circ$  as well, shown by Table 2.

Table 2. Enthalpy and Gibbs Energy of Combustion at 25°C, 1 atm

|          | $\Delta H_C^\circ$ | $\Delta G_C^\circ$ |
|----------|--------------------|--------------------|
| Methanol | -726.52 kJ/mol     | -702.36 kJ/mol     |
| Hydrogen | -285.83 kJ/mol     | -237.18 kJ/mol     |

From reaction (4),  $\Delta H_{MSR}^\circ$  and  $\Delta G_{MSR}^\circ$  themselves imply the theoretical amount of energy and Gibbs-energy (exergy) of the heat required to enable the endothermic MSR reaction.

Therefore, this endothermic heat required has the value of exergy rate ( $\varepsilon$ ), which is defined as:

$$\varepsilon = \frac{\Delta G}{\Delta H}, \quad (5)$$

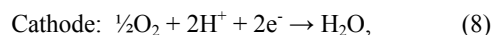
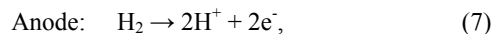
about 0.07 (7%). Based on the Exergy Rate ( $\varepsilon$ ) – Temperature Equation:

$$\varepsilon = 1 - \frac{T_0 \ln(T/T_0)}{T - T_0}, \quad (6)$$

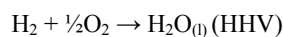
with  $T_0$  as the ambient temperature (25°C), the temperature level of the heat input required for MSR is found to be about 344 K (71°C) for the theoretical/ideal condition.

### 2.3 Fuel cell (FC)

Basic reactions that occur in FC can be viewed



where the overall reaction can be written as:



$$\Delta H_{FC}^\circ = -285.83 \text{ kJ/mol}$$

$$\Delta G_{FC}^\circ = -237.18 \text{ kJ/mol} \quad (9)$$

The reactions in FC as well as MSR will be viewed in High Heating Value (HHV) since the initial state of reactants and final state of products are in equilibrium with ambient state, where this is closely related to the concept of exergy.

Therefore, based on HHV, the maximum theoretical efficiency of FC is

$$\eta_{FC} = \Delta G_{FC}^\circ / \Delta H_{FC}^\circ = 83\%. \quad (10)$$

Nevertheless, this value certainly can't be reached in actual system regarding the irreversibility, potential

and other losses. Hence, in particular for the FC case, the reasonable  $\eta_{FC} = 50\%$  will be used in this calculation.

### 2.4 Integrated system of AHP, MSR, and FC

Figure 3 shows the integrated system of the AHP, MSR and FC. Here we see there's a change in enthalpy of combustion from one mole of methanol to three moles of hydrogen. Based on the Law of Energy Conservation, heat input in the amount of 130.97 kJ must be supplied to the MSR process. This heat input, which comes from the Absorber of AHP, has the temperature level of 71°C (344K). This temperature level is enough for the theoretical case, however, in actual system, it won't work. The conversion of the methanol to hydrogen will be very low or even won't proceed. Therefore, by any means, in order to get a highly-efficient total energy system, the methanol conversion must reach 100% conversion. Empirically, this can be achieved by supplying heat input ( $Q_A$ ) with temperature level  $T_A \geq 200^\circ\text{C}$ .

However, assume that the attempts to decrease this temperature level of MSR could succeed, to say 100% conversion of methanol can be reached in  $T_A = 120^\circ\text{C}$ ,  $160^\circ\text{C}$  or  $200^\circ\text{C}$ . Then, to pick up a case, heat input with energy amount of 130.97 kJ with temperature level  $200^\circ\text{C}$  will have the Gibbs-energy (exergy) of 27.92 kJ. However, only 9.18 kJ of exergy increase will be accepted by the MSR. Then we can view this system that 18.74 kJ of exergy is destroyed. Table 3 also shows the cases for  $120^\circ\text{C}$  and  $160^\circ\text{C}$ . This implies that if efforts to decrease the 100% MSR conversion-temperature level could give fruit, less exergy of  $Q_A$  would be destroyed.

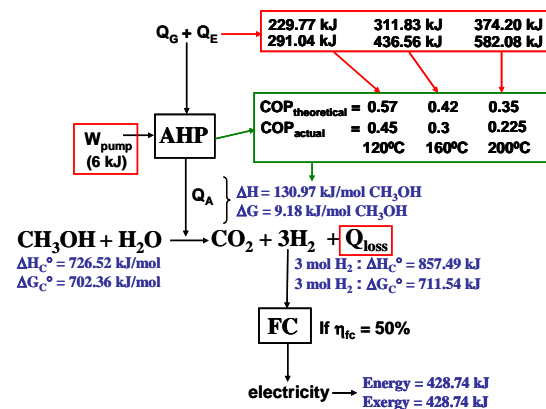


Figure 3. Integrated System of AHP, MSR, and FC Diagrams

Meanwhile, the energy contained in three moles of hydrogen is transferred to the FC. Since the efficiency of the FC with respect to energy is 50%, thus 428.74 kJ of electricity energy will be produced. The exergy of this produced electricity is also 428.74 kJ since electricity has the exergy rate of 100%.

Table 3. AHP Heat Output Exergy Content and Exergy Destroyed

| Temperature | $Q_A$<br>( $\Delta H_{MSR}^\circ$ ) | $\varepsilon$ | Exergy contained | Exergy destroyed |
|-------------|-------------------------------------|---------------|------------------|------------------|
| 120°C       | 130.97<br>kJ                        | 0.1319        | 17.27 kJ         | 8.09 kJ          |
| 160°C       | 130.97<br>kJ                        | 0.1752        | 22.94 kJ         | 13.76 kJ         |
| 200°C       | 130.97<br>kJ                        | 0.2132        | 27.92 kJ         | 18.74 kJ         |

The work required to drive the liquid pumps ( $W_{pump}$ ) in AHP is considered about 6 kW for the actual system.

### 2.5 Hydrogen production system

For the case of hydrogen production, Figure 3 can be viewed in restriction up to the output of MSR. In other words, the Fuel Cell is excluded from the integrated system. The calculation for this special case of hydrogen production efficiency will be presented in section 3.4.

## 3. Results and Discussion

Referring to Figure 3 and AHP data in Table 1, the integrated system total efficiency was calculated for both energy and exergy efficiencies. This energy and exergy efficiencies calculation will be further divided into several cases, i.e. theoretical and actual approximation cases as well as thermodynamic-based and practical-based cases.

### 3.1. Energy Efficiency Calculation

#### a. Theoretical/Ideal Thermodynamic-based Total Energy Efficiency

Theoretical/Ideal case here means the values of energy used in the calculation were the theoretical ones where the COP of AHP used were the theoretical COP and energy content of methanol was the theoretical value as well. "Thermodynamic-based" means that the waste heat input energy to the AHP was included in calculation. Thus, the Theoretical/Ideal Thermodynamic-based Total Energy Efficiency could be written as:

$$\eta_{en,total}^1 = \frac{\text{electricity energy produced}}{CH_3OH \text{ energy} + \text{total AHP heat input energy}} = \frac{428.74 \text{ kJ}}{726.52 \text{ kJ} + (130.97 \text{ kJ} / COP_{AHP})} \quad (11)$$

For the theoretical  $COP_{AHP}$  values of 0.57 (120°C), 0.42 (160°C), 0.35 (200°C); the total energy efficiency will be 44.83%, 41.29%, 38.95% respectively. If work required for liquid pumps ( $W_{pump}$ ) would be included in the denominator of Eq. (11), the total energy efficiency will become 44.55%, 41.05% and 38.73%. We can see that only less than 1% decrease of efficiency occurred. This is why in many cases of AHP efficiency calculation, the work required to drive the pumps could be neglected.

#### b. Theoretical/Ideal Practical-based Total Energy Efficiency.

Since the waste heat input ( $Q_G+Q_E$ ) to the AHP was usually discarded unless it is used in this system, we could practically exclude it in the calculation. This will be named the "Practical-based" and thus the Theoretical/Ideal Practical-based Total Energy Efficiency will be:

$$\eta_{en,total}^2 = \frac{\text{electricity energy produced}}{CH_3OH \text{ energy} + W_{pump}} = \frac{428.74 \text{ kJ}}{726.52 \text{ kJ} + 6 \text{ kJ}} = 58.52\% \quad (12)$$

#### c. Actual-Approximation Thermodynamic-based Total Energy Efficiency

In actual system, however, irreversibility and energy losses will unavoidably occur. Significant losses in AHP such as heat losses in Heat Exchanger as well as heat losses in the MSR reactor should be taken into consideration. Therefore, the COP values of actual AHP system will be used for this case calculation.  $W_{pump}$  required in AHP must be included as well. Besides, assumption of 20% inefficiency with respect to methanol energy in the MSR process will be used. This means that 145.30 kJ of heat loss occurred in the MSR reactor and hence the number of moles of methanol supplied must be increased to compensate this heat loss. In other words, 871.82 kJ of methanol input energy needs to be supplied to the MSR process. This equals the energy of 1.2 moles of methanol. Therefore, this actual-approximation thermodynamic-based total energy efficiency could be written as:

$$\eta_{en,total}^3 = \frac{\text{electricity energy produced}}{CH_3OH \text{ energy} + \text{total AHP heat input energy} + W_{pump}} = \frac{428.74 \text{ kJ}}{871.82 \text{ kJ} + (130.97 \text{ kJ} / COP_{AHP,actual}) + 6 \text{ kJ}} \quad (13)$$

For the actual  $COP_{AHP}$  values of 0.45 (120°C), 0.3 (160°C), 0.225 (200°C); the total energy efficiency will be 36.68%, 32.61% and 29.36% respectively.

#### d. Actual-Approximation Practical-based Total Energy Efficiency

Meanwhile, for the practical case, the actual-approximation practical-based total energy efficiency will be:

$$\eta_{en,total}^4 = \frac{\text{electricity energy produced}}{CH_3OH \text{ energy} + W_{pump}} = \frac{428.74 \text{ kJ}}{871.82 \text{ kJ} + 6 \text{ kJ}} = 48.84\% \quad (14)$$

### 3.2 Exergy efficiency calculation

The exergy efficiency, similarly, will be calculated in previously-defined cases as in energy efficiency calculation.

### a. Theoretical/Ideal Thermodynamic-based Total Exergy Efficiency

In this case, the total exergy efficiency could be written as:

$$\eta_{ex,total}^1 = \frac{\text{electricity exergy produced}}{CH_3OH \text{ exergy} + \text{total AHP heat input exergy}}$$

$$= \frac{428.74 \text{ kJ}}{702.36 \text{ kJ} + \varepsilon_{@80^\circ\text{C}} (130.97 \text{ kJ} / COP_{AHP})}, \quad (15)$$

where the exergy rate of the 80°C heat input is 0.0822. For the theoretical COP<sub>AHP</sub> values of 0.57 (120°C), 0.42 (160°C), 0.35 (200°C); the total exergy efficiency will be 59.44%, 58.89%, 58.48% respectively. If the exergy of the W<sub>pump</sub> would be included in the denominator of Eq. (15), the total exergy efficiency will become 58.95%, 58.41% and 58.00%. Still, relatively small efficiency decrease (less than 1%) occurred, even in the exergy calculation case.

### b. Theoretical/Ideal Practical-based Total Exergy Efficiency

Here, the exergy of the AHP waste heat input was excluded and the total exergy efficiency for this theoretical practical-based will become

$$\eta_{ex,total}^2 = \frac{\text{electricity exergy produced}}{CH_3OH \text{ exergy} + W_{pump}}$$

$$= \frac{428.74 \text{ kJ}}{702.36 \text{ kJ} + 6 \text{ kJ}} = 60.52\% \quad (16)$$

### c. Actual-Approximation Thermodynamic-based Total Exergy Efficiency

With the same assumptions as in the energy efficiency calculation, the actual-approximation thermodynamic-based total exergy efficiency could be written as:

$$\eta_{ex,total}^3 = \frac{\text{electricity exergy produced}}{CH_3OH \text{ exergy} + \text{total AHP heat input exergy} + W_{pump}}$$

$$= \frac{428.74 \text{ kJ}}{842.78 \text{ kJ} + 0.0822(130.97 \text{ kJ} / COP_{AHP,actual}) + 6 \text{ kJ}}, \quad (17)$$

where the exergy rate ( $\varepsilon$ ) of methanol is 96.67%. For the actual COP<sub>AHP</sub> values of 0.45 (120°C), 0.3 (160°C), 0.225 (200°C), the total exergy efficiency for this case will be 49.12%, 48.46% and 47.81% respectively.

### d. Actual-Approximation Practical-based Total Exergy Efficiency

For the practical case, the actual-approximation total exergy efficiency will be:

$$\eta_{ex,total}^4 = \frac{\text{electricity exergy produced}}{CH_3OH \text{ exergy} + W_{pump}}$$

$$= \frac{428.74 \text{ kJ}}{842.78 \text{ kJ} + 6 \text{ kJ}} = 50.51\% \quad (18)$$

### 3.3 Alternative actual-approximation cases

The previous actual-approximation cases, i.e. section 3.1.c, 3.1.d, 3.2.c, and 3.2.d determined that heat losses in MSR reactor could be compensated by supplying more moles of methanol. However, since the moles of hydrogen produced remain constant, there will be remaining unconverted methanol. From the view-point of energy and exergy enhancement, the initial intention of increasing 18% of energy and 1.3% of exergy by converting methanol to hydrogen seems to be no more meaningful. Therefore, the remaining unconverted moles of methanol should be pressed as low as possible and by engineering technique, the heat losses of the MSR reactor could be compensated by supplying more heat input ( $Q_A$ ) to the system. Thus, the production of 3 moles of hydrogen will only require about 1 mole of methanol (not 1.2 moles as before); which means less unconverted methanol will occur. Moreover, the waste heat available is abundant and thus it should not be regarded as limiting reactant in the MSR process.

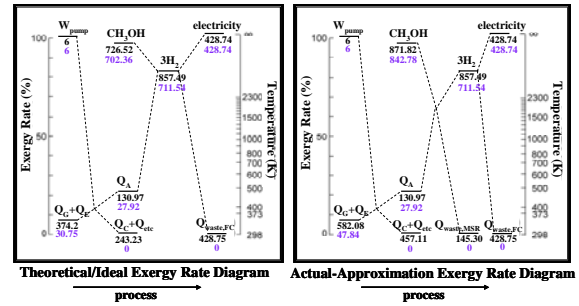


Figure 4. Exergy Rate Diagram of the Integrated System

Consequently, the efficiency of the case 3.1.c, 3.1.d, 3.2.c, and 3.2.d can be improved as follow:

#### 1. Energy case

### c. Alternative Actual-Approximation Thermodynamic-based Total Energy Efficiency

$$\eta_{en,total}^{3,alt} = \frac{\text{electricity energy produced}}{CH_3OH \text{ energy} + \text{total AHP heat input energy} + W_{pump}}$$

$$= \frac{428.74 \text{ kJ}}{726.52 \text{ kJ} + (276.27 \text{ kJ} / COP_{AHP,actual}) + 6 \text{ kJ}} \quad (19)$$

Here we could see that the amount of total heat input in AHP increases since it substitutes the compensation that otherwise supplied by methanol (145.3 kJ). Thus, for the actual COP of 0.45, 0.3, and 0.225; the total energy efficiency will become 31.84%, 25.93% and 21.87% respectively.

d. *Alternative Actual-Approximation Practical-based Total Energy Efficiency*

For the alternative actual-approximation thermodynamic-based case above, the efficiencies seem to decrease compared to 3.1.c. This is certainly true since bigger amount of waste heat energy is required to substitute the compensation energy provided by methanol previously. However, since the waste heat is free and abundant, for the practical-based case, it can be excluded in the calculation and the efficiency will increase significantly as follow:

$$\eta_{en,total}^{4,alt} = \frac{\text{electricity energy produced}}{CH_3OH \text{ energy} + W_{pump}} = \frac{428.74 kJ}{726.52 kJ + 6 kJ} = 58.52\% \quad (20)$$

This is exactly the same as the Theoretical/Ideal Practical-based Total Energy Efficiency (3.1.b).

2. Exergy Case

a. *Alternative Actual-approximation Thermodynamic-based Total Exergy Efficiency*

$$\eta_{ex,total}^{3,alt} = \frac{\text{electricity exergy produced}}{CH_3OH \text{ exergy} + \text{total AHP heat input exergy} + W_{pump}} = \frac{428.74 kJ}{702.36 kJ + 0.0822(276.27 kJ / COP_{AHP,actual}) + 6 kJ} \quad (21)$$

For the actual COP of 0.45, 0.3, and 0.225; the exergy efficiency will become 56.50%, 54.68% and 52.97% respectively. It is increased compared to 3.2.c.

b. *Alternative Actual-approximation Practical-based Total Exergy Efficiency*

$$\eta_{ex,total}^{4,alt} = \frac{\text{electricity exergy produced}}{CH_3OH \text{ exergy} + W_{pump}} = \frac{428.74 kJ}{702.36 kJ + 6 kJ} = 60.52\% \quad (22)$$

shows a significantly high increase in efficiency result which equals case 3.2.b.

3.4. Hydrogen production efficiency

1. Energy Case

In the same way and cases as previous total efficiency calculation, for the case if the output is hydrogen, then we shall get following results:

a. *Thermodynamic-based Efficiency*

$$\eta_{en,H_2}^1 = \frac{\text{Hydrogen energy produced}}{CH_3OH \text{ energy} + \text{total AHP heat input energy} + W_{pump}} \quad (23)$$

= 89.10%, 82.10%, 77.48% (theoretical)  
= 73.36%, 65.23%, 58.73% (actual-approximation),

Table 4. Energy and Exergy Efficiency Calculation Results of the Integrated System of AHP, MSR, and FC

|  |        |        |        |
|--|--------|--------|--------|
| Total Energy Efficiency (Theoretical Thermodynamic-based)          | 44.55% | 41.05% | 38.73% |
| Total Energy Efficiency (Theoretical Practical-based)              | 58.52% | 58.52% | 58.52% |
| Total Energy Efficiency (Actual-approximation Thermodynamic-based) | 36.68% | 32.61% | 29.36% |
| Total Energy Efficiency (Actual-approximation Practical-based)     | 48.84% | 48.84% | 48.84% |
| Total Energy Efficiency (Alt Actual-approx Thermodynamic-based)    | 31.84% | 25.93% | 21.87% |
| Total Energy Efficiency (Alt Actual-approx Practical-based)        | 58.52% | 58.52% | 58.52% |
| Total Exergy Efficiency (Theoretical Thermodynamic-based)          | 58.95% | 58.41% | 58.00% |
| Total Exergy Efficiency (Theoretical Practical-based)              | 60.52% | 60.52% | 60.52% |
| Total Exergy Efficiency (Actual-approximation Thermodynamic-based) | 49.12% | 48.46% | 47.81% |
| Total Exergy Efficiency (Actual-approximation Practical-based)     | 50.51% | 50.51% | 50.51% |
| Total Exergy Efficiency (Alt Actual-approx Thermodynamic-based)    | 56.50% | 54.68% | 52.97% |
| Total Exergy Efficiency (Alt Actual-approx Practical-based)        | 60.52% | 60.52% | 60.52% |

Table 5. Hydrogen Production Energy and Exergy Efficiency Calculation Results

|  |         |         |         |
|--|---------|---------|---------|
| Energy Efficiency (Theoretical Thermodynamic-based)          | 89.10%  | 82.10%  | 77.48%  |
| Energy Efficiency (Theoretical Practical-based)              | 117%    | 117%    | 117%    |
| Energy Efficiency (Actual-approximation Thermodynamic-based) | 73.36%  | 65.23%  | 58.73%  |
| Energy Efficiency (Actual-approximation Practical-based)     | 97.68%  | 97.68%  | 97.68%  |
| Exergy Efficiency (Theoretical Thermodynamic-based)          | 97.84%  | 96.94%  | 96.26%  |
| Exergy Efficiency (Theoretical Practical-based)              | 100.44% | 100.44% | 100.44% |
| Exergy Efficiency (Actual-approximation Thermodynamic-based) | 81.53%  | 80.43%  | 79.35%  |
| Exergy Efficiency (Actual-approximation Practical-based)     | 83.83%  | 83.83%  | 83.83%  |

b. *Practical-based Efficiency*

$$\eta_{en,H_2}^2 = \frac{\text{Hydrogen energy produced}}{CH_3OH \text{ energy} + W_{pump}} \quad (24)$$

= 117% (theoretical)  
= 97.68% (actual-approximation).

For hydrogen production, the actual-approximation cases above assume that there's heat loss in MSR that

counts for 20% of methanol energy and compensated by adding more methanol input.

## 2. Exergy Case

### a. Thermodynamic-based Efficiency

$$\eta_{ex,H_2}^1 = \frac{\text{Hydrogen exergy produced}}{CH_3OH \text{ exergy} + \text{total AHP heat input exergy} + W_{pump}} \quad (25)$$

= 97.84%, 96.94%, 96.26% (theoretical)

= 81.53%, 80.43%, 79.35% (actual-approximation),

### b. Practical-based Efficiency

$$\eta_{ex,H_2}^2 = \frac{\text{Hydrogen exergy produced}}{CH_3OH \text{ exergy} + W_{pump}} \quad (26)$$

= 100.44% (theoretical)

= 83.83% (actual-approximation).

## 3.5. Exergy rate diagram

These theoretical as well as actual-approximation calculations of energy and exergy efficiencies can be visualized by the exergy rate diagrams as shown in Figure 4. These exergy rate diagrams show the energy-conversion processes starting from the AHP to FC. They also describe the enhancement as well as decrease of exergy rate values of various kinds of energy quantities.

## 3.6. Additional discussion

All the energy and exergy efficiencies were summarized in Table 4 and Table 5. For comparison, currently one of the best power plant combustion system that uses the Advanced Combined Cycle (ACC), has the energy efficiency of 54% based on LHV (Low Heating Value)<sup>20</sup>. Therefore, the efficiency of this power plant, on HHV (High Heating Value) based, is about 48.66% where its exergy efficiency is 52.97% as shown in Figure 5. The fuel, natural gas, is a fossil-fuel that will eventually be depleted. Even though the fuel for the power plant is natural gas (methane), if methanol is used instead, the power plant efficiency will be relatively similar<sup>21,22</sup>.

However, this integrated system of AHP, MSR and FC is not without problem. The feedstock to produce methanol is an important issue. Currently, methanol is mostly produced from fossil-fuel as well, since it is economically the most favorable. Therefore, it is necessary for further research to find alternative/renewable resources to produce methanol, as have been done by several research<sup>23,24</sup>. Biomass, agricultural, industrial and other wastes have potential to produce huge amount of methanol.

This integrated system still has many spaces for efficiency improvement. Higher temperature of waste heat input in AHP system (80°C was used in this calculation), more efficient and higher COP of the AHP, higher efficiency of MSR reactor and certainly higher efficiency of FC will further yield significant increase in the total integrated system efficiency.

In particular, hydrogen production cases show high efficiencies due to the principle of waste heat energy recovery/recycling. Here, the low quality waste heat which is difficult to reuse and usually discarded, has been enhanced by the AHP system. This enhanced waste heat is then absorbed by the MSR process to be stored into the high quality chemical energy, i.e. the hydrogen energy. This hydrogen will be further utilized through various hydrogen-related technologies to support the Hydrogen Economy scheme in the future.

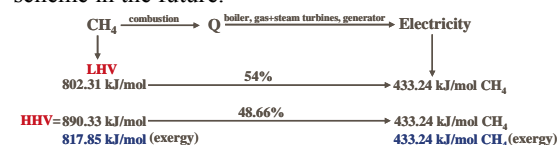


Figure 5. Power Plant Combustion System and Efficiency Analysis.

## 4. Conclusion

With the specified conditions and assumptions, for the MSR temperature of 200°C, the integrated system of AHP, MSR and FC has the energy efficiency of 38.73% and 58.52% for the theoretical thermodynamic-based and practical-based cases; as well as 29.36% and 48.84% for the actual-approximation thermodynamic and practical-based cases, respectively. In term of exergy, it will be 58%, 60.52%, 47.81%, and 50.51% for the respective cases.

Meanwhile, for the hydrogen production efficiency and MSR temperature of 200°C, the thermodynamic-based case will yield 77.48% and 58.73% for theoretical and actual-approximation cases respectively. For practical-based case, it will be 117% (theoretical) and 97.68% (actual-approximation). In term of exergy, the efficiency will be 96.26% and 79.35% for thermodynamic-based; 100.44% and 83.83% for practical-based respectively.

The efficiency of actual-approximation cases can be further improved to approach the theoretical cases by supplying more heat input to compensate the heat loss in the MSR. This is especially significant for the practical-based cases. Moreover, spaces for efficiency improvement in parts of this integrated system are still available.

If this high efficiency integrated system that utilizes the concept of exergy enhancement can be combined with the potential methanol production from renewable resources (including wasted material), it is not impossible that this integrated system could, one day, become a high-efficient and sustainable energy system.

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### References

1. K. Okazaki and M. Akai, Countermeasures to Global Warming by Integration of Coal, Hydrogen and CO<sub>2</sub> Sequestration, and System Evaluation, The 36<sup>th</sup> Clean Coal Seminar, p. 17-46, 2004.
2. K. Okazaki, Significance of Hydrogen Energy Introduction and Technology Prospects, *Petrotech*, **25(8)**, 627-632, 2002.
3. Y. Kozawa, and K. Okazaki, Total Energy System Based on Fuel Cells, *Chemical Engineering*, **65(10)**, 530-533, 2001.
4. K. Okazaki, Clean and Efficient Coal Technology Integrated with Hydrogen Energy Systems, 9<sup>th</sup> Asian Hydrogen Energy Conference 2007, Plenary Lecture, Tokyo, Japan, 17-30, 2007.
5. P. Mathieu, Toward the Hydrogen Era using Near-zero CO<sub>2</sub> Emissions Energy Systems, *Energy*, **29**, 1993-2002, 2004.
6. K. Yoshida, Prospects and challenges of hydrogen energy system. The 2<sup>nd</sup> COE-INEN International Workshop on "Toward Hydrogen Economy", Tokyo, Japan, 2006.
7. K. Okazaki, Exergy Enhancement and Effective use of Low-to-medium-temperature Waste Heat with an Example of Biomass Hydrogenation, *Hydrogen Energy System Society of Japan (HESS)*, **29(1)**, 18-25, 2004.
8. H. Sumitomo *et al.*, Exergy Enhancement of Low Temperature Waste Heat by Methanol Steam Reforming for Hydrogen Production, 8<sup>th</sup> Asian Hydrogen Energy Conference 2005, Beijing, China, 2005.
9. P.J.D. Wild and M.J.F.M. Verhaak, Catalytic Production of Hydrogen from Methanol, *Catalysis Today*, **60**, 3-10, 2000.
10. Y.M. Lin and M. H. Rei, Study on the Hydrogen Production from Methanol Steam Reforming in Supported Palladium Membrane Reactor, *Catalysis Today*, **67**, 77-84, 2001.
11. S. R. Segal *et al.*, Low Temperature Steam Reforming of Methanol Over Layered Double Hydroxide-derived Catalysts, *Applied Catalysis A: General*, **231**, 215-226, 2002.
12. N. Iwasa *et al.*, Hydrogen Production by Steam Reforming of Methanol, *Journal of Chemical Engineering of Japan*, **37(2)**, 286-293, 2004.
13. A. Basile, F. Gallucci and L. Paturzo, A Dense Pd/Ag Membrane Reactor for Methanol Steam Reforming: Experimental Study, *Catalysis Today*, **104**, 244-250, 2005.
14. F. Steimle, Heat Pumps for Waste Heat Recovery and Economical use of Energy. ICCR 1998, Hangzhou, China. *Soc des Ingenieurs de l'Automobile*. P. 209-215, 1998.
15. X. Ma *et al.*, Application of Absorption Heat Transformer to Recover Waste Heat from a Synthetic Rubber Plant, *Applied Thermal Engineering*, **23**, 797-806, 2003.
16. A. Costa *et al.*, Application of Absorption Heat Pumps in the Pulp and Paper Industry for Increased Efficiency and Reduction of Greenhouse Gas Emissions, *PAPTAC 2004*, Montreal, Canada, vol. B. p. 191-195, 2004.
17. D. C. A. Padilla and L. G. Rodriguez, Application of Absorption Heat Pump to Multi-effect Distillation: a Case Study of Solar Desalination, *Desalination*, **212**, 294-302, 2007.
18. N. Inoue *et al.*, COP Evaluation for Advanced Ammonia-based Absorption Cycles, *International Absorption Heat Pump Conference 1994*, New Orleans, USA. ASME, 1994. p. 1-6, 1994.
19. N. Inoue, K. Irie and Y. Fukusumi Y. Analysis on Static Characteristics of Heat Transformer (昇温型吸収ヒートポンプの特性解析). *Trans. of the JSRAE*, **22 (2)**, 173-184, 2005 (in Japanese)
20. Tokyo Electric Power Company (TEPCO). Highly efficient and Environmentally-friendly Yokohama Thermal Power Station. TEPCO Pamphlet, p. 5-8, 2006.
21. Tokyo Electric Power Company (TEPCO). Methanol power generation—demonstration test starts for a power source at peak demand. Japanese High-Technology Monitor, April 5 1993.
22. G. F. Janda *et al.*, High Efficiency Reformed Methanol Gas Turbine Power Plants, Houston, TX: Exxon Chemical Patents Inc, 1999.
23. R.J. Nichols, The Methanol Story: a Sustainable Fuel for the Future, *Journal of Scientific & Industrial Research*, **62**, 97-105, 2003.
24. T. Ekbom, High Efficient Motor Fuel Production from Biomass via Black Liquor Gasification, ISAF XV 2005, San-Diego, USA, 2005.