Heat Recovery of LDG by Utilizing Latent Heat and Reaction Heat for Producing Methanol

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This paper proposes a new heat recovery process of hot gas exhausted from the steelmaking converter by utilizing not only latent heat but also endothermic heat of reaction. The intermittently emitted LD gas was first transferred into continuous, constant-temperature heat source in the form of latent heat in the Phase Change Material (PCM) of copper. Then, the stored heat was supplied to Coke Oven Gas (COG) to induce endothermic reaction of methane steam reforming. Methanol was finally produced from the obtained gas in the proposed system. A heat and material balance model predicted all operating data of the system and then exergy analysis based on the predicted data was conducted to validate the system theoretically. The results showed that the proposed system has a possibility to produce a large amount of methanol corresponding to 20% of total demand in Japan, with only 28% of exergy consumption in the conventional method.

KEY WORDS: steelmaking; LDG heat recovery; PCM; hydrogen; methanol production; chemical recovery; COG reforming; exergy evaluation.

1. Introduction

The Japanese steelmaking industry consumes as much as 11% of total primary energy, and then releases 5% in the form of waste heat. Although many equipments for energy saving have been introduced after two oil crises, the waste of high temperature such as blast furnace (BF) slag and LD converter slag still remains unused. Thus, authors have reported several papers1–9) to save energy and to decrease carbon dioxide emissions. In the steelmaking process the converter has also released high temperature waste gas (LDG) over 1 873 K, as a result of oxygen blowing into the converter. Most of its sensible heat becomes waste in spite of its large potential.6) This is mainly because the temperature of LDG is too high to recover it efficiently by conventional technologies and the emission is intermittent, not constant, due to unsteady operation: that is, charging of hot iron, oxygen blowing for de-carbonization and discharging of steel. In addition, the incomplete sealing system of the converter by skirts makes direct heat recovery of LDG more difficult. The existing Off-Gas (OG) boiler may be effective for recovering the lower temperature part of LDG, however it dose not recover the higher one elementally.6) Therefore, a new technology is needed to utilize LDG heat over 1 273 K in temperature.

The development of a heat storage material for efficient heat recovery of the intermittently emitted, high temperature waste heat10,11) such as combustion waste gas is under consideration. In the companion paper,12) we reported a new heat storage material with large latent heat, so-called Phase Change Material (PCM), in which the encapsulation technology of copper sphere with nickel film based on an electroplating method was mainly examined. Advantages of the PCM system12,13) are the followings;

(1) Heat Source of Constant Temperature: The PCM stores sensible heat in the form of latent heat due to melting and then releases the thermal energy of a fixed melting point of the PCM during the solidification.
(2) High Storage Density: Generally speaking, latent heat of the PCM is 50 to 100 times larger than the sensible heat.
(3) Heat Recovery Without Much Temperature Drop: The PCM system can regenerate thermal energy of high temperature by selecting a melting point of the PCM close to the temperature of waste heat.
(4) Repeatable Utilization: The melting and solidifying procedure of the PCM is elementally repeatable everlasting.

In addition, selection of the coating material of PCM can be flexibly selected. For example, it is reported that the nickel film behaves as an excellent catalyst for methane steam reforming.11)

Recently, a new concept of heat recovery by using an endothermic chemical reaction not sensible heat has been focussed.6) This method is attractive in terms of direct recovery without much temperature drop, because the conventional method based on sensible heat storage by using ceramics or water etc. is indirect one, needing to add a heat exchange. This concept is based on that an endothermic reaction such as methane steam reforming can be combined
to high temperature waste heat for converting its thermal energy into chemical energy. Thanks to the direct combination of waste heat with endothermic reaction we can save large amounts of fossil fuel, because a key phenomena in many industries is usually an endothermic reaction.

The steam reforming of methane is an essential one in the chemical industry or ironmaking industry with the direct reduction for producing hydrogen and carbon monoxide. Thus, as one promising selection, the generated hydrogen and carbon monoxide can be available to synthesize methanol. This would be quite reasonable from a fact that the demand of methanol is drastically increasing for vehicle fuel or a hydrogen source of a fuel cell, etc.

Therefore, the purpose of this paper is to study a new recovery system of LDG waste heat by not only latent heat but also endothermic chemical reaction, in which a detailed operating data was mainly evaluated and then exergy analysis based on the obtained data was carried out to assess the total process. The results will appeal a possibility to realize a new process for co-producing steel and methanol. In other words, the proposed system is contributed to promoting energy saving in the steelworks by reducing the methanol productive energy in the chemical industry.

2. Proposed system

2.1. Conventional Converter

Table 1 gives a material balance of one typical LD converter with a scale of 240 tone of steel. Note that one charge of 250 tone of hot metal to the LD converter by-produces as much as 31 500 Nm$^3$ of LDG with blowing oxygen into the hot metal for de-carbonization. The LDG, recovered and stored by the gasholder, is 65%CO–17%CO$_2$–17%N$_2$–1%H$_2$ in composition and 343 K (70°C) in temperature. The LDG stored is usually effectively used as fuel within the steelworks, for example, for heating blasting air in a hot stove furnace or for generating electricity power. The temperature of LDG, as soon as the generation, becomes very high due to huge exothermic heat of de-carbonization reaction. However the sensible heat of such high temperature gas is not recovered at the present due to technical difficulty, unfortunately.

To utilize the LDG waste heat effectively, we need to keep it as high levels as possible is very crucial for the use of another process from the viewpoint of exergy theory. It is because the thermal energy at higher temperatures has the higher potential to do work more effectively. The previous report concluded that the LDG heat of high temperature, if it is over 1 300 K, must be supplied to the endothermic processes requiring high temperature heat close to 1 300 K, such as coal gasification, natural gas reforming, limestone decomposition, etc. We should never use it for generating hot water of 353 K or steam of 473 K absolutely with much temperature drop, based on the thermodynamic theory that exergy is lost once the temperature drops even if the heat loss is negligible.

2.2. LDG Heat Storage by Latent Heat

The converter releases the LDG only during the period of oxygen blowing. For recovering/storing the intermittently released LDG and then supplying it as heat source with a constant temperature to another process, the utilization of latent heat between solid and liquid by using Phase Change Material (PCM) is very helpful.

In the companion paper, the PCM balls were manufactured and then experimentally validated by the practical use under melting and solidification conditions. In the manufacturing process of the PCM, copper spheres were uniformly coated by nickel with an inserted inert material based on an electroplating method. The results of heating tests showed that the PCM balls have enough strength against cyclic heating and cooling tests and that the surface of the nickel film is very active for reforming methane by steam at the melting point of copper, 1 356 K. It was concluded that the developed PCM balls can not only store

<table>
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<tr>
<th>Inflow</th>
<th>T/ch or Nm$^3$/ch</th>
<th>K (°C)</th>
<th>Pressure</th>
<th>C</th>
<th>H</th>
<th>Ca</th>
<th>Si</th>
<th>P</th>
<th>Mn</th>
<th>Fe</th>
<th>H$_2$O</th>
<th>O$_2$</th>
<th>N$_2$</th>
<th>C$<em>{2}$H$</em>{6}$</th>
<th>H$_2$</th>
<th>CO</th>
<th>CO$_2$</th>
<th>%</th>
<th>t/ch</th>
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<td>Hot metal</td>
<td>250</td>
<td>1623 (1350)</td>
<td>11.3</td>
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<td>0.3</td>
<td>0.7</td>
<td>236.9</td>
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<tr>
<td>Subsidiary raw material</td>
<td>20</td>
<td>293 (20)</td>
<td>0.0</td>
<td>6.2</td>
<td>1.2</td>
<td>0.7</td>
<td>2.7</td>
<td>0</td>
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<tr>
<td>Blast oxygen</td>
<td>14500</td>
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<td>0.9</td>
<td>0.3</td>
<td>0.7</td>
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<tr>
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<td>3509</td>
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<td>0.9</td>
<td>0.3</td>
<td>0.7</td>
<td>236.9</td>
<td>21</td>
<td>79</td>
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<td></td>
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<tr>
<td>Cooling water for skirt</td>
<td>71</td>
<td>291 (18)</td>
<td>0.9</td>
<td>0.3</td>
<td>0.7</td>
<td>236.9</td>
<td>21</td>
<td>79</td>
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<tr>
<td>Cooling water for blowing lance</td>
<td>138</td>
<td>291 (18)</td>
<td>0.9</td>
<td>0.3</td>
<td>0.7</td>
<td>236.9</td>
<td>21</td>
<td>79</td>
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<tr>
<td>Water for collecting dust</td>
<td>330</td>
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<td>0.3</td>
<td>0.7</td>
<td>236.9</td>
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<tr>
<td><strong>Sum</strong></td>
<td></td>
<td></td>
<td>11.3</td>
<td>0.9</td>
<td>0.3</td>
<td>0.7</td>
<td>236.9</td>
<td>100</td>
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<tr>
<th>Outflow</th>
<th>T/ch or Nm$^3$/ch</th>
<th>K (°C)</th>
<th>Pressure</th>
<th>C</th>
<th>H</th>
<th>Ca</th>
<th>Si</th>
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<th>H$_2$O</th>
<th>O$_2$</th>
<th>N$_2$</th>
<th>C$<em>{2}$H$</em>{6}$</th>
<th>H$_2$</th>
<th>CO</th>
<th>CO$_2$</th>
<th>%</th>
<th>t/ch</th>
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<tr>
<td>Steel</td>
<td>240</td>
<td>1873 (1600)</td>
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<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>239.5</td>
<td>100</td>
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<td>Recovered steam</td>
<td>21</td>
<td>452 (178)</td>
<td>0.1</td>
<td>10.3</td>
<td>0.0</td>
<td>16.9</td>
<td>1.3</td>
<td>64.8</td>
<td>16.9</td>
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<td>LD gas</td>
<td>31500</td>
<td>343 (70)</td>
<td>0.1</td>
<td>10.3</td>
<td>0.0</td>
<td>16.9</td>
<td>1.3</td>
<td>64.8</td>
<td>16.9</td>
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<tr>
<td>Cooling water for blowing lance</td>
<td>138</td>
<td>303 (30)</td>
<td>0.1</td>
<td>10.3</td>
<td>0.0</td>
<td>16.9</td>
<td>1.3</td>
<td>64.8</td>
<td>16.9</td>
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<tr>
<td>Water for collecting dust</td>
<td>330</td>
<td>293 (20)</td>
<td>0.1</td>
<td>10.3</td>
<td>0.0</td>
<td>16.9</td>
<td>1.3</td>
<td>64.8</td>
<td>16.9</td>
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<tr>
<td>Waste steam</td>
<td>0.9</td>
<td>373 (100)</td>
<td>0.1</td>
<td>10.3</td>
<td>0.0</td>
<td>16.9</td>
<td>1.3</td>
<td>64.8</td>
<td>16.9</td>
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<tr>
<td><strong>Sum</strong></td>
<td></td>
<td></td>
<td>10.9</td>
<td>0.0</td>
<td>0.3</td>
<td>2.6</td>
<td>240.5</td>
<td>100</td>
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waste heat of high temperature, release heat source of a constant temperature, but also behave as an excellent catalyst for the steam reforming. From these findings, the proposal of a new process for recovering LDG heat by using latent heat of the PCM and endothermic heat of methane steam reforming, looks quite reasonable as shown in Fig. 1.

Table 2 gives the various properties of the PCM for the high temperature applications. After reviewing them from large latent heat per cubic-meter, reasonable price and high thermal conductivity, copper was selected as the PCM in this study. The PCM material, its shape or its equipment for high temperature application is still under investigation, because it strongly depends on each objective process condition.

2.3. LDG Heat Recovery by Endothermic Reaction

In general, a key reaction in other industries is always an endothermic one, in which fossil fuel is consumed to obtain exothermic heat of combustion. Therefore, the combination between LDG heat and endothermic reaction will lead to the saving energy if possible. In this study the steam reforming reaction of methane of Eq. (1) was selected as a combination reaction for the heat recovery of LDG.

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad \Delta H_{298} = 206 \text{ kJ/mol} \quad \ldots (1)
\]

Figure 3 shows the operating conditions of the proposed process, in which both latent heat and reaction heat are utilized for the recovery of LDG heat. As methane source, Coke Oven Gas (COG) was selected. Operating data of this process depend on some parameters as mentioned later.
3. Method

3.1. Operating Data Evaluation

Figure 4 shows an algorism for predicting operating data of the proposed process based on a heat and material balance. In this process, COG was constantly supplied into the PCM reactor as a source of methane at a constant flowing rate. The composition of COG was H₂/N₂/CH₄/CO/CO₂/H₂O = 58.22/2.84/29.2/7.78/1.96 (mol%). The assumed packed bed reactor of PCM is indirectly heated by LDG heat. In this process, the following fundamental equations were derived.

A) Overall heat balance:

\[
\Delta Q = Q_{IN} - Q_{OUT} = t_b(Q_g + f_{CH_4} Q_R) V_{COG,IN} + t_{NB}(Q_g + f_{CH_4} Q_R) V_{COG,IN}\]

B) Heat stored by PCM:

\[
t_{NB}(Q_g + f_{CH_4} Q_R) V_{COG,IN} = \frac{Q_L}{H_{11005}} W_{PCM}\]

The detailed procedure to evaluate operating data is as follows:

1) Input data of initial conditions; LDG's temperature (T_{LDG,IN}), flow rate (V_{LDG}), chemical composition (C_{LDG}), oxygen blowing time (t_b), time until the next blowing period (t_{NB}), inlet COG's chemical composition (C_{COG,IN}) and current of flow rate (\alpha).

2) Calculate equilibrium chemical composition (C_{COG,OUT}) of the outflowing COG in the help of the commercial software code of thermodynamics: ASPEN PLUS.

3) Input the inflowing rate of the COG (V_{COG,IN}) as an initial condition. This is added by \alpha in the iteration loop.

4) Calculate the heat (\Delta Q) required for the complete steam reforming of methane, expressed by Eq. (2), and then evaluate weight of PCM (W_{PCM}) for storing the heat by Eq. (3).

5) Calculate the sensible heat of the inflowing LDG (\Delta T) and then evaluate the temperature drop (\Delta T) of COG after the heat exchange. Temperature dependence of average specific heat of COG and LDG was incorporated.

6) Evaluate amounts of hydrogen (V_{H_2}) and methanol production from this system.

7) Increase V_{COG,IN} at the interval of \alpha until (T_{LDG,IN} - \Delta T) is less than T_{MP} or a ratio of V_{COG,IN}/V_{LDG} is over 1.85. This value was determined from operating data of typical integrated steelworks, as given in Table 3.

8) Display the calculated parameters.

3.2. Evaluation of the System with Methanol Synthesis

Figure 5 shows a flow sheet of a conventional methanol synthesis system. It is industrially consisted of three processes; a methane steam-reforming furnace, a methanol synthesis converter and a methanol refining tower. Table 3 shows the operating conditions of the integrated steel works.

Table 3. Operating conditions of the integrated steel works.

<table>
<thead>
<tr>
<th>Item</th>
<th>Value</th>
<th>Unit</th>
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<tbody>
<tr>
<td>Fuel ratio of blast furnace</td>
<td>385</td>
<td>kg/thm</td>
</tr>
<tr>
<td>COG</td>
<td>604.4</td>
<td>Nm³/t-coke</td>
</tr>
<tr>
<td>Capacity of converter</td>
<td>232.7</td>
<td>Nm³/thm</td>
</tr>
<tr>
<td>LDG</td>
<td>250</td>
<td>t/hm/charge</td>
</tr>
<tr>
<td>COG/LDG</td>
<td>126</td>
<td>Nm³/thm</td>
</tr>
<tr>
<td>thm: ton of hot metal</td>
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</tbody>
</table>

Fig. 4. Algorism for evaluating effect of COG flowrate on the PCM weight, hydrogen generation, methanol production and energy consumption.

Fig. 5. Material flow of a conventional system for methanol production.
synthesis reactor and a distillation tower. In the methane steam-reforming furnace, methane has also been burnt to get reaction heat. For comparison between this conventional methanol production system and the new one using the syngas from LDG, exergy analysis was carried out, in which exergy loss in all of each process from a raw material to a product was evaluated, summarized and then the total exergy loss was quantitatively evaluated. This methodology has been recently called as Exegetic Life Cycle Assessment (ELCA).14)

4. Results and Discussions

4.1. Analysis of the LDG Heat Recovery Process

Figure 6 shows the calculated equilibrium compositions of the mixture gas of COG and steam, in which methane is mainly reformed by steam and carbon dioxide. With increasing temperature, methane and water decrease and nitrogen as inert gas shows a constant value. In contrast, carbon monoxide and hydrogen increase, because the above-mentioned reactions proceed with temperature. The process proposed here takes copper as the PCM, thus note that its melting point is 1 356 K at which the equilibrium composition is \( \text{H}_2/\text{O}_2/\text{N}_2/\text{CH}_4/\text{CO}/\text{CO}_2/\text{H}_2\text{O} = 76.77/0/1.52/0.03/20.61/0.13/0.95 \) (vol%).

In the previous study,11) the mixture gas of COG and steam was introduced into the pencil reactor of packed beds of the PCM balls and then the gas composition at the outlet of the reactor was monitored by a gas chromatography. The results showed that the PCM packed beds changed the mixture gas to the equilibrium composition quickly thanks to nickel of the PCM ball surface. The catalyst property of the developed PCM balls was experimentally validated as shown by marks. Those are measured compositions of hydrogen and carbon monoxide that agreed with the equilibrium values calculated around the temperature of 1 356 K.

Figure 7 shows the relationship of the temperature drop of LDG; \( \Delta T \), the heat recovered; \( \Delta Q \), and the hydrogen...
generated; \( V_{H_2} \) against the rate of the inflowing COG; \( V_{COG,IN} \). As soon as the temperature of the mixture of COG and steam increased by the LDG heat, reactions of methane reforming occurred. As a result, the three parameters of \( DT \), \( DQ \) and \( V_{H_2} \) increased linearly with \( V_{COG,IN} \). \( DT_{MAX} \) is necessarily 217 K because the inlet temperature of LDG was assumed to be 1573 K and the outlet one was not less than the melting point of the PCM. Under the condition that \( DT \) was 217 K, the Case C was that \( DQ \) was 11.6 GJ/charge, \( V_{COG,IN} \) was 50 mol/s and the possible hydrogen generation was 291 Nm\(^3\)/charge.

The weight of needed PCM is an important parameter for designing this equipment. Figure 8 shows the relationship between the temperature drop; \( DT \), and the weight of PCM; \( W_{PCM} \), at different conditions of non-blowing period; \( t_{NB} \). The results show that in the reference case of 15 min of non-blowing period, for recovering \( DT = 217 \) K’s sensible heat of LDG generated from steel of 240 ton, 6.5 ton of copper is needed, and maximum \( DT_{MAX} \) of 217 K, 28 ton (see arrows). As typical operating conditions of LD converter, the blowing oxygen period of 15 min and the non-blowing period of 15 min for discharging the steel and charging the hot metal were selected. As expected, shortening the period of non-blowing is effective for decreasing the PCM weight absolutely. Also, it can be seen that increasing the latent heat of the PCM itself is effective for that. For example, beryllium having a latent heat nine times larger than copper (see Table 2), decreases the PCM weight drastically. In this case, only 3 ton of the PCM is needed for recovering \( DT = 217 \) K’s LDG heat, as the double-dotted line shows. In comparison to the capacity of the converter of 240 ton, these values of the PCM weight would be reasonable for constructing the equipment. In contrast, we need to remember that the study of the PCM with larger density of heat storage is also effective for compacting the equipment.

### 4.2. Evaluation of the Proposed System with Methanol Synthesis

In order to evaluate the overall proposed system with methanol production, three cases (A–C) were selected as shown in Fig. 7.

The obtained hydrogen can be easily changed to methanol by adding appropriate carbon monoxide. Figure 9 shows possible methanol production evaluated at the different cases mentioned above where this value and annual steel production by BF-LD system 7×10\(^7\) ton in Japan were available. Methanol production were evaluated as 2.8 kg/thm in case A, 5.6 kg/thm in case B and 9.4 kg/thm in...
case C. Note that these values mean quite large one, in comparison to 37.1 kg/thm at present. This value of 37.1 was calculated by dividing 2.6×10^6 ton methanol by 7×10^7 ton steel annually in Japan. Based on the case C, we can produce as much as 6.6×10^7 ton of methanol annually from waste heat of LDG. This result suggests that the steelmaking converter has a possibility to be a leading producer of methanol in Japan.

Figure 10 shows comparison of the total exergy loss between the conventional and the proposed system. In evaluating the conventional system of methanol production, all operating data of each process from a raw material to the product of methanol were collected, and introduced into the equation of exergy. The exergy loss in the process was determined by difference between inflowing and outflowing one, and then was summarized as total exergy loss in the system. The results show that the reformer is the most exergy-consuming process, taking 72% of total loss. In contrast, the value of total exergy loss in the proposed system was regarded as one in the conventional systems without the steam reforming. Therefore, exergy loss in the proposed one was only 28% in comparison to the conventional one.

5. Conclusions

Based on the developed PCM technology for the high temperature application, a heat recovery system of LDG by utilizing latent heat and endothermic heat of reaction was newly proposed and investigated. The following conclusions were obtained:

1) Operating data of the process predicted by a simple model of heat and material balance showed that much hydrogen generates due to the steam reforming of COG under the reasonable amount of PCM.

2) The steelmaking converter with the proposed process can be a leading producer of methanol in Japan, probably producing 6.6×10^7 ton annually, corresponding to 20% of the total demand.

3) The proposed system can produce methanol with only 28% of total exergy loss in the conventional method. This provides a new concept of symbiotic steelworks that can produce not only steel but also methanol.

Nomenclature

- \( C_{\text{COG,IN}} \): Composition of COG at inlet (–)
- \( C_{\text{COG,OUT}} \): Composition of COG at outlet (–)
- \( C_{\text{LDG}} \): Composition of LDG (–)
- \( C_{\text{PCM}} \): Composition of PCM (–)
- \( \Delta f \): Average specific heat (J·K⁻¹·mol⁻¹)
- \( f_{\text{CH}_4} \): Content of CH\(_4\) (CH\(_4\)·mol/mol)
- \( \Delta H \): Latent heat (i=1 per unit mol (kJ/mol), i=2 per unit kg (kJ/kg), i=3 per unit volume (kJ/m\(^3\)), i=4 per unit yen (K/day))
- \( k \): Thermal conductivity (W/m·K)
- \( M \): Molecular weight (g/mol)
- \( Q_{\text{g}} \): Sensible heat of COG from \( T_{\text{COG,IN}} \) to \( T_{\text{mp}} \) (kJ/mol)
- \( Q_{\text{IN}} \): Inflowing sensible heat of LDG (kJ/thm)
- \( Q_{\text{OUT}} \): Outflowing sensible heat of LDG (kJ/thm)
- \( Q_{\text{R}} \): Heat of reaction (kJ/CH\(_4\)-mol)
- \( \Delta Q \): Recovered LDG sensible heat (kJ/thm)
- \( T_{\text{COG,IN}} \): Temperature of inflowing COG (K)
- \( T_{\text{COG,OUT}} \): Temperature of outflowing COG (K)
- \( T_{\text{MP}} \): Melting point of PCM (K)
- \( T_{\text{LDG,IN}} \): Temperature of inflowing LDG to the recovering process (K)
- \( t_b \): Blowing time (s)
- \( t_{\text{NB}} \): Non-blowing time (s)
- \( T_{\text{LDG,OUT}} \): Temperature of inflowing LDG to the recovering process (K)
- \( t_{\text{LDG}} \): Temperature of outflowing LDG to the recovering process (K)
- \( \Delta T \): Temperature drop (K)
- \( \Delta T_{\text{MAX}} \): Maximum temperature drop (K)
- \( V_{\text{COG,IN}} \): Flow rate of COG at inlet (mol/s)
- \( V_{\text{COG,OUT}} \): Flow rate of reformed COG at outlet (mol/s)
- \( V_{\text{LDG}} \): Flow rate of LDG (Nm\(^3\)/thm)
- \( V_{\text{H}_2} \): Hydrogen generated (Nm\(^3\)/charge)
- \( W_{\text{PCM}} \): Weight of PCM (ton)
- \( \alpha \): Increment of flow rate (–)

REFERENCES


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