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Utilization of Low Grade Iron Ore (FeOOH) and Biomass Through Integrated Pyrolysis-tar Decomposition (CVI process) in Ironmaking Industry: Exergy Analysis and its Application

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Effective utilization of low grade iron ore (FeOOH) and biomass represents a promising method to reduce the dependency on fossil fuels and decrease raw material costs in the ironmaking industry. A process system diagram was made and a comparison of exergy losses in conventional methods was conducted to evaluate the proposed system, integrated pyrolysis-tar decomposition over a porous ore through Chemical Vapor Infiltration (CVI) process. As the main product, the CVI ore was employed for energy storage based on carbon deposition and pre-reduced ore, Fe₃O₄ as a product of proposed system that consisted of three units: pyrolysis, CVI, and dehydration-separation. The exergy of CVI ore increased significantly owing to exergy recovery through tar decomposition. In the basis of 3.86%wt carbon deposition (experimental value) and producing of 1 000 kg metallic Fe, the exergy loss of the proposed system was found to decrease by about 17.6% compared to that in conventional systems by the recovery of both chemical and thermal tar exergy. The exergy loss decreased drastically to 37.0% when the expected carbon deposition was attained (10%wt). The CVI ore offered great chance to replace the coke breeze as a heat source in sinter plant. With regard to experimental value, the sinter plant could be operated without using additional coke breeze when the CVI ore content was 70% to total input ore. The total enthalpy of CVI ore consisted of the oxidation of deposited carbon and Fe₃O₄ in the ratio of 60.2% and 39.8%, respectively. Based on these results, the proposed system proffered effective biomass and low grade ore utilization as well as led to decrease in CO₂ emissions by the ironmaking industry.

KEY WORDS: biomass; tar decomposition; exergy analysis; sinter plant; coke breeze saving.

1. Introduction

The ironmaking industry is one of the most energy-intensive industries in the world and consumes 24 EJ/year, which constitutes around 5% of the total global energy consumption.¹⁾ The primary energy source is fossil fuels, and such ironmaking is one of the biggest contributors to CO₂ emissions, 3–4% of the total global emissions.^{1,2)} Several programs have been initiated worldwide to reduce fossil fuel utilization and CO₂ emissions, such as ULCOS in the EU, COURSE50 in Japan, and AISI in the USA.³⁾ In addition, a simple way to resolve emission concerns is to use biomass resources in the ironmaking industry. Pyrolysis and gasification serve as the primary steps in the utilization of biomass energy by converting it into char, tar, and gas. Tar contains highly condensable hydrocarbons and may cause issues, such as pipe plugging, condensation, and tar aerosol formation.^{4,5)} Several researchers have attempted to remove tar and eliminate problems such as adsorption-absorption and catalytic decomposition.⁶⁾ However, the results are still

unsatisfactory because of technical and catalyst problems.

The effective utilization of low-grade ores such as goethite, FeOOH, in the modern ironmaking industry is highly required to solve the problems related to the depletion and shortages of high-grade iron ores. The drawback of low-grade ores containing goethite as a raw material is the presence of a large amount of combined water (CW) in the ores, which necessitates additional energy for the dehydration process. However, it has been reported that the dehydration of goethite at 450°C with a heating rate of 3°C/min in an air creates micropores ranging from 2 to 4 nm in size and a BET specific surface area as high as 70 m²/g.⁷⁾ Because of these, Miura *et al.*⁸⁾ proposed iron ore/carbon composite (IOC) by introducing carbonaceous material into the pores to enhance the reduction rate of iron ore. The reduction rate of an IOC sample prepared using FeOOH reagent and thermoplastic carbon resin is dramatically enhanced and proceeds at temperatures as low as 700°C.

The integrated pyrolysis-tar decomposition over low-grade ores through Chemical Vapor Infiltration (CVI) is one of the most promising methods for the effective utilization of biomass and low-grade ores in the ironmaking industry.

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In this method, volatile matter, tar, and pyrolysis gas are introduced to a porous iron ore for a tar-decomposition process that produces highly valuable syngas (CO and H_2) and carbon materials that infiltrate and deposit within the pores of the iron ore. Under certain conditions, the conversion of tar in the decomposition process is 20–30 wt% for the pyrolysis of lignite coal and Palm Kernel Shell (PKS) biomass.⁹⁾ In addition, indirect iron ore reduction by CO and H_2 and conversion from Fe_2O_3 to Fe_3O_4 , simultaneously occur during tar decomposition. Therefore, the method offers benefits such as removal of tar, effective use of low-grade ores and prereduced ores containing deposited carbon. As the main product, the ore containing deposited carbon, namely CVI ore exhibits high reactivity during the reduction reaction that started at 750°C primarily because of the nanoscale contact of iron ores and carbon.¹⁰⁾

To truly understand the energy efficiency and complexity of the proposed method, a specific analysis was definitely required. Exergy analysis based on the second law of thermodynamics may be the best method to assess the energy efficiency of the proposed method and to compare it with existing systems.^{11,12)} Therefore, an exergy analysis was performed using the developed process system diagram to evaluate the advantages of the proposed method over conventional methods. The sinter plant is the second biggest contributor of CO_2 emissions after the blast furnace in the ironmaking process because of the utilization of coke breeze and coke oven gas (COG) as energy sources.¹³⁾ The utilization of the CVI ore containing deposited carbon and a prereduced ore could be initiated in the sinter plant. The deposited carbon within the iron ore pores could serve as an energy source

for the sintering process. Thus, the consumption of coke breeze in sinter plants could be minimized in order to achieve lower CO_2 emissions. The objectives of this study are to propose a process system diagram for the CVI process and compare its exergy analysis with conventional processes. In order to examine the feasibility of the process, the exergy analysis was processed based on previous published experimental results. In addition, a feasibility study of CVI ore utilization in sinter plants was discussed in terms of energy consumption and coke breeze utilization.

2. Analysis Method

2.1. System Definition

The process system diagram was developed with a strict boundary with regard to use of the energy generated from Palm Kernel Shell (PKS) biomass in the pyrolysis process. The exergy analysis comparison was carried out based on the proposed system (case 1) and conventional system (case 2), as briefly explained below.

2.1.1. Case 1: Proposed Integrated Pyrolysis-tar Decomposition (CVI Process) System

Figure 1 shows the proposed system which was composed of integrated pyrolysis-tar decomposition for the recovery of tar energy using low-grade iron ores. This system was composed three units, pyrolysis, CVI, and dehydration-separation. In the pyrolysis unit, PKS biomass was fed at atmospheric pressure and 873 K . As an endothermic process, the unit was supplied with heat generated through the combustion of recycled pyrolysis gas (after separation).

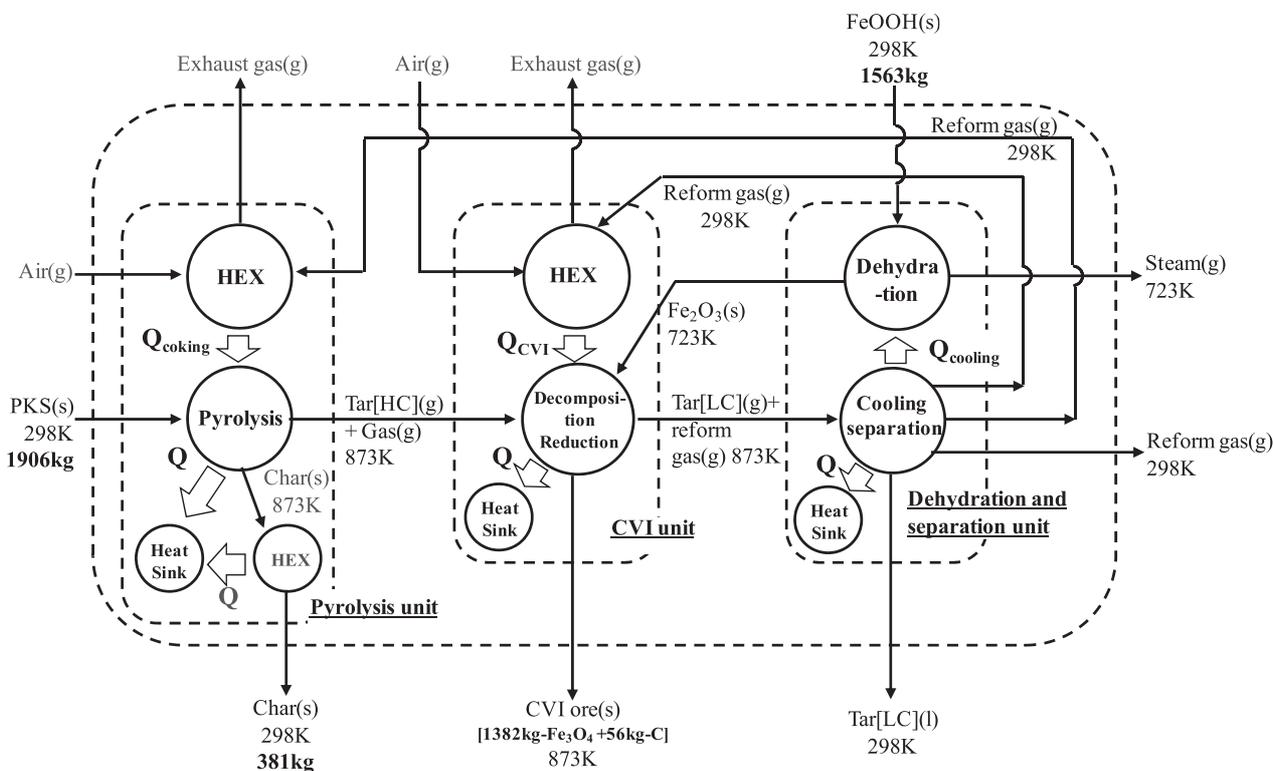
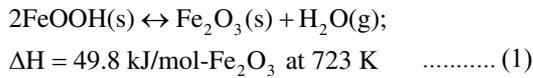
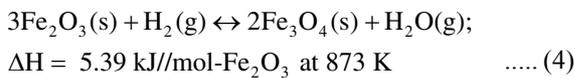
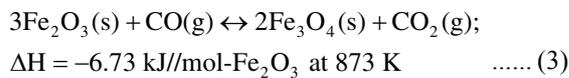
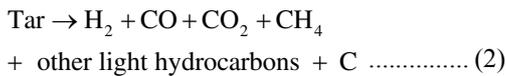


Fig. 1. Proposed system for utilization of PKS biomass and low grade iron ore (FeOOH) to produce **381 kg-char** and **1 000 kg-Fe** through integrated pyrolysis-tar decomposition (CVI process). PKS: Palm Kernel Shell biomass, HC: Heavy hydrocarbon, LC: Light hydrocarbon, HEX: Heat Exchanger, Heat sink means environment, and the dotted line is the boundary of system.

Solid product char was taken directly from the unit and used as an energy source for combustion in another unit while the volatile matter (tar and gas) was transported to the CVI unit for tar decomposition. The low-grade ore, goethite, was dehydrated at 723 K under air to create porous ores based on the following reaction:



The dehydration energy was provided by waste heat from the cooling process of the mixture, in addition to tar and gas following the CVI process. The porous ore and volatile matter from the pyrolysis unit were delivered to the CVI unit for tar decomposition (2) and reduction (3–4) based on the following reaction.



Simultaneously to the tar decomposition, the carbon product infiltrated and deposited in the porous ore to produce an iron ore containing carbon material. In addition, the indirect reduction of the iron ore (Fe₂O₃ to Fe₃O₄) also took place with the use of H₂ and CO, both of which were produced from pyrolysis and tar-decomposition. Thus, the CVI unit resulted in the prereduced iron ore containing a carbon material, CVI ore which could be sent to the next processing unit such as the sinter plant or blast furnace. After the CVI process, the mixture of unreacted tar (light hydrocarbon) and reform gas was transported into a separation unit for cooling. The amount of condensable hydrocarbon in the

mixture was smaller because of the decomposition process, and it was possible to recover the heat of the mixture for iron-ore dehydration. The total carbon content of unreacted tar was 22% less than that in the tar product obtained from the conventional system.⁹⁾ The reform gas product can be recycled as a heat source for several endothermic units such as pyrolysis, CVI, and dehydration. The remaining reform gas could be applied as an energy source in other ironmaking processes. The chemical energy of cooled un-reacted tar can be unrecovered again within the system and delivered outside of the ironmaking industry. Therefore, the proposed system offers both thermal and chemical energy recovery through CVI and separation units.

2.1.2. Case 2: Conventional Pyrolysis and Dehydration Systems

The conventional system is a common existing method for biomass pyrolysis system, which consists of pyrolysis and a separation unit, as shown in Fig. 2(a). In order to evaluate the exergy losses, conventional pyrolysis was carried out in a similar way to the proposed process. Unlike the proposed system, the volatile product consisting of tar and gas could not be directly utilized as an energy source because of the large amount of condensable heavy hydrocarbon. Thus, a separation process must be completed first by cooling the volatile mixture. Finally, the gas product, which was free of tar, could be used as an energy source in the pyrolysis and endothermic units. The liquid tar was collected and sent outside of the system. Therefore, the conventional system never recovered the energy of tar material because of handling and technical difficulties. In order to utilize the low grade ore (FeOOH) for ironmaking, the additional energy (gas fuel) was supplied for dehydration process as shown in Fig. 2(b). The porous ore, Fe₂O₃ could be sent to a sinter plant or blast furnace to produce metallic Fe.

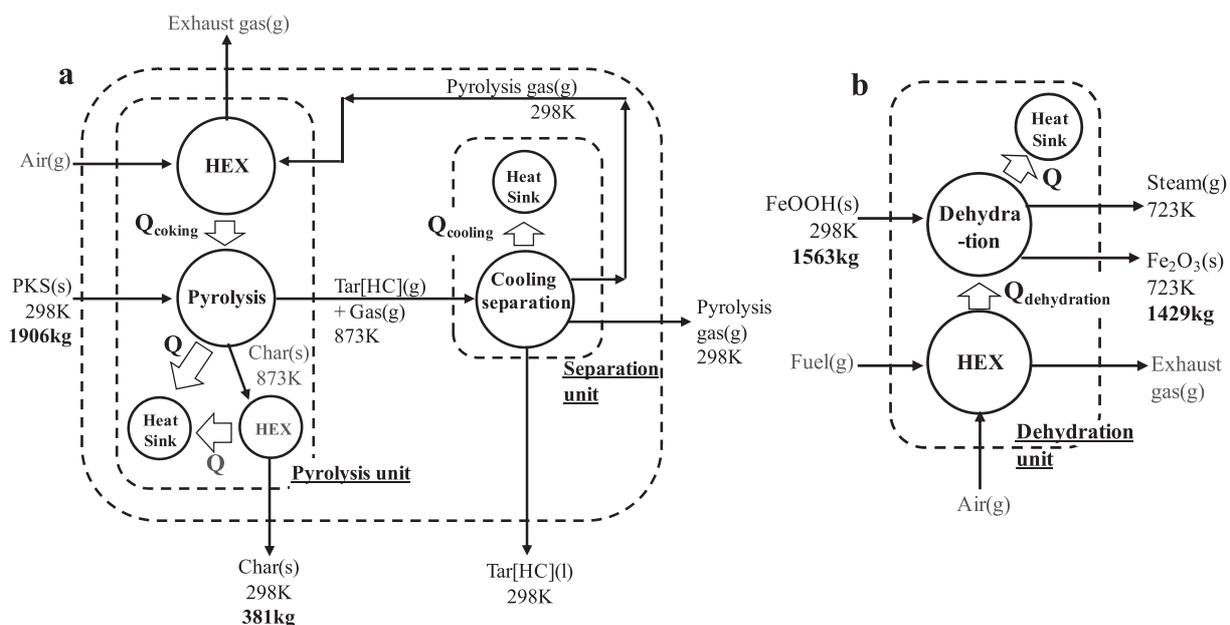


Fig. 2. Conventional system for (a) utilization of PKS biomass and producing of 381 kg-char through pyrolysis process and (b) dehydration process to produce 1 000 kg-Fe from low grade iron ore (FeOOH) in the ironmaking industry. PKS: Palm Kernel Shell biomass, HC: Heavy hydrocarbon, LC: Light hydrocarbon, HEX: Heat Exchanger, Heat sink means environment, and the dotted line is the boundary of system.

2.2. Exergy Analysis

2.2.1. Mass Balance and Operation Data

According to the experimental data obtained under conditions,⁹⁾ the material flow of both the conventional and proposed systems was calculated for producing 381 kg char and 1 000 kg metallic Fe, as listed in **Table 1**. The ratio of PKS to the porous ore was similar in the experiment condition, 4:3 (weight ratio). **Table 2** shows the operation data used in that analysis. The carbon content within the iron ore was 3.86 wt%, as explained previously.⁹⁾ The high heating value (HHV) of PKS and charcoal were estimated using the Dulong equation¹⁴⁾ as follows:

$$HHV [kJ/kg] = 337C + 1442 \left(H - \frac{O}{8} \right) + 93S \dots\dots (5)$$

where C, H, O, and S are the percentages of carbon, hydrogen, oxygen, and sulfur in the solid fuel, respectively.

2.2.2. Calculation Method

Based on the material flow and operation data given above, an exergy analysis was performed to evaluate the

Table 1. Material flow of both conventional (pyrolysis-dehydration) and proposed systems (pyrolysis-tar decomposition) in each unit. Basis: 1 000 kg of metallic Fe.

Conventional	Pyrolysis process				Dehydration process	
	Pyrolysis		Separation		Dehydration	
Material [unit]	Input	Output	Input	Output	Input	Output
PKS [kg]	1906.1	0.0	0.0	0.0	0.0	0.0
Char [kg]	0.0	381.2	0.0	0.0	0.0	0.0
Tar [kg]	0.0	567.1 ^{a)}	567.1	567.1	0.0	0.0
Pyrolysis gas ¹⁾ [Nm ³]	291.7	909.5	909.5	909.5	0.0	0.0
Goethite ore (FeOOH) [kg]	0.0	0.0	0.0	0.0	1563.0	0.0
Porous ore (Fe ₂ O ₃) [kg]	0.0	0.0	0.0	0.0	0.0	1429.6
Steam [Nm ³]	0.0	0.0	0.0	0.0	0.0	180.9
Fuel gas [Nm ³]	0.0	0.0	0.0	0.0	42.9	0.0
Air [Nm ³]	1 002.7	0.0	0.0	0.0	251.6	0.0
Exhaust gas [Nm ³]	0.0	1 203.4	0.0	0.0	0.0	284.5

Proposed	Pyrolysis		CVI		Dehydration-separation	
	Input	Output	Input	Output	Input	Output
PKS [kg]	1906.1	0.0	0.0	0.0	0.0	0.0
Char [kg]	0.0	381.2	0.0	0.0	0.0	0.0
Tar [kg]	0.0	567.1 ^{a)}	567.1	478.0 ^{b)}	478.0	478.0
Pyrolysis gas ¹⁾ [Nm ³]	316.7	909.5	987.0	1 017.8 ^{c)}	1 017.8	1 017.8
Goethite ore (FeOOH) [kg]	0.0	0.0	0.0	0.0	1563.0	0.0
Porous ore (Fe ₂ O ₃) [kg]	0.0	0.0	1429.6	0.0	0.0	1429.6
CVI ore (Fe ₃ O ₄ +C) [kg]	0.0	0.0	0.0	1438.0	0.0	0.0
Steam [Nm ³]	0.0	0.0	0.0	0.0	0.0	180.9
Air [Nm ³]	971.4	0.0	237.5	0.0	0.0	0.0
Exhaust gas [Nm ³]	0.0	1 197.9	0.0	292.9	0.0	0.0

Input : recycling gas after separation; a) Heavy hydrocarbon; b) Light hydrocarbon; c) Reform pyrolysis gas.

benefit of proposed system. The exergy analysis was used to assess the feasibility of qualitatively converting the available energy into usable energy in the form of work by the following equation:

$$\Delta\varepsilon = \Delta H - T_0\Delta S \dots\dots\dots (6)$$

The total exergy consisted of chemical exergy (ε_C), thermal exergy (ε_T), pressure exergy (ε_P), and mixing exergy (ε_M). The detailed equations for each kind of exergy are given below:

$$\varepsilon = \varepsilon_C + \varepsilon_T + \varepsilon_P + \varepsilon_M \dots\dots\dots (7)$$

$$\varepsilon_C = \sum n_i \varepsilon_i^0 \dots\dots\dots (8)$$

$$\varepsilon_T = \left(\sum n_i C_{pi} \right) \left[T - T_0 - T_0 \ln(T / T_0) \right] \dots\dots\dots (9)$$

$$\varepsilon_P = \left(\sum n_i \right) RT_0 \sum \left[\ln(P / P_0) - (1 - P_0 / P) \right] \dots\dots (10)$$

$$\varepsilon_M = RT_0 \sum \left[n_i \ln \left(n_i / \sum n_i \right) \right] \dots\dots\dots (11)$$

where ε : exergy [kJ/mol], H: enthalpy [kJ/mol], S: entropy [J/molK], n : mol of the substances [mol], C_p : specific heat at constant pressure [kJ/molK], T_0 : reference temperature [K], T : actual temperature [K], P_0 : reference pressure [atm], P : actual pressure [atm], and R : gas constant [J/molK]

The exergy loss (EXL) was calculated as the difference between the exergy of the input material (ε_{in}) and that of the output material (ε_{out}) in each unit of the system. The reference exergy (ε^0) was described as the chemical exergy of each substance at 298 K and 1 atm calculated based on the Gibbs free energy. The exergy calculation was made based on the following assumptions:

1. The exergy of solid fuel was equal to HHV, according to Rant's approximation.¹⁶⁾

Table 2. Operation and enthalpy data which used for exergy analysis.

(a) Palm Kernel Shell (PKS) and biochar elemental analysis.

Material	C	H	N	O	Enthalpy [MJ/kg]
PKS	49.5	5.7	0.8	44	16.7
PKS char	79.8	3.1	0.4	15.6	28.1

(b) Composition of pyrolysis, reform pyrolysis and fuel gases [%volume].

Material	H ₂	CO	CO ₂	CH ₄	N ₂	Enthalpy [MJ/Nm ³]
Pyrolysis gas	15.7	44.5	23.9	13.9	0.0	14.1
Reform pyrolysis gas	24.2	31.7	29.9	12.4	0.0	12.9
Fuel gas (COG)	53.6	6.9	2.6	29.2	5.9	20.3

(c) Material enthalpy data.

Material	Enthalpy [MJ/kg]	Note
PKS tar	21.6	Cp : 4.22E-3T[kJ/kg-tar K] ¹⁵⁾ Enthalpy of HC and LC was similar
Deposited carbon	28.1	Similar with char product
Iron ore	0.0045	Fe ₂ O ₃ and FeOOH (CW : 8.2%wt)
Porous ore	0.35	Fe ₂ O ₃ at 723 K
CVI ore	1.01	Fe ₃ O ₄ at 873 K
Steam	3.38	Superheated steam (723 K, 1 atm)

HC: Heavy hydrocarbon, LC : Light hydrocarbon.

- The enthalpy of unreacted tar (LC) (after the CVI process) was identical to the tar from the pyrolysis process (HC) because of difficulties in analyzing the unreacted tar. In addition, the exergy of tar was equal to 0.975 HHV, as gleaned from Rant's approximation for liquid fuel.¹⁶⁾
- The exergy of the deposited carbon was similar to char pyrolysis product.
- Adiabatic process was done in each unit. The pressure and temperature of outflow stream in each process was assumed to be similar with the condition inside of process.
- The requirement energy of pyrolysis, CVI, and dehydration unit were supplied by the complete combustion of the recycled gas product in each unit. Energy loss was computed and collected as a heat sink to maintain the law of energy conservation.
- To ensure complete combustion, the amount of input air exceeded 20% of the volume of the theoretical calculation.

3. Results and Discussion

3.1. Exergy Analysis

Figure 3(a) shows the exergy flowchart of the conventional pyrolysis system used for producing 381 kg char. The width flow expresses the exergy quantity while the black block arrows refer to the exergy flow of each unit. It is clear

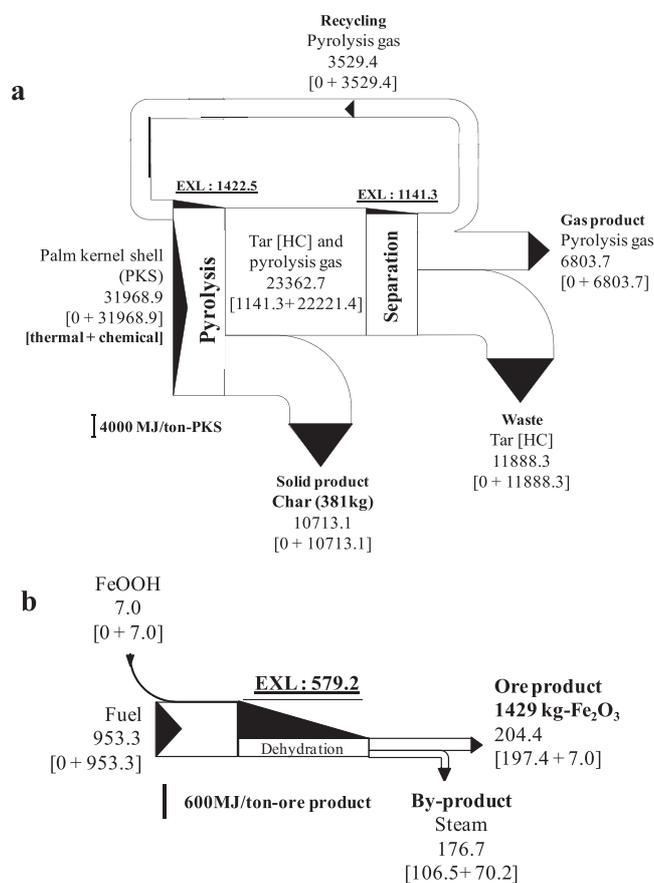


Fig. 3. Exergy flowchart of the conventional process (a) for producing of 381 kg-char by pyrolysis of Palm Kernel Shell (PKS) biomass and (b) for producing of 1000 kg-Fe from low grade iron ore (FeOOH).

that only 33.5% of PKS input exergy was converted into char exergy and could be directly utilized in the other unit. This may be related to the original composition of the biomass, which consisted of large volatile matter, around 65.4 wt%.⁹⁾ Thus, the biggest portion of PKS exergy passed directly to the separation unit. By using this unit, clean gas was recovered which contained 32.3% of the PKS exergy input. A part of this gas exergy was utilized in the pyrolysis unit while the remaining gas was delivered to another unit. It means that the tar material still comprised of 37.2% of PKS input exergy and was not utilized in the ironmaking process. The total exergy of the output material was smaller than those of the input materials in all units, indicating that each process suffered exergy losses owing to the exergy consumption required to run the process. In the pyrolysis unit, the exergy loss was 4% of the total input exergy and was mainly used for the decomposition and destruction of PKS solid fuel. Meanwhile, the exergy loss in the separation unit was 4.9% of the total input and was primarily composed of thermal exergy from cooling.

On the other hand, conventional dehydration was carried out to produce 1000 kg metallic Fe using fuel gas as shown in Fig. 3(b). Obviously, the process consumed a significant amount of exergy which 60.3% of input exergy was lost for removing of the -OH group from the iron ore as in reaction (1). This process also generated steam as a byproduct which contained around 18.4% of input exergy. Therefore, the exergy flowchart illustrated that the largest amount of PKS exergy was transferred into the tar material and was not recovered in the ironmaking process. Moreover, the utilization of low grade iron ore (FeOOH) required high additional energy in the dehydration process.

Integrated pyrolysis-tar decomposition through CVI process was proposed to recover as much PKS exergy as possible using porous ores. By similar basis to conventional system, 381 kg char and 1000 kg Fe products, the exergy analysis of proposed system was conducted and the flowchart was showed in Fig. 4. The exergy of the pyrolysis unit was similar to the conventional system. In the proposed system, the volatile matter (tar and pyrolysis gas) was transported to the CVI unit for tar decomposition over porous ores. Unlike the conventional system, to create a porous ore, a low-grade iron ore was heated using waste heat generated from the cooling process. In addition to the porous ore, complete dehydration process resulted in superheated steam (723 K, 1 atm) with exergy of 176.7 MJ and could be utilized in another unit as an energy source. The volatile matter was introduced with the porous ore in the CVI unit for tar decomposition, carbon deposition, and reduction. As shown in Fig. 3, the CVI ore exergy increased to a significantly higher value than the input exergy of the CVI unit because of due to carbon deposition and reduction reaction. The carbon material contained a large amount of exergy, while Fe₃O₄, the reduction product, released a large amount exergy during the oxidation process. The high exergy of CVI ore could be utilized to decrease the energy consumption in an ore-processing unit such as a sinter plant or blast furnace. The exergy loss in this unit was quite small, around 1.6%, compared to other units because of the limited tar conversion during the process. It is well known that the large amount of decomposition material requires a significant

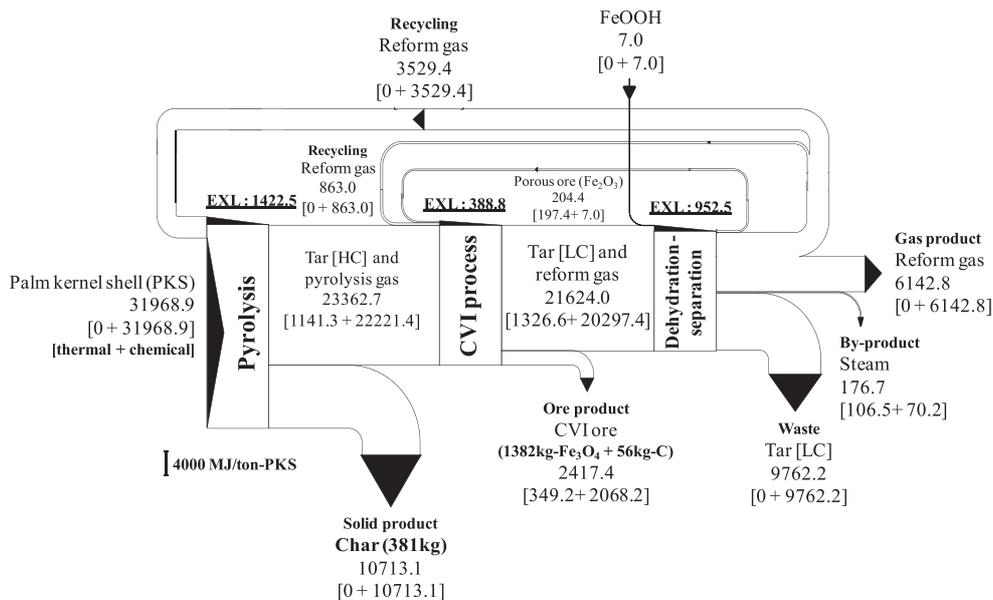
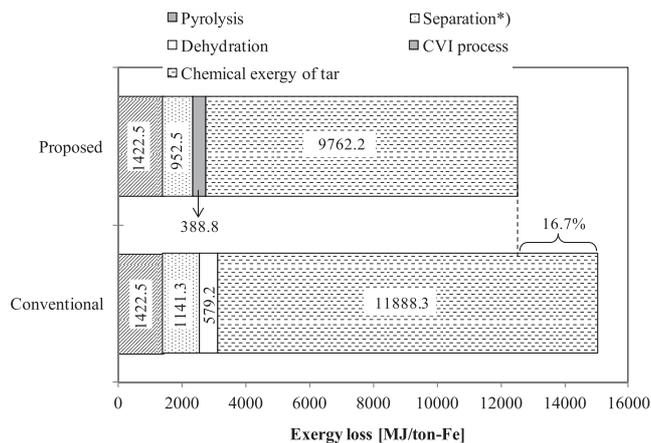


Fig. 4. Exergy flowchart of the proposed system for utilization of biomass and low grade iron ore (FeOOH) to produce 381 kg-char and 1000 kg-Fe through integrated pyrolysis-tar decomposition (CVI process). The integrated process showed that the CVI process increased utilization of PKS exergy by decreasing the tar exergy outflow.

amount of endothermic heat and result in large exergy consumption. Therefore, the CVI unit offers an advantage in terms of tar exergy recovery by producing a CVI ore containing carbon and a pre-reduced ore, Fe₃O₄. Furthermore, the remaining exergy of the unreacted tar and gas product was delivered to the separation unit to simultaneously perform the thermal exergy recovery and cooling process. The application of waste heat for heating the iron ore allows the dehydration process of proposed system to proceed without using any external energy source. Similar to the conventional system, clean gas was recovered and utilized in the other endothermic units such as the pyrolysis, CVI, and dehydration units. The amount of the discharged tar exergy from this unit was less than the conventional system, indicating that the proposed system reutilized the tar exergy to generate a useful product.

3.2. Comparison of Exergy Loss

Figure 5 shows a comparison of exergy losses in both a conventional and proposed system for producing 318 kg char and 1000 kg metallic Fe. The total loss which was obtained from exergy losses in each unit and outflow tar exergy can be determined by using the assumption that the exergy of char and gas product could be employed in other unit through simple conversion method. The separation process in the proposed system allowed for recovery of thermal exergy from gas and unreacted tar for the dehydration process. Obviously, the proposed system based on integrated pyrolysis-tar decomposition was effective in recovering the chemical exergy of tar using porous low-grade iron ores. In addition, the waste heat recovery in the dehydration of iron ore in the proposed system constituted a promising method to reduce the total exergy loss. Thus, the proposed system decreased the exergy loss by around 16.7% through the recovery of both chemical and thermal tar exergy. The decomposition of the tar component into a lighter hydrocarbon and the carbon deposited in the iron-ore pores successfully



*) In the proposed system, the separation process was integrated with ore dehydration (heat recovery)

Fig. 5. Comparison of exergy losses showed that the proposed system decreased exergy losses compared to a conventional system by recovering both chemical and thermal exergy. Basis 1000 kg-Fe.

decreased the total exergy losses.

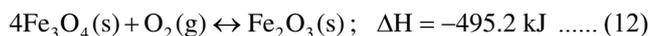
Based on the experimental values, the amount of deposited carbon within the porous ore was lower than the expected, 10%wt. This value was calculated by using the remaining pore volume of the porous ore after the carbon deposition process.^{7,9)} Figure 6 shows the exergy losses and ore product for both conventional and proposed system with different amounts of deposited carbon. As the carbon deposition originated from tar decomposition, increasing the carbon deposition enhanced the ore product exergy and decreased the chemical tar exergy outflow. Therefore, the expected value of carbon deposition declined significantly of total exergy loss. In addition to exergy loss, this circumstance improved also the overall efficiency of biomass utilization in ironmaking process, meaning that a similar amount of biomass input, 1906 kg PKS resulted in higher exergy of the ore product and smaller exergy losses.

3.3. Application of Sinter Plant

The main purpose of the sinter plant is to prepare an iron ore as a suitable feedstock for the blast furnace through an agglomeration process. In the existing system, this process shows high energy consumption and produces a large amount of CO₂ from the combustion of coke breeze and COG. To produce sinter, an iron ore and lime (CaO) are heated and melted at high temperatures. Therefore, the sinter plant is promising unit in the ironmaking industry to effectively utilize the CVI ore. The deposited carbon within the CVI ore could replace the coke breeze as an energy source in the sinter plant. **Figure 7** shows the schematic diagram of a sinter plant that utilized the CVI ore as a product of integrated pyrolysis-tar decomposition over porous iron

ores. In addition to the deposited carbon, the reform pyrolysis gas could also be used as an energy source and substitute for COG. By using this system, the consumption of coke breeze and CO₂ emissions could be reduced.

The main energy source for ore agglomeration in the sinter plant comes from the combustion of solid fuel through an oxidation process. In addition to the deposited carbon, the CVI ore mainly contained prereduced iron ore, Fe₃O₄ as a result of indirect reduction in the CVI unit. Based on the Gibb's free energy, the oxidation of Fe₃O₄ into Fe₂O₃ would occur spontaneously in the sinter plant through reaction (12).



Using the large supply of O₂ from the input air, this reaction occurred completely without any CO₂ generation. The reaction heat of this reaction could act as additional energy for the combustion and agglomeration processes in the sinter plant. In addition to the carbon content, this represented another benefit of the CVI ore, and therefore, it could also act as an energy-storage system in the ironmaking process.

In the existing plant, 1 061 kg of the total iron ore was fed into the sinter plant with 37 kg of coke breeze as energy source to produce 1 ton of sinter. **Figure 8** shows the enthalpy of the CVI ore at different ratios compared to the total input ore for 1 ton of sinter product. The horizontal line indicates the minimum coke enthalpy input in the existing system. It is clear that the enthalpy of total input ore (original ore and CVI ore) was enhanced at a higher ratio of CVI ore because of the amount of deposited carbon and Fe₃O₄. The total enthalpy of CVI ore was supplied by two different sources, namely re-oxidation of Fe₃O₄ and deposited carbon with ratio of 39.8% and 60.2% respectively. The enthalpy of total input ore became more than the minimum coke enthalpy when the CVI ore content was above 70% of the total input ore. This indicated that the CVI ore enthalpy was sufficient for the sintering process without the addition of any coke breeze. Accordingly, the oxidation enthalpy of Fe₃O₄ also had a significant effect on the total enthalpy of

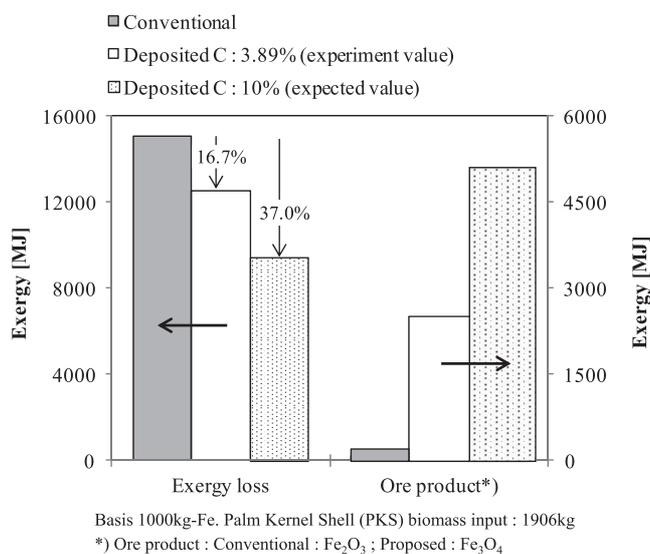


Fig. 6. Comparison of exergy losses and ore product for both conventional and proposed system at different amount of deposited carbon showed that the expected value of deposited carbon decreased significantly of exergy loss and enhanced dramatically of ore product exergy.

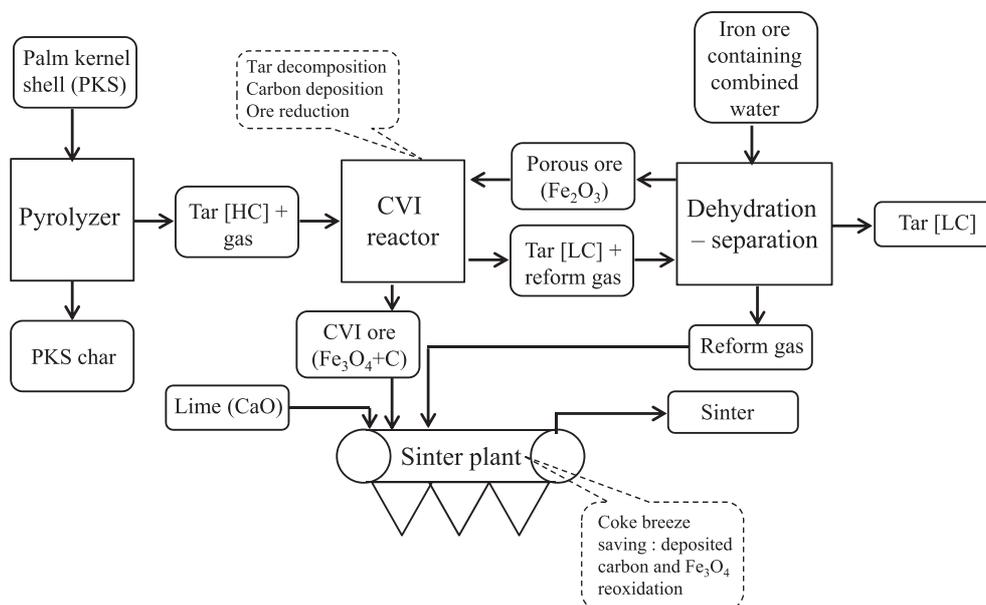


Fig. 7. Schematic diagram of CVI ore application in the sinter plant showed that the carbon deposited in the ore had a high potential to reduce the consumption of coke breeze in the ironmaking industry.

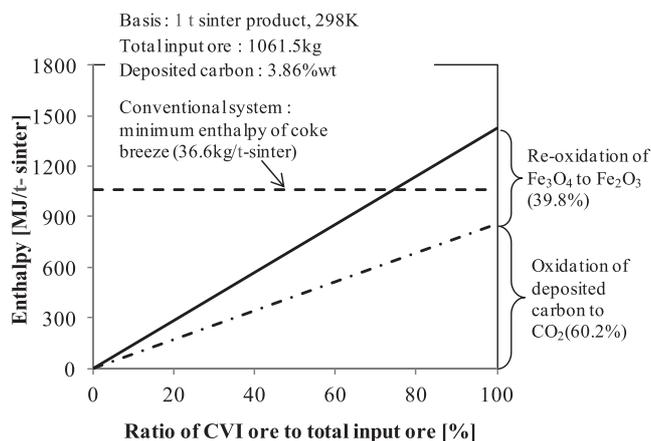


Fig. 8. Enthalpy content of the input iron ore in the sinter plant showed that the input enthalpy of CVI ore was higher than the minimum coke enthalpy at ratios of CVI ore above 70%.

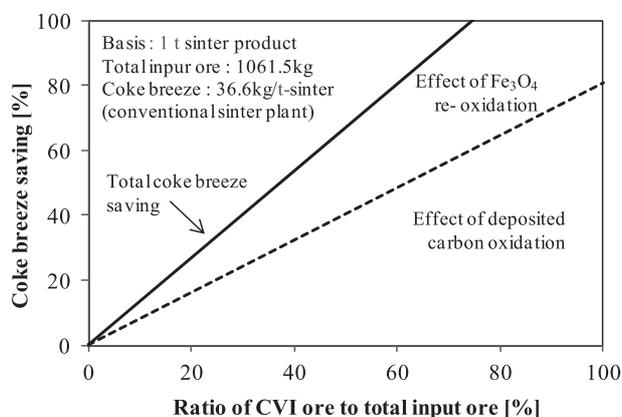


Fig. 9. Effect of CVI ore utilization on the consumption of coke breeze in sinter plant showed that the proposed system offered an extensive amount of coke breeze savings.

the CVI ore.

Based on the enthalpy content of the input ore, the amount of coke breeze was estimated at different ratios of the CVI ore, as shown in Fig. 9. The amount of coke breeze saving had a linear correlation with the CVI ore input to the sinter plant, and a larger coke saving was achieved at a higher ratio of the CVI ore to the total input ore. When the ratio of the CVI ore was 40%, the consumption of coke breeze in the sinter plant decreased to 14.4 kg, and more than 60% was saved as compared to the existing system. The coke breeze saving could become 100% when the CVI ore content was above 70% of the total input ore, meaning that the sinter plant could proceed without addition of coke breeze. Based on these results, the application of the CVI ore in a sinter plant led to extensive decreases in coke breeze and CO₂ emissions in the ironmaking process.

4. Conclusions

A process system diagram was constructed and a compar-

ison of exergy analysis with conventional methods was conducted to assess the advantages of integrated pyrolysis-tar decomposition for the utilization of low-grade ores and biomass in the ironmaking industry. In addition, the benefits of CVI ores utilization in sinter plants were also discussed. The main results can be summarized as follows:

(1) A process system diagram of the integrated pyrolysis-tar decomposition through CVI process was successfully constructed. It consisted of three units: pyrolysis, CVI, and dehydration-separation. The iron ore was utilized for energy storage in this system through deposited carbon within the pores of the ore and Fe₃O₄. The energy requirements of this system were sufficiently supplied via the recycling of pyrolysis gas.

(2) The exergy of CVI ore enhanced drastically in the CVI unit because of the reduction reaction and carbon deposition as a result of tar decomposition. The total exergy losses decreased by 17.6% compared to a conventional system by recovering the chemical and thermal tar exergy. When the carbon deposition reached the expected value (10%wt), the total exergy losses declined significantly to around 37.0% compared to a conventional. Thus, the proposed system is a promising method for recovery chemical and thermal tar exergy using porous low-grade iron ores.

(3) In the sinter plant, the amount of the deposited carbon was sufficient to completely replace coke breeze when the CVI ore content was above 70% of the total input ore. The total enthalpy of CVI ore was sourced by re-oxidation of Fe₃O₄ and deposited carbon with the ratio of 39.8% and 60.2% respectively. The application of the CVI ore in a sinter plant resulted in an extensive decrease in the coke breeze and CO₂ emissions in the ironmaking industry.

These results demonstrate that the proposed system is a promising method for the effective utilization of biomass and for decreasing CO₂ emissions in the ironmaking industry.

REFERENCES

- 1) C. Xu and C. Da-qiang: *J. Iron Steel Res. Int.*, **17** (2010), 1.
- 2) M. Yellishetty, P. G. Ranjith and A. Tharumarajah: *Resour. Conserv. Recycl.*, **54** (2010), 1084.
- 3) J. Fu, G. Tang, R. Zhao and W. Hwang: *J. Iron Steel Res. Int.*, **21** (2014), 275.
- 4) L. Devi, K. J. Ptasiński and F. J. Janssen: *Biomass Bioenerg.*, **24** (2003), 125.
- 5) M. A. Diez, R. Alvarez and J. L. Cimadevilla: *Fuel*, **114** (2013), 216.
- 6) A. Paethanom, S. Nakahara, M. Kobayashi, P. Prawisudha and K. Yoshikawa: *Fuel Process. Technol.*, **104** (2012), 144.
- 7) R. B. Cahyono, N. Yasuda, T. Nomura and T. Akiyama: *Fuel Process. Technol.*, **119** (2014), 272.
- 8) K. Miura, K. Miyabayashi, M. Kawanari and R. Ashida: *ISIJ Int.*, **51** (2011), 1234.
- 9) R. B. Cahyono, A. N. Rozhan, N. Yasuda, T. Nomura, H. Purwanto and T. Akiyama: *Energ. Fuel*, **27** (2013), 2687.
- 10) S. Hosokai, K. Matsui, N. Okinaka, K. Ohno, M. Shimizu and T. Akiyama: *Energ. Fuel*, **26** (2012), 7274.
- 11) T. Hiraki and T. Akiyama: *Int. J. Hydrogen Energ.*, **34** (2009), 153.
- 12) Y. Shudo, T. Ohkubo, Y. Hideshima and T. Akiyama: *Int. J. Hydrogen Energ.*, **34** (2009), 4500.
- 13) H. Yabe and Y. Takamoto: *ISIJ Int.*, **53** (2013), 1625.
- 14) S. Kathiravale, M. N. Yunus, K. Sopian, A. H. Samsuddin and R. A. Rahman: *Fuel*, **82** (2003), 1119.
- 15) C. Li and K. Suzuki: *Renew. Sust. Energ. Rev.*, **13** (2003), 594.
- 16) N. Yasuda, T. Tsuchiya, N. Okinaka and T. Akiyama: *Int. J. Hydrogen Energ.*, **37** (2012), 9706.