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Feasibility of an Advanced Waste Heat Transportation System Using High-temperature Phase Change Material (PCM)

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A waste-heat transportation (HT) system whose operation depends on the latent heat (LH) of high-temperature phase change material (PCM) is effective in reducing carbon dioxide (CO₂) emission from industries. This paper describes 1) the use of the binary eutectic mixture NaOH/Na₂CO₃ as a PCM to realize the HT system, 2) the feasibility of HT system using this PCM from viewpoints of energy requirements, exergy loss, and CO₂ emissions. In this study, we examined the thermophysical properties of the PCM and its chemical stability with reference to the heat transfer medium of the HT system by differential scanning calorimetry and thermogravimetry-differential thermal analysis. We observed that NaOH/Na₂CO₃ had a LH of fusion of 252 kJ/kg and a melting point (MP) and a freezing point (FP) of 285±1°C that was suitable for the HT system. There were no significant changes in the chemical and physical properties after aging for 500 h during phase change when dibenzyltoluene was used as the heat transfer medium. On the contrary, in the system analysis, the operating data in the proposed system—as well as in a conventional heat supply system—were calculated based on heat and material balances. The results show it has only 9.5% of the energy requirements, 39.7% of the exergy loss, and 19.6% of the CO₂ emissions of conventional systems that lack heat-recovery capabilities.

KEY WORDS: phase change material (PCM); latent heat; waste heat; CO₂ emission; heat storage; transportation.

1. Introduction

Recently, the use of phase change material (PCM) for thermal energy storage (TES) has attracted considerable attention. In particular, a waste-heat transportation (HT) system involving the use of a PCM helps reduce carbon dioxide emission. In previous studies,^{1–3)} an energy transportation system that can be used to recover industrial waste heat at low temperatures (<200°C) has been proposed. This system involves the use of PCMs with low melting points (MP) and large latent heat (LH); PCMs such as erythritol (MP: 118°C, LH: 340 kJ/kg) and sodium acetate trihydrate (MP: 58°C, LH: 264 kJ/kg) can be used in this system. This system functions as follows. A mobile LH accumulator recovers industrial waste heat and distributes it over wide areas for municipal uses, instead of industrial uses. The waste heat is stored in the form of LH by melting of PCM; the PCM is then transported to the city in container tanks. By solidifying the PCM, the waste heat stored in it can be used to heat water, which can be supplied for municipal purposes. Thus, this technique does not require the combustion of fossil fuels. This system has many benefits; it helps in recovering and supplying waste heat efficiently, conserving fossil fuel, and reducing CO₂ emissions. The mass to be transported in the container tank can

be minimized because this system involves direct heat exchange between the PCM and the oil, used as the heat transfer medium and does not require heavy equipments such as shells and tubes.^{4,5)}

As the next stage in this research, the reduction of CO₂ emission in the industrial side in the help of the energy transportation system is now under contemplation.⁶⁾ The concept of exergy based on the second law of thermodynamics indicates that the use of a system involving thermal cascading utilization minimizes exergy loss. In other words, the thermal combination between high-temperature industries and nearby medium- or low-temperature industries has great potential for reducing CO₂ emission by reducing the consumption of fossil fuels in the medium- or low-temperature industries. For example, a large amount of waste heat is produced at high temperatures in steelworks. The sensible heat of hot rolls at temperatures of 300–400°C is not recovered at all and emitted to air. On the contrary, the distillation tower used for the separation of benzene, toluene, and xylene (BTX) is one of the most promising candidates for supplying waste heat. In fact, some plants that are involved in the production of BTX from coal tar are located in the vicinity of steelworks. In these plants, temperatures of approximately 200–300°C are attained by the combustion of coke oven gas (COG).

Therefore, in the present study, we proposed the advanced HT system using high-temperature PCM (MP <200°C) which can efficiently recover waste heat at high temperatures emitted from steelworks and supply the heat to chemical plants. **Figure 1** shows the concept of the advanced HT system using high-temperature PCM and **Fig. 2** shows a schematic diagram of HT container.²⁾ The PCM used in this system should have large LH, should be chemically stable with respect to the oil used as the heat transfer medium, and should not exhibit supercooling.

This study can be separated into two sections: experimental and system analysis.

The purpose of the experimental section is to investigate the use of binary eutectic mixture NaOH/Na₂CO₃ as PCM in a HT system for high-temperature applications. The PCMs were examined from mainly two viewpoints: (1) thermophysical properties such as the MP, freezing point (FP), and LH and (2) chemical stability with reference to

the heat transfer medium upon repeated heating and cooling. The studies were carried out by using differential scanning calorimetry (DSC) and thermogravimetric and-differential thermal analysis (TG-DTA).

In addition, the purpose of the system analysis section is to investigate the feasibility of the proposed system using above mentioned PCM; feasibility is mainly evaluated in terms of energy requirements, exergy loss, and CO₂ emissions by comparing conventional system which uses the combustion heat of fossil fuels without transportation.

2. Experimental

2.1. Materials

Chemical reagents NaOH (99.0% purity) and Na₂CO₃ (99.0% purity) were used without further purification. They were mixed in air to give their eutectic compositions: 82.9wt%NaOH–17.1wt%Na₂CO₃.

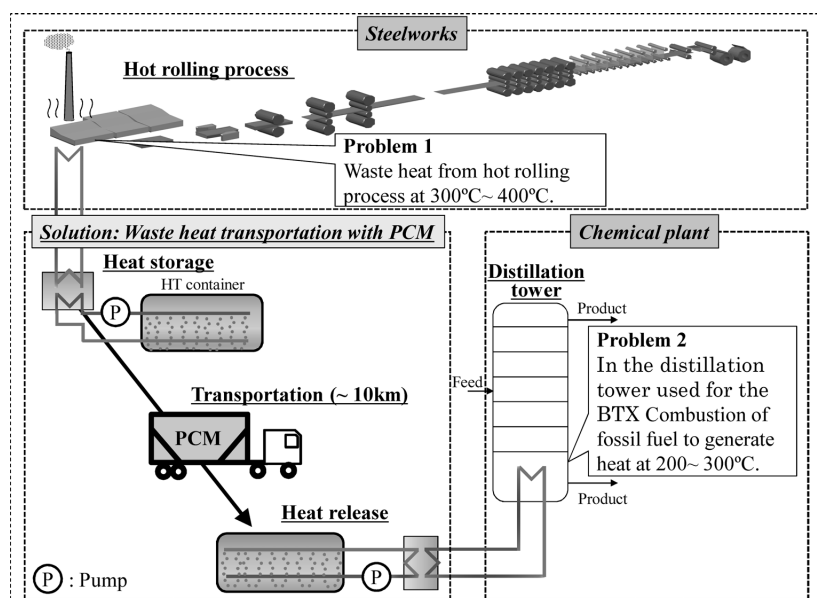


Fig. 1. Concept of the advanced HT system using high-temperature PCM.

(a) Schematic diagram of HT container

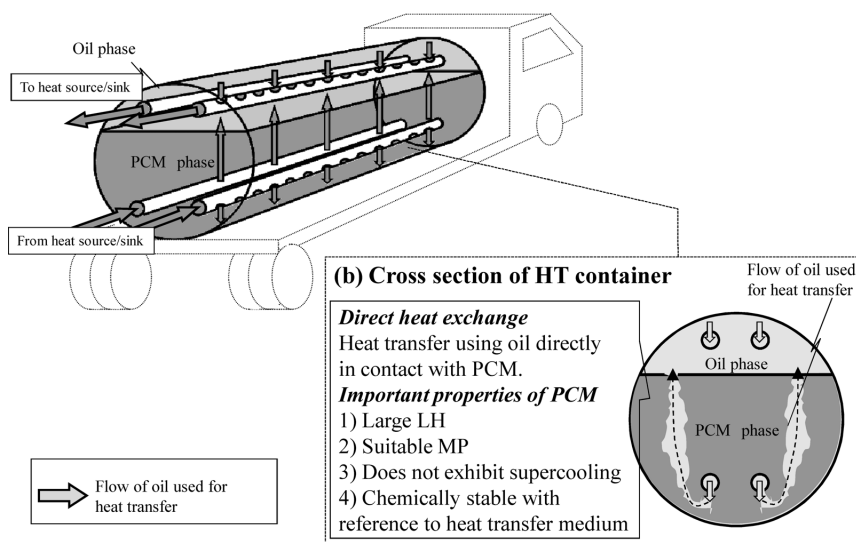


Fig. 2. (a) Schematic diagram of HT container,²⁾ (b) cross section of HT container.

Table 1. Thermophysical properties of dibenzyltoluene (heat transfer medium).⁷⁾

Material	Molecular weight [g/mol]	Density [kg/m ³]	Boiling point [°C]	Freezing point [°C]	Firing point [°C]
dibenzyltoluene	271	1.04 at 20 °C	> 390	< -30	212

Dibenzyltoluene which has a high boiling point of 390°C, low vapor pressure head, and low viscosity was selected as the candidate of heat transfer medium. This material can be used for the recovery of waste heat at medium or high temperature. **Table 1** lists the thermophysical properties of dibenzyl toluene.⁷⁾

2.2. Techniques for Thermal Characterization

Thermogravimetric and differential thermal analysis (TG-DTA) and differential scanning calorimetry (DSC) were applied for thermal characterization of the samples. Conditions for the TG-DTA were: temperature regime from room temperature to 350°C, heating rate of 10 K/min, samples mass about 10 mg in an open alumina crucible under argon gas flow of 500 mL/min with alumina as reference. DSC recording were taken from room temperature to 350°C, heating or cooling rate of 5 K/min, in open alumina crucibles under argon gas flow of 50 mL/min against alumina as reference. Calibration was performed against temperatures and enthalpies of melting of indium, tin and lead.

2.3. Chemical Stability of PCM with Reference to the Heat Transfer Medium

To evaluate the thermal stability of the eutectic mixtures of NaOH/Na₂CO₃ as PCM and its compatibility with dibenzyltoluene as the heat transfer medium, aging tests were performed by DSC. Before performing the tests, the PCM was heated at 120°C in vacuum for 12 h to remove water, and then the PCM was placed in a stainless steel crucible that contained the dibenzyltoluene, and finally the crucible was quickly sealed.

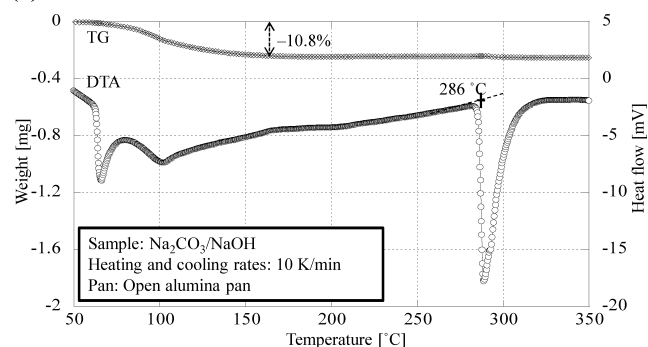
Conditions for the DSC measurements were as follows; the closed stainless steel container including PCM and dibenzyltoluene was maintained at 320°C for long periods up to 500 h. Five hundred hours is enough long period because according to the previous study it is expected that liquid PCM contacts heat transfer medium for only several hours in heat storage or release.^{1,2)} The DSC measurements for the samples were made intermittently.

2.4. Results and Discussions

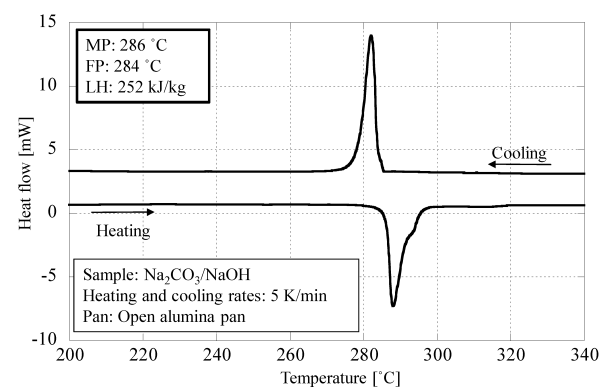
2.4.1. Thermophysical Properties of Na₂CO₃/NaOH

Figure 3(a) shows the TG-DTA curves of Na₂CO₃/NaOH that were obtained during heating at a rate of 10 K/min. Three endothermic peaks are observed in the DTA curve. The first peak observed between 60°C and 80°C was probably caused by the dehydration of the hydrates of Na₂CO₃ and NaOH. The second peak observed between 80°C and 160°C was caused by the evaporation of water. As observed from the TG curve, the mass of the sample started decreasing from the starting point of the first peak of the DTA curve to approximately 160°C, which is the endpoint of the second peak of the DTA curve. This trend in the TG curve indicated the dehydration of hydrates and

(a) TG-DTA curves



(b) DSC curves

**Fig. 3.** (a) TG-DTA curves and (b) DSC curves of eutectic mixtures of NaOH/Na₂CO₃.

the evaporation of water. The third peak of the DTA curve was observed at approximately 300°C, and was caused by the melting of Na₂CO₃/NaOH. Moreover, the mass loss of the sample remained constant from 160°C, which corresponds to the temperature at which evaporation of water is complete, to 350°C, which corresponds to the end of the measurement. This shows that Na₂CO₃/NaOH has sufficiently low vapor pressure and does not decompose; hence, it can be used as PCM up to 350°C.

Figure 3(b) shows the DSC curves of Na₂CO₃/NaOH that were obtained during heating and cooling at rates of 5 K/min. A sharp endothermic peak corresponding to a large LH of 252 kJ/kg was observed at 286°C during heating, and a sharp peak was observed at 284°C during cooling. The MP of the sample: 286°C was almost similar to the value reported in previous studies.⁸⁾ The results revealed that Na₂CO₃/NaOH had little supercooling tendency. In addition, the LH of the sample: 252 kJ/kg is enough large value for applying to the proposed system. This value is approximately similar to sodium acetate trihydrate (MP: 58°C, LH: 264 kJ/kg) which was applied to the above mentioned waste heat transportation system using PCM for recovery of waste heat at low temperature (under 200°C), and it is large in comparison with other PCM candidates such as nitrate, nitrite, hydroxide, and their mixtures which have MP with 200–300°C.^{9,10)}

2.4.2. Chemical Stability of PCM with Reference to the Heat Transfer Medium

Figure 4 shows the changes in MP, FP, and LH of Na₂CO₃/NaOH after it was kept in contact with dibenzyltoluene in the closed stainless steel container for several

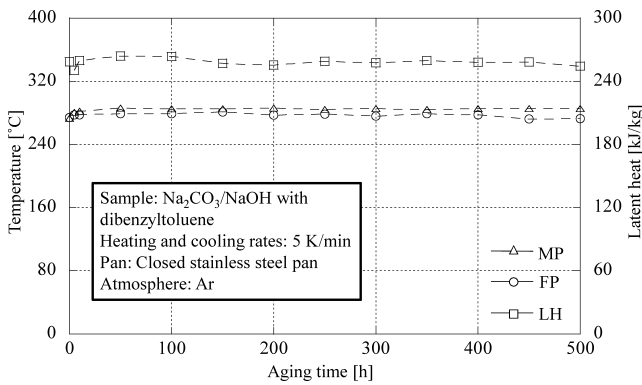


Fig. 4. Changes in MP, FP, and LH of $\text{Na}_2\text{CO}_3/\text{NaOH}$ after it was kept in contact with dibenzyltoluene in the closed stainless steel container for several hours at 320°C .

hours at 320°C . It is evident that the MP, FP, and LH of fusion do not change after aging for 500 h in dibenzyltoluene. This result indicates that $\text{Na}_2\text{CO}_3/\text{NaOH}$ is chemically stable with reference to dibenzyltoluene and also thermally stable. In conclusions, $\text{Na}_2\text{CO}_3/\text{NaOH}$ can be used as PCM in the proposed waste heat transportation system with direct heat exchanger.

3. System Analysis

3.1. Details of System Analysis

3.1.1. Conventional System

Figure 5(a) shows a process system diagram for Case 1, *i.e.*, a conventional system that uses the combustion heat of COG on site to obtain hot oil at 250°C .

3.1.2. Waste Heat Transportation System Using PCM (Proposed)

Figure 5(b) shows a process system diagram for Case 2, Waste heat transportation system using PCM. This system comprises three unit-systems (also see Fig. 1): heat storage, transportation, and heat release. The heat-storage system comprises two sub-systems: a heat-exchange system between the waste heat and the oil as the heat-transfer medium, and a heat-storage system that stores heat in a container by melting PCM. The transportation system coordinates heat delivery between the producing industry and the point of demand by using a container truck. The heat-release system comprises two sub-systems: 1) a heat-release system that recovers the transported heat by solidifying PCM during heat exchange between melting PCM and flowing oil into the container, and 2) a heat-exchange system to supply hot oil to BTX plant during heat exchange between the oil flowing from the container and the oil flowing from BTX plant. Note that the transported oil is used as an intermediary fluid and circulating between the container and heat exchanger. In this study, the eutectic mixtures of $\text{NaOH}/\text{Na}_2\text{CO}_3$ was selected as the PCM.

3.2. Calculation Method

Enthalpy was calculated using the following equations:

(A) Enthalpy of material at T (K):

$$H = mC_p(T - T_0) \quad \text{.....(1)}$$

(B) Enthalpy of PCM at T (K):

$$H_{\text{PCM}} = m_{\text{PCM}}C_{p,\text{PCM},l}(T - T_m) + m_{\text{PCM}}Q_{L,f} + m_{\text{PCM}}C_{p,\text{PCM},s}(T_m - T_0) \quad \text{.....(2)}$$

Exergy is used to evaluate the qualitative change from the available energy to the unusable energy, in the form of work. The thermal exergy is defined by the following equations.

(C) Exergy of material at T (K):

$$\varepsilon = mC_p \left\{ T - T_0 - T_0 \ln \left(\frac{T}{T_0} \right) \right\} \quad \text{.....(3)}$$

(D) Exergy of PCM at T (K):

$$\varepsilon = m_{\text{PCM}}C_{p,\text{PCM},l} \left\{ T - T_m - T_0 \ln \left(\frac{T}{T_m} \right) \right\} + m_{\text{PCM}}Q_{L,f} \left(1 - \frac{T_0}{T_m} \right) + m_{\text{PCM}}C_{p,\text{PCM},s} \left\{ T_m - T_0 - T_0 \ln \left(\frac{T_m}{T_0} \right) \right\} \quad \text{.....(4)}$$

Note that environmental temperature T_0 was 298 K for the whole calculation.

Table 2 shows the enthalpy and exergy of fossil fuel, together with the conversion factor of CO_2 emissions of fossil fuel and electricity.¹¹⁾

(E) The intermediary energy that is either released or accepted is given by

$$\Delta H = H_{\text{out}} - H_{\text{in}} \quad \text{.....(5)}$$

Intermediary energy is defined as energy that is either released by or accepted into a process. The calculation of enthalpy balance is represented in the form of a flow diagram. Finally, energy requirements, exergy losses, and CO_2 emissions are evaluated on the basis of the energy supplied in the different cases. By using Eqs. (6), (7), and (8), the abovementioned parameters are calculated on the basis of the energy required for producing supply hot oil of 1 GJ.

$$\text{INH} = \frac{H_{\text{input}}}{H_{\text{supply}}} \quad \text{.....(6)}$$

$$\text{EXL} = \frac{\varepsilon_{\text{loss}}}{H_{\text{supply}}} \quad \text{.....(7)}$$

$$\text{ECO}_2 = \frac{W_{\text{CO}_2}}{H_{\text{supply}}} \quad \text{.....(8)}$$

CO_2 emissions, expressed as W_{CO_2} , were calculated according to the guidelines provided for calculating greenhouse effect gases.¹¹⁾ Analyses were performed, based on the following assumptions:

- (1) In Case 2, the distance of transfer of the waste heat from the steelworks to the chemical plant was 10 km, and the truck's fuel consumption of diesel oil was 2 km/L.
- (2) In Case 2, the laden weight of the container was 2.0×10^4 kg; a PCM weight of 1.75×10^4 kg and a heat-transfer oil weight of 2.5×10^3 kg were included.

(a) Case 1; Conventional (b) Case 2; Proposed

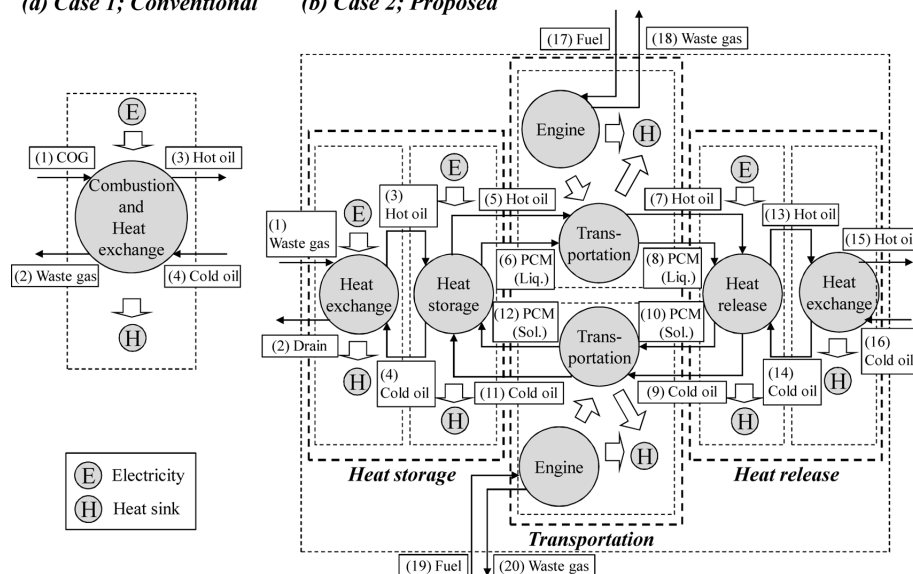


Fig. 5. (a) Process system diagram of Case 1; a conventional system that uses the combustion heat of a COG on site, (b) process system diagram of Case 2; a proposed latent heat transportation system. Note that open circle, a process; solid-line arrow, flow of the substance; open arrow, flow of intermediary energy; dotted line, system boundary.

Table 2. Enthalpy and exergy of diesel oil and COG, together with the conversion factor of CO₂ emission of them and electricity.

	Enthalpy	Exergy	Conversion factor
Diesel oil	38.2 MJ/L	37.7 MJ/L*	0.0686 kg-CO ₂ /MJ
COG**	21.1 MJ/Nm ³	19.8 MJ/Nm ³ *	0.0403 kg-CO ₂ /MJ
Electricity	-	-	0.378 kg-CO ₂ /kWh

*Calculated by Rant's equation

**Coke Oven Gas (H₂/N₂/CH₄/CO/CO₂)

Table 3. Assumed temperature of in- and out-flowing materials.

Case 1: Fossil fuel combustion (Conventional)

No.	Material	Temperature (K)
(1)	Fossil fuel (COG)	-
(2)	Waste gas	298.15
(3)	Hot oil into chemical plant	523.15
(4)	Cold oil from chemical plant	483.15

Case 2: Waste heat transportation with PCM (Proposed)

No.	Material	Temperature (K)
(1)	Waste gas from steelwork	673.15
(2)	Waste gas after heat exchange	623.15
(3)	Hot oil flowing from container	623.15
(4)	Cold oil flowing into container	603.15
(5)	Hot oil after heat storage	603.15
(6)	Liquid PCM after heat storage	603.15
(7)	Hot oil after transportation	602.15
(8)	Liquid PCM after transportation	602.15
(9)	Cold oil after heat release	543.15
(10)	Solid PCM after heat release	543.15
(11)	Cold oil after transportation	542.15
(12)	Solid PCM after transportation	542.15
(13)	Hot oil flowing from container	543.15
(14)	Cold oil flowing into container	523.15
(15)	Hot oil flowing into chemical plant	523.15
(16)	Cold oil flowing from chemical plant	483.15
(17)	Fuel for wheel track	-
(18)	Waste gas from the track	298.15
(19)	Fuel for wheel track	-
(20)	Waste gas from the track	298.15

- (3) The above mentioned experimental values were used as the latent heat and MP of the PCM: eutectic mixtures of Na₂CO₃/NaOH. The specific heat of the NaOH⁽¹²⁾ was assumed as the those of the PCM. Specific heat and density of dibenzyltoluene as heat transfer oil were 2.50 kJ/kg·K and 850 kg/m³,⁽⁷⁾ respectively. In addition, the constant value of specific heat of oil and the PCM, and density of oil were employed for the whole calculation.
- (4) The heat loss in each process was ideally zero, except in the transportation processes. The temperature drop of 1 K during the transportation processes was assumed.
- (5) The generation of waste heat at a temperature of 400°C was not considered.
- (6) In Case 1, the combustion efficiency of the fossil fuel was 95%, and the electric power was ignored.
- (7) In Case 2, heat storage or release rate were 1 MW, and power of pumps to flow intermediary fluid in both heat storage and release process were 20 kW.
- (8) **Table 3** lists the assumed temperatures of the materials that were changed before and after each process.

3.3. Results and Discussion

This study analyzed two systems used for supplying hot oil at 250°C. The enthalpy and exergy of the in- and out-flowing materials for producing hot oil of 1GJ in the different cases are shown in **Table 4**. **Figure 6** shows the energy requirements, exergy losses, and CO₂ emissions for produc-

ing hot oil of 1 GJ at 250°C. Case 1 consumed fossil fuel, while Case 2 consumed electric power for heat-storage and heat-release operations and fossil fuel to transport the container. CO₂ emissions were calculated from consumed energies. The energy requirements, exergy losses, and CO₂ emissions of Cases 2 were considerably lower than those of Case 1; Case 2 had an energy requirement of 9.5%, an exergy loss of 39.7%, and CO₂ emission of 19.6% of Case

addition, as the results of the calculation, Case 2, the proposed system, can supply 7.00 GJ/1 cycle.

Figure 7(a) shows an exergy flow diagram for Case 1, (b) shows that for Case 2. It is clear that in Case 1, a very large exergy loss generates the fossil fuel combustion for heating the heat-transfer medium to 250°C. On the contrary, although Case 2 needs many processes for supply thermal energy of waste heat to chemical plants, small exergy loss generates since Case 2 does not combust the fossil fuel for heating.

4. Conclusions

In this study, the thermophysical properties and chemical stability of the binary eutectic mixture NaOH/Na₂CO₃, a new PCM candidate, was experimentally studied by thermal analysis and the feasibility of an advanced waste heat transportation system using high-temperature PCM for recovery of high-temperature waste heat and supply it to a BTX distillation tower was investigated under reasonable assumptions. We observed the following:

(1) Na₂CO₃/NaOH could be used up to 350°C as PCM because it had sufficiently low vapor pressure and did not decompose.

(2) Na₂CO₃/NaOH (MP: 286°C; FP: 284°C) had a sufficiently large LH (252 kJ/kg) and had little supercooling tendency.

(3) Na₂CO₃/NaOH was chemically stable with reference to dibenzyltoluene, which was used as the heat transfer medium. DSC analysis showed that its thermophysical properties were constant even after aging for 500 h.

(4) The waste heat transportation system using the binary eutectic mixture NaOH/Na₂CO₃ (Case 2) supplied the heat of 7.00 GJ/1 cycle at 250°C.

(5) The waste heat transportation system (Case 2) had energy requirements, exergy losses, and CO₂ emissions that were 9.5%, 39.7%, and 19.6% those of a conventional system that uses fossil fuel on site (Case 1), respectively.

All the results indicated a possibility that the proposed waste-heat transportation system with direct heat exchanger using Na₂CO₃/NaOH and heat transfer medium of dibenzyltoluene can reduce CO₂ emission in the industrial side, in addition to the municipal side.

Nomenclature

C_p	: Specific heat (J/g K)
$C_{\text{PPCM},s}$	: Specific heat of solid PCM (J/g K)
$C_{\text{PPCM},l}$	: Specific heat of liquid PCM (J/g K)
E_{CO_2}	: Ratio of CO ₂ emissions rate (g/J)
EXL	: Ratio of exergy loss (—)
H	: Enthalpy (J)
H_{in}	: Input enthalpy of a process (J)
H_{input}	: Input enthalpy of a system (J)
H_{out}	: Output enthalpy of a process (J)
H_{supply}	: Enthalpy of supplied oil to chemical plant (J)
INH	: Ratio of inflowing enthalpy (—)
m	: Mass (g)
$Q_{L,f}$	: Latent heat of fusion (J/g)
T	: Temperature (K)
T_m	: Melting point (K)
T_0	: Environmental temperature (K)
W_{CO_2}	: Weight of CO ₂ emissions (g)
ε	: Exergy (J)
$\varepsilon_{\text{Loss}}$	: Exergy loss (J)

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