FEASIBILITY OF WASTE HEAT RECOVERY FROM MOLTEN SLAG

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ABSTRACT

This paper describes a feasibility study of direct heat recovery system from high temperature wastes over 1700 K by using chemical reaction, in which enthalpy-exergy diagram, so-called *thermodynamic compass*, is introduced for evaluating various systems. Blast furnace slag was taken as an example for the evaluation and popular endothermic reactions in the cement production, the chemical industry, *etc.* were selected as a combination process for the heat recovery. Exergy analysis of cement and methanol plants was also carried out for further discussion.

The results showed that decomposition of limestone, reforming of methane and gasification of carbon are the most promising for heat recovery of the high temperature wastes; various slag and LD gas, from a viewpoint of effective use of exergy, not energy. This also appeals a possibility of next generation symbiotic steelworks with heat cascade utilization, rather than heat recovery.

Keywords; ironmaking, steelmaking, high temperature waste, exergy, chemical reaction, limestone decomposition, methane reforming, carbon gasification.

1. INTRODUCTION

Not a small waste heat reportedly exists in the steelmaking industry, due to technical difficulties. In typical steelworks, recovery ratio of outflow heat is still 17.5 % in enthalpy basis[1] and 25.3 % in exergy basis, despite of aggressive introduction of some energy saving equipment after the two oil crises. High temperature heat of blast furnace (BF) slag, LD converter slag, electric furnace slag, and LD gas (LDG) is not almost recovered in spite of its high potential energy. Slag emits its sensible heat to atmosphere; in contrast sensible heat of LDG is partially recovered by off-gas (OG) boiler in the form of *latent and sensible heats* of steam, however, the recovery ratio is still only 30 to 40 % in enthalpy basis[1]. In particular, high temperature region just above the converter is remaining without recovery.

Regarding to BF slag, the heat recovery process based on *air blast method* has researched in 1980's as a national project[2], however, unfortunately, it has never been realized. In this process, thermal energy of slag transfers to *sensible heat* of hot air. Recently, another trial to recover waste heat of the BF slag in the form of *sensible heat* of hot water after the wet granulation is also reported. In other words, these heat recovery processes are based on utilization of sensible heat with/without latent heat. They greatly contributes to recovery of waste heat simply, easily and economically. However, nowadays, more sophisticated, alternative way is needed from global aspect such as earth warming. That is, the new way must promote ecological-efficiency, in which more products should be obtained by less energy.

Utilization of reaction heat, instead of latent heat and sensible heat, is quite attractive from viewpoints of energy storage/transportation and connection to other industry. Nevertheless, this method has rarely been reported as far as we know. Therefore, the aim of this paper is to study *chemical heat recovery* of high temperature wastes theoretically, in which various endothermic reactions were mainly examined as a combination process by using the enthalpy-exergy diagram. The results will not show only methodology to determine best chemical heat recovery system, but also offer new idea on combination of steelmaking with different industries.

2. THEORY

Concept of the enthalpy-exergy diagram, which is originally proposed and named as *thermodynamic compass* by Ishida[3], was employed for comparing heat recovery systems using a chemical reaction. Detail of this concept was recently given by us elsewhere[4], thus

only its framework is explained here.

The *system* consists of several processes in general. The *process* means physical or chemical change, in which materials, enthalpy and exergy are in- and out-flowing. Difference of enthalpy and exergy is calculated by subtracting in-flow value from out-flow one and expressed by Δ. For the system evaluation, we have only to summarize all of Δ values within a system. This method is simple, but very powerful tool for the system design, too. In this method, first and second laws of thermodynamics within a system, expressed by equations (1) and (2), are discussed. First law means energy conservation and second one, exergy reduction. Under these constraints, exergy loss is clearly evaluated in the schematic diagram.

$$\sum_{j} \Delta H_j = 0 \qquad (1)$$

$$\sum_{j} \Delta \varepsilon_j \leq 0 \qquad (2)$$

We can plot any kinds of process as a vector of (ΔH, $\Delta \varepsilon$) in the enthalpy-exergy diagram. Thus, a system is evaluated by a synthesis of process vectors. Noteworthy point is that slope of the vector, $\Delta \varepsilon / \Delta H$, is defined as energy level, A, indicating energy quality. In particular, energy level of thermal energy is simply expressed by the following equation when specific heat is assumed to be constant:

$$A = \frac{T - T_0}{T} \qquad (3)$$

Here, T is temperature (K) of thermal energy and T_0, environ-mental one (K) (=298K). It means that steeper vector has higher quality of energy.

The possile system condition is also clearly judge-able in the diagram. The system is feasible only when the synthesized vector of the process vectors shows negative direction just on the Y-axis, for meeting the two conditions of Eqs. (1) and (2). In addition, length of the synthesized vector; that is, exergy loss, corresponds to degradation of energy. The system with shorter synthesized vector, thus, should be selected for the effective use of exergy.

3. METHOD

As high temperature waste from steelworks, molten BF slag is selected in this study as an example, then its cooling phenomena to room temperature is taken as an *objective process.* The point is high temperature, 1773 K, of slag. This method will be also applicable easily to other wastes; such as different slags and LDG.

Conditions of the molten slag is determined for the system evaluation:

1) Slag composition is four component system of 43%CaO-35%SiO$_2$-15%Al$_2$O$_3$-7%MgO.

2) Average specific heat of the slag is 59.7 (J/K mole).

3) Temperature of the slag is 1773K (1500), meaning A=0.846.

4) Enthalpy of the slag recovered is 200MJ, corresponding to 2271 mole or 143.5 kg.

5) Sensible heat of the slag is recovered completely without heat loss.

As refrigerant of the molten slag, nine chemical reactions, popular in other industry, are selected in this study. Table 1 indicates the reactions selected, together with enthalpy change, exergy change, possible reaction temperature under normal pressure and energy level. Note that they all are endothermic reactions with relative large of reaction heat, for recovering sensible heat of the slag. They are also key reactions in other industries; for example, cement production (2), coal gasification ((3)(4)), hydrocarbon reforming ((5) to (8)). Hydrogen production due to water decomposition (1) and methanol decomposition (9) are selected as reference. Reverse reaction (9) is also proposed for energy transportation in the development of ecological town[5]. Each reaction plays a role of a *combination process* in the system design.

Table 1   Endothermic reactions selected for thermo-chemical recovery of high temperature wastes over 1700 K.

No.	Reaction	Enthalpy ΔH[kJ]	Exergy $\Delta \varepsilon$ [kJ]	$T_{\Delta G=0}$ [K]	A $(=\Delta \varepsilon / \Delta H)$ [−]
1	$H_2O \rightarrow 0.5O_2 + H_2$	242	229	5400	0.945
2	$CaCO_3 \rightarrow CaO + CO_2$	178	130	1110	0.731
3	$C + CO_2 \rightarrow 2CO$	172	122	1020	0.708
4	$C + H_2O \rightarrow CO + H_2$	131	91	982	0.694
5	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	247	171	964	0.691
6	$CH_4 + H_2O \rightarrow CO + 3H_2$	206	142	960	0.689
7	$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$	165	114	957	0.688
8	$C_3H_8 + 3H_2O \rightarrow 3CO + 7H_2$	498	298	742	0.598
9	$CH_3OH \rightarrow CO + 2H_2$	90	25	410	0.278

From the above conditions of slag, we first draw a vector of the objective process in the enthalpy-exergy diagram. Then, a vector of the combination process appears because slope is given by energy level, A, in Table 1 and length is determined from the constraint of first law of thermodynamics. Finally, we can evaluate the system consisting of the two processes, by obtaining the following three valuable findings:

1) feasibility of the system,

2) value of exergy loss of the system and

3) material balance of product and reactant.

4. RESULTS AND DISCUSSION

4.1 Thermo-chemical transformation

Figure 1 shows the enthalpy-exergy diagram for the system having two processes; molten slag as an objective process and reaction (1) as a combination process. Vector having 0.945 in slope was drawn to be the same horizontal length of the vector from the constraint of thermodynamic first law, Eq (1). Resultant of both vectors, expressed by a white arrow, appeared upward on the y-axis, not downward. Obviously, this dose not obey the second law of thermodynamic, thus we can recognize that this system is impossible under this condition. In fact, theoretical temperature of water decomposition is over 5000 K, as listed in Table 1; this result is easily understandable. Water electrolysis is also explained by a fact that electricity, instead of the slag, has 1 of energy level.
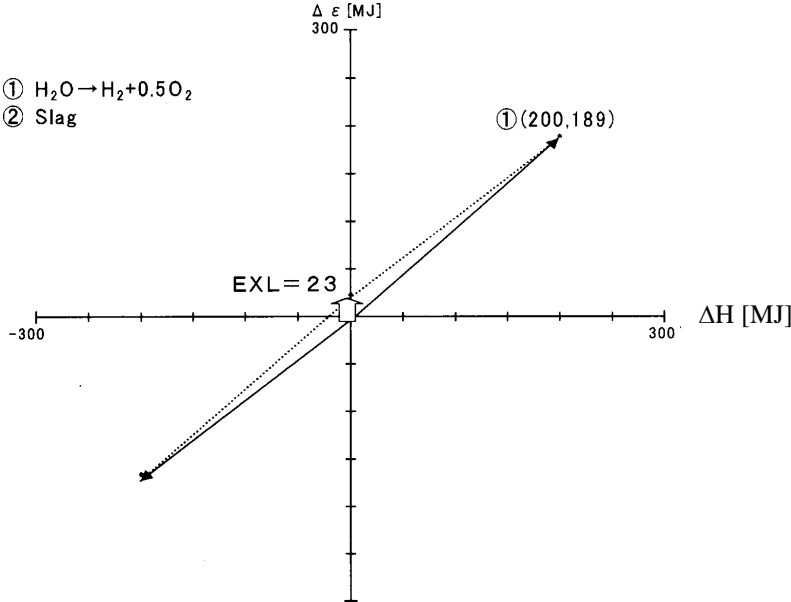

$\Delta \varepsilon$ [MJ]

① $H_2O \rightarrow H_2 + 0.5 O_2$
② Slag

①(200,189)

EXL = 23

ΔH [MJ]

Figure 1 Enthalpy-exergy diagram for heat recovery of the slag by using the reaction $H_2O \rightarrow H_2 + 0.5O_2$

Similarly, Figs. 2 and 3 are obtained for reactions (2) and (4) to (7) as a combination process. In contrast, all of these systems are possible because a resultant vector shows negative direction on the y axis. Length of this vector means exergy loss (EXL) of the system. It is 20 MJ for reaction (2), and 28 MJ for reactions from (4) to (7). Both of these values are relatively small because vector's slope of the two is very close. Interestingly, the latter equations have the same value due to the same slope.
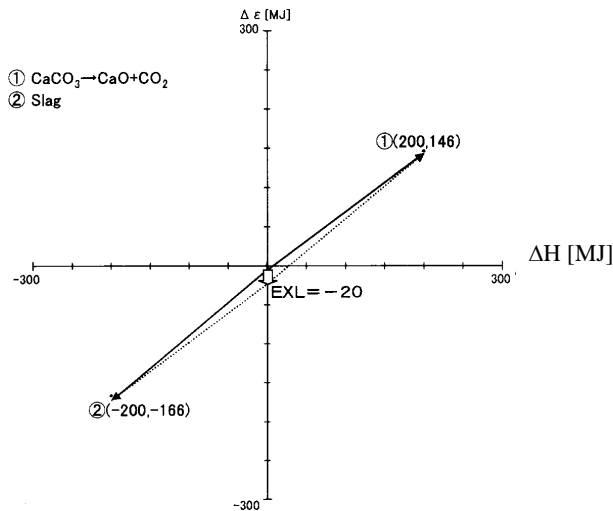
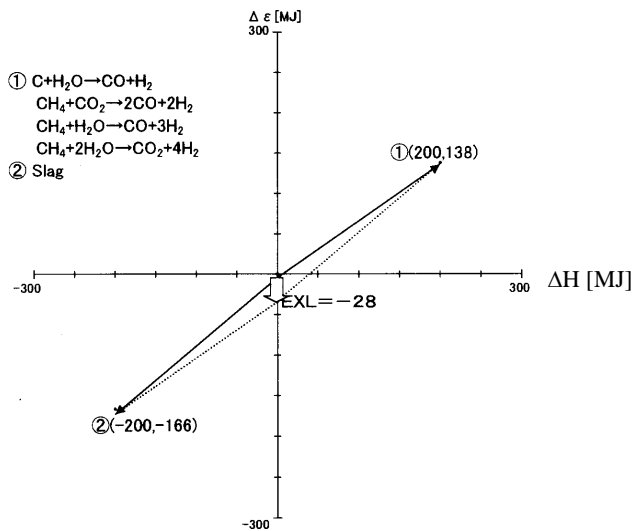**Figure 2 Enthalpy-exergy diagram for heat recovery of the slag by using the reaction $CaCO_3 = CaO + CO_2$**

Figure 3 Enthalpy-exergy diagram for heat recovery of slag by using the reaction: $C+H_2O=CO+H_2$, $CH_4+CO_2=2CO+H_2$, $CH_4+H_2O=CO+3H_2$, $CH_4+2H_2O=CO_2+4H_2$

Note that hydrogen does generate due to reactions (4) to (7), although it is difficult due to reaction (1), as shown in Fig.1. For example, this reason could be explained by using Fig.4, in which reaction (6), $CH_4+H_2O \rightleftharpoons CO + 3H_2$, is divided into two elemental equations; $H_2O \rightleftharpoons H_2+0.5O_2$ and $CH_4 + 0.5O_2 \rightleftharpoons 2H_2 + CO$. It is found that steep slope of the former endothermic reaction (vector 1) is improved by the latter exothermic one (vector 2). As a result, the vector of reaction (6) (vector 3) has more gentle slope than that of an objective process (vector 4). Partial oxidation of methane (vector 2) with very steeper slope than 1 is rare and attractive reaction for improving a combination process. It is, thus, also focussed as a fuel cell[6], in which it does not make only electricity, but also, thermal energy and reducible gas of CO and H_2.
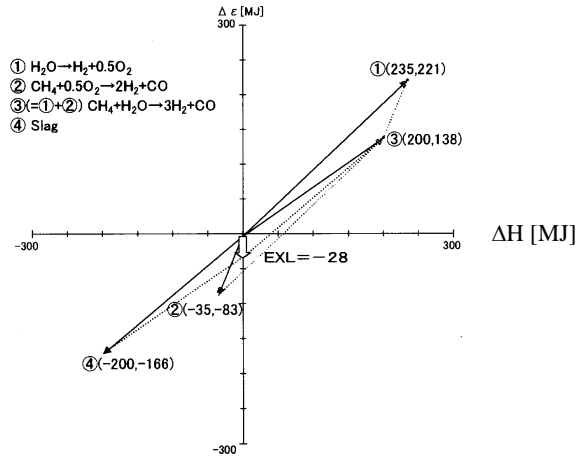
Figure 4 Enthalpy-exergy diagram for heat recovery of the slag by using the two reactions: $H_2O=H_2+0.5O_2$ and $CH_4 +0.5O_2=2H_2+CO$, in which the latter vector adjustably degrades former one by relieving steep slope.

4.2 Conventional steam and hot water recovery

In comparison to conventional heat recovery methods based on sensible heat, the two cases are additionally evaluated:

1) Generation of steam of 573 K (300°C) from cold water 398 K (25°C), and

2) Heating of water from 298 K (25°C) to 353 K (80°C).

Since energy level; that is, vector slope, is easily calculated from eq.(3), we can obtain Figs.5 and 6. They indicate each EXL for both cases; -84 MJ in the steam generation system and –135 MJ in the water heating system. These large EXLs are induced by too gentle slope of the combined process in comparison to Figs.2 and 3. The result suggests that we should design the system *mildly* for decreasing EXL; more concretely speaking, smaller difference of slope between an objective process and a combination process is better for saving exergy. Based on this precept, idea of the steam generation recovery for high temperature waste is wrong.
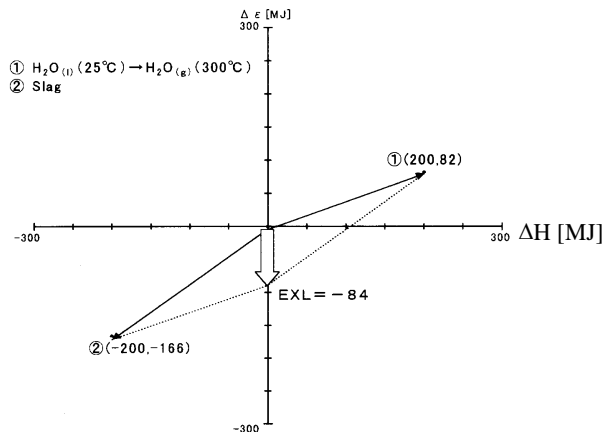

Figure 5 Enthalpy-exergy diagram for heat recovery of the slag by generating

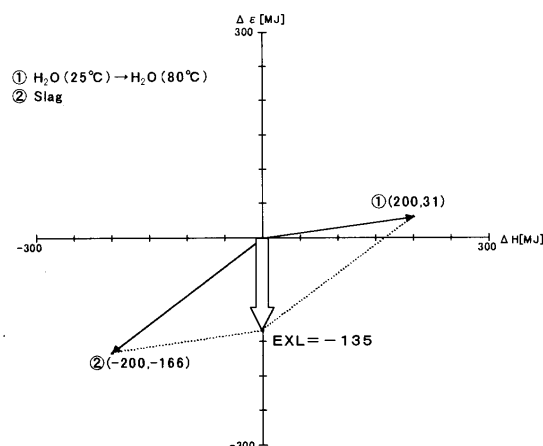**steam of 573 K (300ºC) form cold water of 298 K (25ºC)**

Figure 6 Enthalpy-exergy diagram for heat recovery of the slag by heating water from 298 K (25ºC) to 353 K (80ºC)

4.3 Overall evaluation

All of the results are summarized in Table 2. Value of EXL depends significantly on the reaction as a combination process, because of its slope difference. Loss ratio of the EXL to the molten slag enthalpy; EXL/H_{slag}, ranges from 0.1 to 0.675. In particular, least value is 0.1 for reaction (2), 0.12 for reaction (3) and 0.14 for reactions from (4) to (7). Reactions (8) and (9), having 0.23 and 0.55, should be used for the recovery of middle temperature waste, not high one.

The enthalpy-exergy diagram also gives information of material balance of reactant and product, as listed in Table 2. Here, weight of underlined reactant, W_r, is calculated, together with ratio to slag; W_r/W_{slag}. For example, ratio of limestone to slag; 0.783, means that molten slag of 30Mt/year has a possibility to treat limestone of 23.5Mt/year or to produce lime (cement) of 13.2(=23.5x0.56) Mt/year. In addition, the molten slag can makes as much as six times hot water of 353 K, however we should recognize that its energy degradation reaches as much as 67.5 % in the loss ratio. The steam recovery system, although slightly better than the hot water one, has the same situation on the loss ratio.

The present wet granulation process is fundamentally environment-polluting, requesting post-drying process, as follows; 1) necessity of huge amount of water for quenching the slag, 2) water pollution by catching alkali from the slag, and 3) air pollution by generation of sulfuric hydrogen. Therefore, new environmentally friendly process recovering both heat and material of the slag should be developed in the closed system, based on thermo-chemical transformation proposed here if possible. For this purpose, reaction rate of methane steam reforming on molten slag was reported for the first time[7]. The reaction was correlated by a

60

rate equation in the form of first order. The results also suggested that enlargement of surface area of the slag due to dry granulation is key technology.

Table 2 Theoretical exergy loss for heat recovery of the molten slag.

No.	Reaction	EXL(MJ)	$\frac{EXL}{H_{slag}}(MJ/MJ)$	W_r*(kg)	$\frac{W_r}{W_{slag}}(kg/kg)$
1	H_2O $0.5O_2+H_2$	impossible	-	none	-
2	$\underline{CaCO_3}$ $CaO+CO_2$	20	0.1	112.4	0.783
3	$\underline{C}+CO_2$ $2CO$	24	0.12	13.9	0.097
4	$\underline{C}+H_2O$ $CO+H_2$	28	0.14	18.3	0.128
5	$\underline{CH_4}+CO_2$ $2CO+2H_2$	28	0.14	11.3	0.079
6	$\underline{CH_4}+H_2O$ $CO+3H_2$	28	0.14	13.6	0.095
7	$\underline{CH_4}+2H_2O$ CO_2+4H_2	28	0.14	17.0	0.118
8	$\underline{C_3H_8}+3H_2O$ $3CO+7H_2$	46	0.23	17.7	0.123
9	$\underline{CH_3OH}$ $CO+2H_2$	110	0.55	71.1	0.495
10	$\underline{H_2O(l)\ 25}$ $H_2O(g)\ 300$	84	0.42	67.0	0.467
11	$\underline{H_2O\ 25}$ $H_2O\ 80$	135	0.675	865.8	6.033

*Amount of underlined reactant

Moreover, application of these thermo-chemical recovery concept using equations (3) to (7) to LDG recovery is more promising. It is well known that iron is very good catalyst for them[8]. There is a lot of iron powder within a converter and, in addition, a gas holder for LDG already exists there. Therefore, we can easily obtain hydrogen enriched LDG after introducing reactant gas immediately above the converter. Once hydrogen enriched gas is obtained, there are many applications such as methanol production and electricity generation. For example, such gas has extremely higher generation ratio of electricity; 45-50%, in contrast steam has, at most, 10-15% in the ratio.

4.4 Cement production and methanol production

At the same time, contribution of selected reactions on the existing plant was studied for further discussion. Cement production and methanol production were selected here.Portland cement[8] is normally produced by a rotary kiln with suspension pre-heater, so called NSP kiln process as shown in Fig.7. Limestone, $CaCO_3$, is first pulverized and then roasted to be clinker in the kiln. After that, clinker is finally crushed for cement product. As a fuel of rotary kiln, coal or oil is consumed to heat up to approximately 1773K (1400°C).

According to the system analysis of the plant with 3700 t/day, total exergy consumption is 1.882 GJ/t-cement (see Table 3). The NSP kiln process consumed as much as 94.3% of this value. In contrast, BF cement is normally produced by mixing Portland cement and wet granulated BF slag with weight ratio of 50:50. Therefore, decomposition of limestone by sensible heat of molten slag is quite reasonable, cost-effective and helpful to cement-making. Since this reaction occurs without any catalyst, it looks very easy for the practical use.

Methanol production system[10] consists of six processes, as shown in Fig.8; reformer, separator1, compressor, reactor, separator2 and refining tower. Based on reliable operating data of the 1000 t/day plant, exergy analysis was carried out. After carefully heat and mass balances were checked, the exergy loss was evaluated in each process. The results are that total exergy loss is 8.40 GJ/t-MeOH in the overall system, in which the most consuming process is reformer, 6.09 GJ/t-MeOH (see Table 3). This value reaches as much as 72.5 %. Therefore, if the slag makes CO and H2 by its sensible heat, it is possible that methanol production fee will be drastically decrease.

Regarding to direct reduction system with shaft furnace or fluidized bed, the most energy-consuming process is also the steam reformer for producing reducible gas CO and H_2. Therefore, merit of new system for producing CO and H_2 by using sensible heat of molten slag is quite obvious.
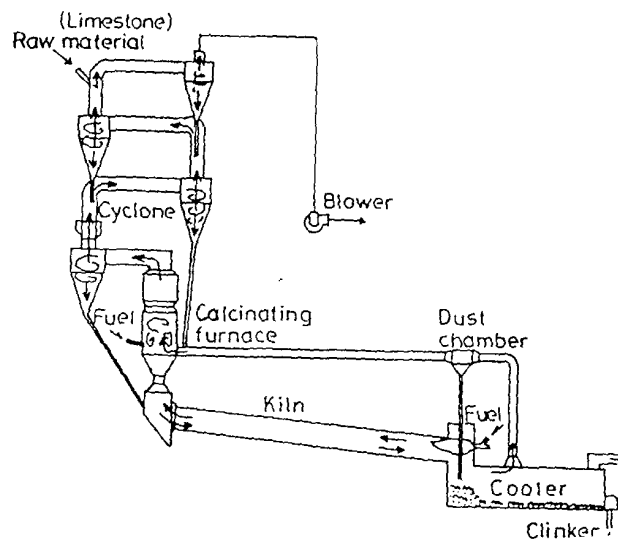

Figure 7 Conventional NSP kiln process for cement production, in which not a small fuel, such as coal, is consumed mainly for thermal decomposition of limestone.
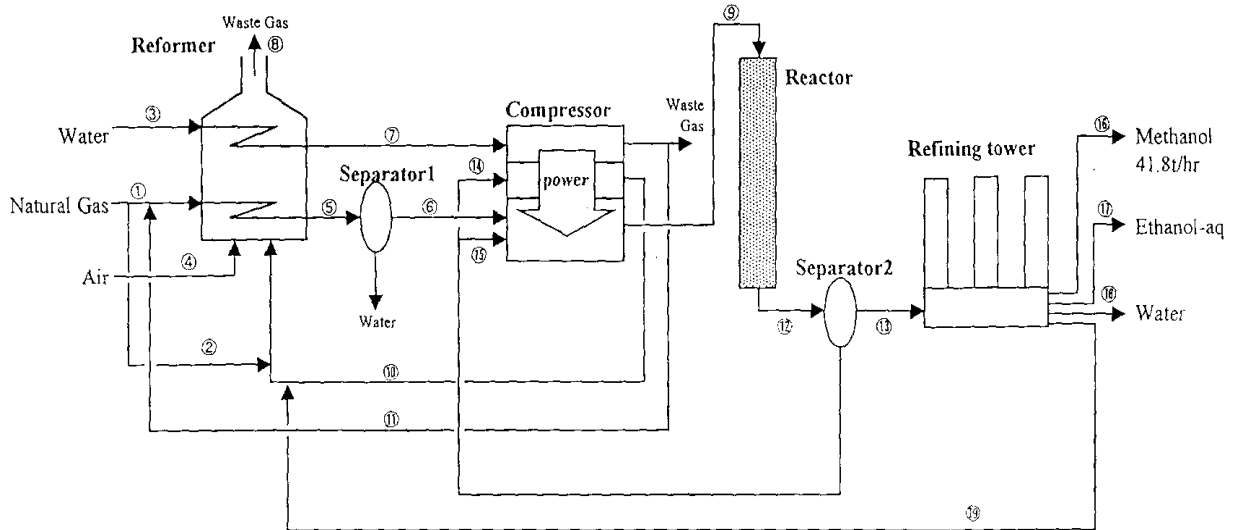
Figure 8 Conventional methanol production system consisting of six processes, in which the first stage, for natural gas reforming to produce CO and H_2, is the most energy-consuming process.

Table 3 Exergy loss in the existing industrial plant, in which underlined value could be saved by thermo-chemical recovery of high temperature wastes from steelmaking industry.

Cement production system

Process	Crushing of raw material	NSP kiln	Crushing of clinker	Total
EXL (GJ/t-cement)	0.042	<u>1.776</u>	0.064	1.882

Methanol production system

Process	Reformer	Separator1	Compressor	Reactor	Separator2	Refining tower	Total
EXL (GJ/t-ethanol)	<u>6.09</u>	0.03	0.59	0.65	0.10	0.94	8.40

5. CONCLUSION

It is often said that thermal energy has lager potential if having higher temperature, however the conventional heat balance method can not explain this engineering sense. To overcome this problem, the enthalpy-exergy diagram was introduced for discussing heat recovery method of high temperature wastes from steelmaking industry. A possibility of thermo-chemical method was mainly examined, in which nine endothermic reactions, together with conventional sensible heat methods using generating steam and hot water, are discussed for recovering the molten slag heat.

The following conclusions were obtained:

1) Utilization of thermal decomposition of limestone ($CaCO_3 \rightleftharpoons CaO+CO_2$), natural gas reforming ($CH_4+CO_2 \rightleftharpoons 2CO+2H_2$, $CH_4+H_2O \rightleftharpoons CO+3H_2$, $CH_4+2H_2O \rightleftharpoons CO_2+4H_2$), and coal gasification ($C+H_2O \rightleftharpoons CO+H_2$, $C+CO_2 \rightleftharpoons 2CO$) are least exergy loss system among eleven systems.

2) Conventional heat recovery method using hot water is most exergy consuming. The steam generation is also highly exergy consuming. These method are better than nothing, but is not suitable for the recovery of high temperature heat.

3) Analysis of an existing plant demonstrates that much exergy is consumed for inducing the above-mentioned reactions; its ratio is 94.3 % for thermal decomposition in the cement production system and 72.5 % for natural gas steam reforming in the methanol production system.

The conclusions appeal absolute merit of thermo-chemical transformation using molten slag or hot LD gas. This study is fundamentally based on equilibrium theory; thermodynamics, thus next stage will be addressed to the process development under kinetic theory for the practical use in the next century.

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