

Thermal Energy Utilization of High Temperature Ash: Current Situation and Prospects

Taikun Yin,^{a,b} Xinya Huang,^{a,b} Sen Yao,^{a,b} and Gang Li^{a,b,*}

Not only is the use of waste heat an important way for companies to reduce fuel costs but it is also an important step in achieving the goal of decreasing peak carbon dioxide emissions. Solid fuels still make up a large proportion of China's energy consumption structures, and the amount of ash generated and the remaining thermal resources are enormous. When considering coal alone, the theoretical recoverable amount of waste heat associated with the ash can be as much as 15.87 Mt of standard coal per year. An analysis of thermal energy utilization of high temperature ash (TEUHA) was conducted. It was found that the existing direct utilization method had a thermal efficiency in the range of 12% to 92%. However, the process is complicated, and the heat carrier is susceptible to contamination. Indirect utilization could avoid pollution issues, but heat loss was severe and maximum thermal efficiency was calculated as only 59%. Combined with the waste heat characteristics of the ash and the heat demand, a "Point-Point" model of TEUHA using phase-change materials as the heat carrier is proposed. This approach not only avoids ash pollution to the thermal environment, but it also increases the energy harvesting efficiency and realizes a high-quality utilization of thermal energy.

DOI: 10.15376/biores.18.3.4866-4883

Keywords: High temperature ash; Theoretical available energy; Direct utilization methods; Indirect utilization methods; Phase-change heat carrier

Contact information: a: College of Mechanical and Electrical Engineering, Henan Agricultural University, Zhengzhou 450002, China; b: Key Laboratory of New Materials and Facilities for Rural Renewable Energy, Ministry of Agriculture & Rural Affairs, Zhengzhou 450002, China;

* Corresponding author: ligang@henau.edu.cn

INTRODUCTION

In recent years, because of the growing demand for energy and overconsumption of traditional energy sources, global energy scarcity, environmental pollution, and other phenomena have gradually intensified. Although global total primary energy use and per capita energy use decreased in 2020 as a result of the novel coronavirus, they remain enormous at 556.63 billion and 71.4 GJ, respectively. According to the Electronic Industries Association (EIA), the total global consumption of primary energy will continue to increase at an annual rate of 1.2% to 960.79 billion GJ by the year 2050 (Zhao *et al.* 2020). As the largest developing country, China not only exhibits uneven energy structure development, but also the rate of growth in energy demand and consumption is much greater than in other countries, achieving 4.97×10^3 Mt standard coal and 2.2% in 2020, respectively (National Bureau of Statistics 2021). Given that China's energy use intensity is 39.6% higher than the global average and that energy production is in short supply,

programs to address future increases in international energy prices and energy security are urgently needed.

Renewable energy integration and reduced energy consumption are the primary measures to address China's current energy crisis (Ouyang *et al.* 2022). While promoting a low-carbon economy, the development of renewable energy is vulnerable to environmental factors and lacks universality. Reducing the use of energy includes two ways. One is to reduce production directly to reduce energy demand, and the other is to improve energy efficiency. Under the background of deepening industrialization reform in China, the former is obviously not of practical significance. Therefore, improving energy efficiency will become the main trend of energy utilization in China.

Industrial waste heat refers to the general term for the energy content of waste products produced in industrial production. This article deals mainly with two components of heat. One is associated with heat capacity multiplied by changes in temperature. The other is the enthalpy of phase-change, as when a liquid becomes a solid due to cooling. Heat is wasted whenever hot materials are exposed directly to the environment, rather than being used to heat up incoming materials to a process. The work to perform waste heat recovery is of great importance for industrial energy conservation and emission reduction as well as the energy efficiency of the entire industrial process. For the solid fuel (coal, biomass, and so on) consumption industry, the waste heat is mainly present in byproducts, such as waste gas and ash (Zhang *et al.* 2013). In cases where the waste heat from byproducts directly supplies the next process without transformation, the loss of heat can be relatively low. Most of the waste heat from waste gas can be recovered by a low-temperature coal saver or air preheater (*i.e.* types of heat-exchangers), and the saved heat can be used to heat some of the condensate or preheat the fuel (Men *et al.* 2019). This is a relatively mature procedure. On the whole, the waste heat of products and high-temperature waste gas has been captured with reasonable efficiency. However, due to high temperature ash corrosion and deposition (Wang *et al.* 2014; Qi *et al.* 2016), the remaining forms of heat use recovery have been limited. Current research is focused on the recycling of high-quality waste heat resources and the use of ash particles (Barati and Jahanshahi 2019).

Given the objective of reducing “carbon peak” consumption, reduction of fossil fuel consumption is a crucial prerequisite, while full TEUHA is an important way to improve the efficiency of heat utilization (Zhong *et al.* 2023). This is a critical technical means of reducing energy consumption and thereby reducing the carbon peak after analyzing the technical bottlenecks affecting TEUHA and developing an efficient utilization technology to improve energy utilization efficiency. The objective of this work was to analyze the characteristics of common ash and calculate the theoretical available energy of high temperature ash in China. After a review of the current status of TEUHA, a method for recycling waste heat from ash using phase-change materials based on phase-change heat storage is proposed in this work.

CHEMICAL COMPOSITION AND ENERGY VALUE OF ASH

Ash is the main byproduct of solid fuel consumption process. It is generally composed of two parts. One is the deposit formed by light fly ash particles after melting in the combustion chamber, and the other is the bottom slag formed by the mixture of molten ash, under-burned fuel particles, and some impurities (Agrela *et al.* 2019). The traditional type of ash in China is dominated by blast furnace ash in the metallurgical industry.

However, in recent years, the rapid development of biomass power plants has led to an increase in the production of biomass ash. The chemical fractions of blast furnace ash, several common biomass ash, and the ash of a biomass power plant in China are compared in Table 1.

Table 1. Chemical Composition of Ash

Kinds	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	MnO	FeOx	Reference
Blast furnace ash	/	1-18	8-24	28-38	/	30-56	0.5-2	0.5-1	Barati <i>et al.</i> (2011)
Pine shavings	0.44	1.60	1.96	11.84	1.32	35.88	/	2.94	Xiao <i>et al.</i> (2011)
Poplar tree	1.49	3.52	8.96	23.76	6.70	23.76	0.52	6.39	Berra <i>et al.</i> (2015)
Sycamore leaf	1.12	5.93	1.88	24.95	11.58	28.37	/	1.79	Xiao <i>et al.</i> (2011)
Rice straw	0.14	1.64	0.09	75.38	11.95	1.60	0.27	0.10	Thy <i>et al.</i> (2006)
Wheat straw	0.80	1.82	0.77	57.47	16.55	2.80	0.07	0.39	Thy <i>et al.</i> (2006)
Maize straw	/	9.10	2.80	44.70	19.00	13.50	/	2.40	Wang <i>et al.</i> (2014)
Rice husk	0.03	0.50	0.37	63.77	1.42	0.44	0.05	2.65	Khoo <i>et al.</i> (2013)
Peanut shells	5.60	6.10	10.71	43.13	9.61	10.81	/	3.96	Umamaheswaran and Batra (2008)
Ash from biomass power plants	1.92	4.06	9.70	40.37	4.17	23.25	/	11.85	/

Table 1 shows that the ash obtained from the combustion of solid fuels contains predominantly Si, Ca, Mg, Al, and Fe, with a high alkaline oxide composition. In particular, biomass ash, such as pine shavings, poplar tree, and sycamore leaf, and blast furnace ash are rich in calcium silicate, which is an ideal filler and alternative material in the preparation of cement and concrete (Barati *et al.* 2011). It has been shown that the addition of ash is beneficial for improving the compressive strength of cement (Al-Kutti *et al.* 2019), promoting the densification of the microstructure of concrete mixes (Qudoos *et al.* 2019), and also effectively reducing the carbon dioxide emissions during the production of silicate cement (Thomas *et al.* 2021). However, limited by the low thermal conductivity of ash itself and the complex composition, the remaining thermal utilization needs to be further developed. Figure 1 shows the variation of thermal conductivity of coal-fired ash at different times under the non-stationary method test (Wu *et al.* 2020). It can be found that with the increase of temperature at a certain temperature, during the sample preparation process, the water accumulated inside the ash due to moisture absorption is gradually evaporated, and the increase of ash porosity leads to the decrease of thermal conductivity until it becomes stable (Cui and Wang 2019). The average value of the thermal conductivity of the ash sample is only 0.3030 W·m⁻¹·K⁻¹. To promote the heat exchange effect of high-temperature ash and to improve the efficiency of ash waste heat recovery, granulation operations are generally performed on high-temperature ash (Barati and Jahanshahi 2019).

The granulation process can be divided into two types. One is wet granulation using pressurized water and the other is dry granulation using large amounts of air. Although wet pelletizing can produce ash with high glass phase on a large scale, the thermal energy in the high temperature ash is severely wasted, and only a small portion of the thermal energy is converted into internal energy of water vapor and flushing water. Moreover, the pelletizing process is accompanied by the generation of H₂S, SO₂, and other harmful gases, which can be harmful to the environment. Dry pelletizing can effectively reduce pollution while efficiently recovering the thermal energy in the form of hot gas, steam, or chemical energy from the high temperature ash residue, which will be described later.

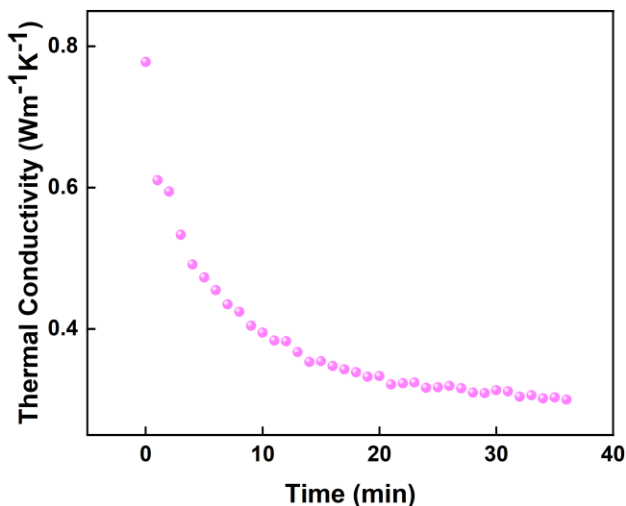


Fig. 1. Variation of thermal conductivity of coal combustion ashes at different times

Theoretical Available Energy of Ash

Solid fuels are the mainstay of China's energy consumption, of which the total annual coal consumption is approximately 3 Gt of standard coal, and the biomass available for energy production is approximately 600 Mt annually. The annual generation of ash from coal combustion is close to 600 Mt under the amount of ash from standard coal is estimated at 20%, and the annual generation of ash from biomass is approximately 40+ Mt, based on the average ash generation of dry-based biomass, 6.8% (Vassilev *et al.* 2013). Both ash types contain a great deal of thermal energy, and their energy can be used either directly or indirectly, but because research on the use of biomass ash waste heat is limited, in this section, only the theoretical energy available from coal-burning ash is analyzed. At present, China's coal consumption is mainly concentrated in the electric power, steel, building materials, and other industries, and their corresponding consumption in 2019 was 54%, 18%, and 12%, respectively (National Energy Information Platform 2020). Carnot's theorem states that, conditional on the form of utilization, heat exchange efficiency, temperature of the low-temperature heat source, and other factors, provided only its influence is considered by the low temperature heat source temperatures. Table 2 shows the theoretical energy available from HA in the three main coal consuming industries (Das *et al.* 2007; Feng *et al.* 2019; Ishaq *et al.* 2019; Liao *et al.* 2019). The theoretical maximum available energy formula was derived by Eq. 1,

$$Q = Cm(T_1 - T_2)\left(1 - \frac{T_2}{T_1}\right) \quad (1)$$

where Q is the theoretical maximum available energy (kJ), C is the specific heat capacity of ash, $1.2 \text{ kJ}/(\text{kg}\cdot^\circ\text{C})$, m is the mass of ash (kg), T_1 is the temperature of ash (K), and T_2 is the temperature of the low temperature end of the waste heat utilization, 323 K.

Table 2. Coal Consumption and Ash Generation in China's Power, Steel and Building Materials Industries in 2019

Name	Coal Consumption (Mt of Standard Coal)	Ash Generation (Mt)	Ash Temperature (K)	Theoretical Available Energy (GJ)	Percentage of Total Energy (%)	Converted Standard Coal Volume (Mt of Standard Coal)
Power Industry	1518.92	303.78	1123 to 1223	2.25×10^8	48	7.68
Steel Industry	506.31	101.26	1723 to 1923	1.44×10^8	31	4.91
Building Materials Industry	337.54	67.50	1773	9.61×10^7	21	3.28

As can be observed in Table 2, influenced by the forms of energy utilization and coal combustion, the temperature of ash in the electric power, iron, and building materials production industries varies greatly. The coal combustion ash of iron and building materials industries are super-high temperature ash with high energy density. From the perspective of energy utilization, the electric power industry has high energy utilization efficiency, whereas the iron and steel and building materials industries have low energy utilization efficiency, which matches the characteristics of their high energy consumption industries. From the perspective of theoretically available energy, the total available energy of the three major coal-burning industries is 4.65×10^8 GJ, which is equivalent to 15.87 Mt of standard coal, of which the power industry's available energy accounts for up to 48%. Overall, this demonstrates that China's ash waste heat resources are highly abundant and have high potential for recovery.

THERMAL ENERGY UTILIZATION OF ASH

There are currently two main forms of using thermal energy of high temperature ash (TEHA): Direct utilization and indirect utilization (Barati and Jahanshahi 2019). The direct utilization method uses high temperature ash directly as a heat source or reagent, with a short duration of action and high efficacy, but it is not applicable to heating compatible media. Indirect utilization uses heat exchange medium as an intermediary to achieve heat transfer, effectively avoiding the impact caused by direct contact with the ash but generally requiring a larger surface area for heat exchange and a higher cost of use.

Methods of Direct Utilization

The direct utilization of ash waste heat is the direct transfer of the energy possessed by the high temperature ash to the heated body, which mainly includes two forms of wet waste heat utilization and dry waste heat utilization (Qiu *et al.* 2019). The wet method, *i.e.*,

the water quenching method, is the most widely used, but it has a large consumption for water resources and has the disadvantages of low heat utilization rate and environmental pollution (Wang *et al.* 2016; Tan *et al.* 2020). The current optimization process of water quenching method mainly focuses on the waste heat utilization of flushing water, but the environmental problems caused by it still have not been effectively solved, so the more economical and environmentally friendly dry method has been developed rapidly in comparison. Early researchers recovered the remaining heat by using air and other heat transfer media in direct contact with the high temperature ash, but it was found that all the methods except centrifugal granulation had obvious shortcomings due to factors such as high process cost, low operating efficiency, and system instability. Recently, researchers have combined TEHA recovery with hydrogen preparation, CO₂ recovery, and biomass resource utilization (Sun *et al.* 2015). They have found that when ash waste heat recovery is combined with reforming for hydrogen production, ash not only can act as a heat carrier, but it also can play the role of catalyst, which has good significance for the application of blast furnace ash waste heat in hydrogen production. It is a good match between ash waste heat recovery and coal gasification reaction, which not only can utilize waste heat, but it also can reduce CO₂ emissions. Combining ash waste heat recovery with municipal waste treatment can promote green development and realize waste heat resource utilization at the same time. All these studies have achieved some success in TEHA recovery and utilization, but most of them have remained in the experimental stage because of some shortcomings. A comparative analysis of the research on the TEUHA directly is provided in Table 3.

Table 3. The Technical Situation of TEUHA Directly

Researcher/Institution	Method	Thermal Efficiency (%)	Insufficiency	Reference
Merotec	Solid particle impact method	65	Heat exchange air is easily contaminated and less efficient for energy use.	Qi <i>et al.</i> (2012)
Ishikawajima-Harima Heavy Industries and Sumitomo Metal	Single drum dry slag-granulation	60	Smaller handling capacity, heat exchange air is easily contaminated and less efficient for energy use.	Dai <i>et al.</i> (2008)
Pickering	Granulation by spinning cup	59	High power consumption and high costs, heat exchange air is easily contaminated.	Mao <i>et al.</i> (2013)
CSIRO, Akiyama	Granulation by spinning disc	58.5	Heat exchange air is easily contaminated, its heat cannot be used directly.	Mao <i>et al.</i> (2013)
Kasai	Methane-steam reforming reaction	---	Complex process with large reactor volumes	Kasai <i>et al.</i> (1997)

Mizuochi, Akiyama	Granulation by spinning cup + Methane-steam reforming reaction	92	Combined application with the rotary cup method to be tested in industrial trials	Mizuochi <i>et al.</i> (2001)
Purwanto	Methane-CO ₂ reforming reaction	---	The H ₂ content in the synthesis gas is relatively low, and further purification is required.	Purwanto and Akiyama (2006)
Liu, Li, Duan	Coal gasification	74.4	Complex process with large reactor volumes	Duan <i>et al.</i> (2015)
Zhao	Urban waste gasification	---	Lack of suitable reactor, further separation of reaction residue from ash required	Zhao <i>et al.</i> (2010)
Luo	Biomass pyrolysis and gasification	---	Lack of suitable reactor, further separation of reaction residue from ash required	Luo <i>et al.</i> (2012)
Qin	Pyrolysis of printed circuit boards	12	Lack of suitable reactors and low heat recovery efficiency	Qin <i>et al.</i> (2012)
Sun	Pyrolysis and gasification of sludge	---	Lack of suitable reactor, further separation of reaction residue from ash required	Sun <i>et al.</i> (2015)
Luo	Pyrolysis and gasification of sludge	---	Lack of suitable reactor, further separation of reaction residue from ash required	Luo and Feng (2016)
Hu	Pyrolysis of waste tires	55.94	Lack of suitable reactor, further separation of reaction residue from ash required	Hu <i>et al.</i> (2018)
Yao, Xie	Bio-oil steam reforming reaction	---	Lack of suitable reactors, relatively low hydrogen production	Yao <i>et al.</i> (2017), Xie <i>et al.</i> (2019)
Ishaq	Copper-chlorine (Cu-Cl) cycle	32.5	Complex process and high cost	Ishaq <i>et al.</i> (2019)

As shown in Table 3, there have been limited studies on the heat recovery efficiency of the TEUHA directly, and the highest efficiency is known for the recovery of ash waste heat by methane reforming reaction. However, the reaction temperature of methane reforming reaction is generally high, and the system is at a standstill when the temperature does not match, which is not applicable to the waste heat recovery of power plant ash. From the perspective of heat utilization of the heat exchange medium, because of the poor heat storage capacity of air and other media, and susceptibility to ash pollution, there is a larger demand for heat transfer medium. However, its heat cannot be directly used, thus causing the overall thermal efficiency to become low. From the perspective of the utilization process, most chemical processes need to be equipped with corresponding chemical plants,

and the corresponding reactions need to be carried out at a specific temperature range, so a large amount of ash is required to maintain a constant temperature, which makes some direct utilization technology of TEHA require larger reactor volume, larger floor space, and higher investment cost.

Some researchers have performed optimization studies of the traditional method of physical dry heat recovery. To investigate the effect of gas flow rate and ash mass flow rate on the rate of heat recovery, Wang *et al.* (2020) simulated the fragmentation behavior of the ash during the pelletization process by gas quench and improved the nozzle on this basis and concluded that the rate of heat recovery could be improved by as much as 18.6% with the optimal parameters. Following numerical analysis of the motion of ash particles and heat transfer characteristics in the gas quench method, Fan and Wang (2019) found that the addition of water vapor spray to the cooling gas stream could noticeably improve the cooling effect of the ash particles and the rate of heat recovery could be increased by up to 5%. Improving the gas flow rate and the addition of spray are generally beneficial because they can improve the total amount of heat transfer medium per unit time, but these operations themselves increase the energy consumption even further.

For the development of new processes, Tan *et al.* (2018) proposed a combined centrifugal-air quenching granulation technology for the membrane splitting mode of high temperature ash during centrifugation and used it to establish a fluidized bed-based ash waste heat recovery system. The waste heat from the ash in this system is absorbed partly by the water-cooled wall around the granulator and partly by the cold air in the fluidized bed. Based on theoretical analysis, the resulting heat recovery can be over 70%. Liao *et al.* (2019) proposed a combined cold-heat-electric system based on the organic Rankine cycle to realize the waste heat recovery of ash from coal fired power stations. Increasing the turbine inlet temperature superheat is considered beneficial in improving system exergy efficiency, but increasing the temperature of the condenser reduces the thermal efficiency of the system. These studies provide new ideas for the recovery of waste heat from ash, but their economics and applicability require further analysis given the complexity of the process.

Methods of Indirect Utilization

The indirect method is the indirect transfer of the energy possessed by high-temperature ash to the heated medium through heat exchangers, *etc.*, and the isolation of the ash from the medium, such as water, through the pipe wall.

Table 4. Technical Situation of TEHA Indirect Utilization

Researcher/ Institution	Method	Heat Transfer Medium	Thermal Efficiency (%)	Insufficiency
Kawasaki Steel	Mechanical agitation	Water	59	Large slag particle size and low heat recovery efficiency
Sumitomo Metal	Mechanical agitation	Water	50	Large slag particle size and low heat recovery efficiency
JFE (formerly Nippon Kokan KK)	Dry slag- granulation using twin drums	Organic liquid	40	Unstable system operation and low heat recovery efficiency
Mitsubishi Heavy Industries and JFE	Wind quenching	Air, Water	41	High energy consumption, and low heat recovery efficiency

However, because of the low thermal efficiency, there is less relevant research, and it is currently mainly used in the granulation stage of liquid high-temperature ash. The research on the indirect utilization of waste heat technology for high temperature ash is shown in Table 4 (Wang *et al.* 2014).

As can be observed in Table 4, more comprehensive studies of TEUHA indirectly technology were conducted in Japan in the early days. However, the mechanical agitation method and the twin drums method have failed to achieve commercial application of these technologies because of the serious phenomenon of mechanical wear and tear, poor system stability, and low quality of ash particles. The wind-quenching method suffers from high energy consumption and low profitability. Although the indirect utilization method avoids the pollution of the heat exchange medium by the ash, the stored heat of heat exchanger cannot be utilized, and as the number of heat transfer increases, the heat loss in the whole process keeps increasing and the energy quality decreases with each step. As a result, the thermal efficiency regarding the indirect type of TEUHA method is only in the range of 41% to 59%, and the exergy efficiency is generally low.

Comprehensive Comparison and Analysis of TEUHA Technology

The current process flow of TEUHA is shown in Fig. 2.

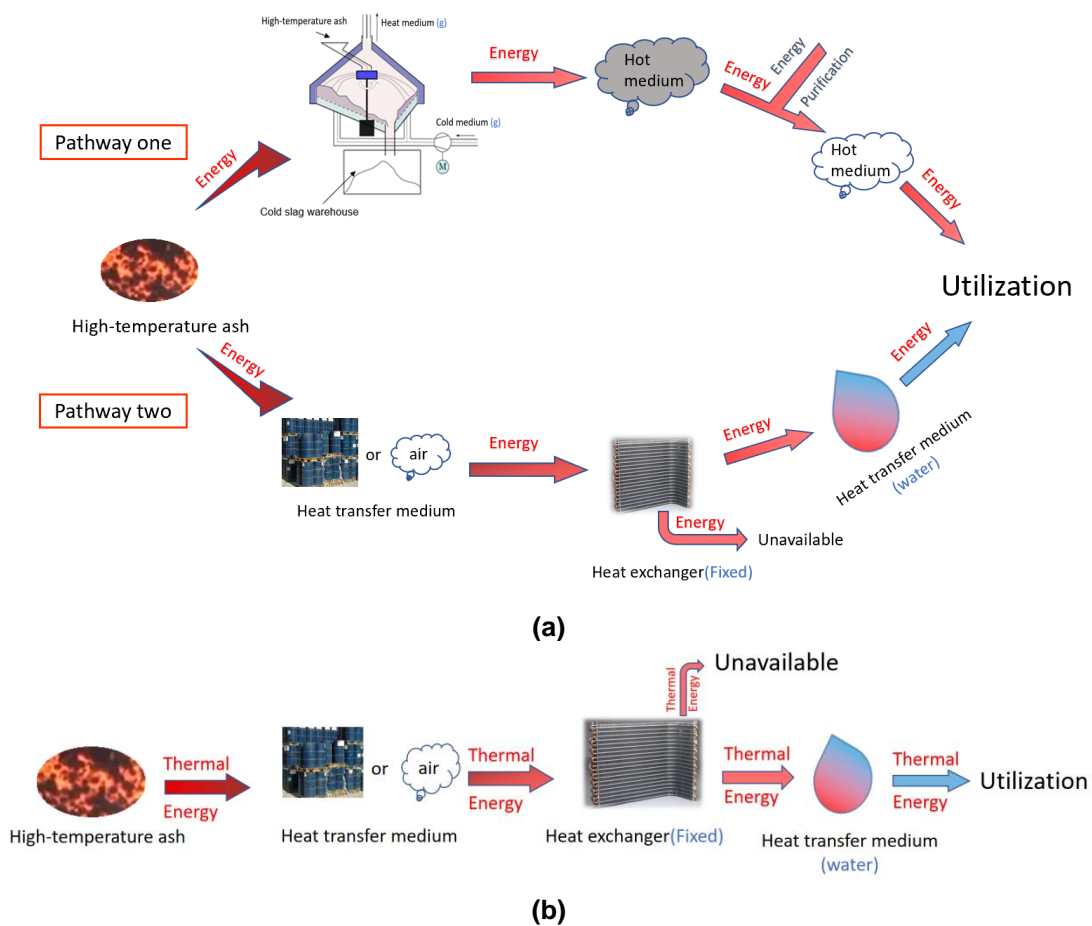


Fig. 2. The process flow diagram of TEUHA: (a) The process flow diagram of TEUHA directly; (b) The process flow diagram of TUEHA indirectly

Figure 2(a) shows the TEUHA directly benefiting from the use of ash waste heat for the direct heating of media, such as air or the direct energy supply for chemical reactions, has a higher thermal efficiency. However, the heat carriers obtained from the existing direct utilization process are mostly gaseous, which will be mixed with impurities in the process of contact with the ash, requiring additional energy to purify the heat carriers. Specifically, in some gasification reactions of biomass pyrolysis, not only is additional energy input required to separate and purify the syngas generated, but the mixture of tar produced by the reaction and the cold ash may also have an impact on the further utilization of the cold ash. Figure 2(b) shows that the TEUHA process first transfers the waste heat of ash to the first heat exchange medium, then it transfers the heat from the first heat exchange medium to the second heat exchange medium through a heat exchanger. Its overall thermal efficiency is lower than that of the direct utilization method because of the multi-stage heat transfer phenomenon of the indirect method and the fact that the hot material's own heat cannot be used directly. Thus, it is of great significance to realize efficient recovery and TEUHA by integrating the advantages and disadvantages of direct and indirect utilization of TEHA, simplifying the process on the premise of direct heat transfer, and using the medium with high heat storage capacity to recover ash waste heat while avoiding the pollution of ash to materials.

Applications of Phase-change Materials

Phase-change materials have been widely used in industrial waste heat recovery, solar thermal utilization, and power plant peaking because of their advantages of high energy storage density, long heat storage time, and controllable phase-change temperature (Nazir *et al.* 2019; Mahian *et al.* 2021).

Table 5. The Application of Phase-change Materials in Waste Heat Recovery

Reference	Phase-change Material	Heat Source	Temperatures of Phase-change (°C)
Akram <i>et al.</i> (2018)	Paraffin Wax	The surface of cement kiln	68
Zhang <i>et al.</i> (2017)	Acetamide /Expanded Graphite	The off gas emitted by highly concentrated photovoltaic module	71.50
Dal Magro <i>et al.</i> (2017)	Al-Si Alloy	The off gas emitted by steel industry	576
Soni <i>et al.</i> (2018)	Cu/Erythritol	Industrial waste heat at low temperature (< 200 °C)	100 - 150
Valenti <i>et al.</i> (2020)	Paraffin Wax	The off gas emitted by industrial laundry	40 - 130
Wang <i>et al.</i> (2022)	Al-Si/ SiCN	Industrial waste heat at high temperature (> 500 °C)	571 - 574
Anagnostopoulos <i>et al.</i> (2021)	Solar salt/ Red mud	Industrial waste heat at medium temperature (≤ 400 °C)	200 - 250
Kawaguchi <i>et al.</i> (2020)	Zn-Al Alloy	Industrial waste heat at medium-high temperature (400 °C to 500 °C)	437 - 512
Li <i>et al.</i> (2021)	Al/Al ₂ O ₃	Industrial waste heat, high temperature (> 600 °C)	624 - 654

These attributes not only can effectively solve the problem of new energy volatility, but they also have important significance in accelerating the low carbon transition of the energy system and will occupy an important position in future energy supply and consumption. The application of phase-change materials in waste heat recovery is described in Table 5.

As shown in Table 5, the development of phase-change materials has gradually shifted to the direction of composite phase-change materials because of the problems of subcooling and low thermal conductivity of single phase-change materials. To solve the problems of indefiniteness and easy leakage during phase-change materials, the development of composite phase-change materials has focused on shaped phase-change materials. It can also be seen that phase-change materials can play a good transit role in waste heat recovery and utilization but are mostly used in the recovery of waste heat from exhaust gases or as a heat transfer fluid within heat exchangers. This is because of the greater susceptibility of conventional formed phase-change materials to contamination in the environment surrounding the ash, as well as the difficulty of subsequent separation and reuse after mixing with ash. Through combining the current situation of TEUHA and phase-change heat storage and making the phase-change material after metal encapsulation as a phase-change heat carrier directly mixing with solid high-temperature ash to recover the waste heat, can meet the current demand of TEUHA processing. A brief description of the concept of using a phase-change heat carrier to recover TEHA is shown in Fig. 3.

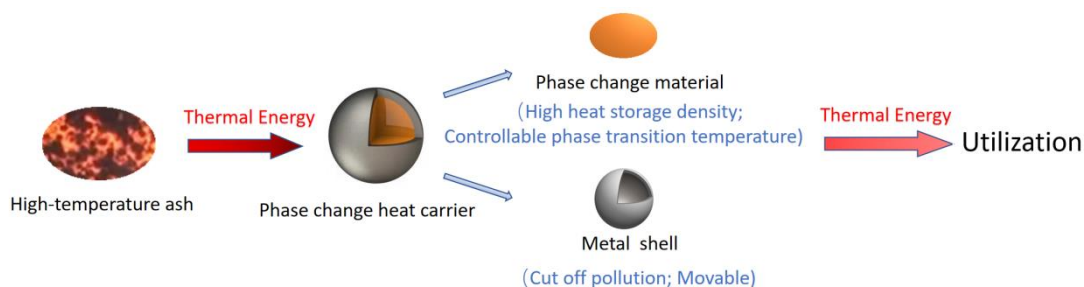


Fig. 3. The conceptual diagram of using phase-change heat carrier to recover TEHA

As can be observed in Fig. 3, the “metal shell + phase-change material” model can not only avoid the pollution of the heated medium by the ash, but it also can achieve a large amount of storage of TEHA while enhancing the heat transfer effect. Meanwhile, for ash at different temperatures, materials with phase-change temperature matching can be selected to recover waste heat. For example, alloy phase-change materials can be used to recover TEHA above 400 °C (Kawaguchi *et al.* 2020). After the heat transfer is complete, organic phase-change materials such as stearic acid can be used to recover the residual TEHA (Chen *et al.* 2013), realizing the gradual recovery of the overall TEHA. Based on those, an experiment was carried out to recover the heat energy of ash ($T \leq 300^\circ\text{C}$) by using heat carrier with stearic acid (melting point of 68 °C, phase-change enthalpy of 200 J/g, purchased from Macklin Co. Ltd., Shanghai, China) as the core material of heat carrier. The system is shown in Fig. 4. In this experiment, after the heat carrier and ash were mixed and heat exchanged in the stirring device according to a certain mass ratio, the heat carrier was screened out by magnetic adsorption. The effects of mixing mass ratio (spherical heat carrier: ash) and heat source temperature (ash temperature) on the recovery of waste heat were studied. The specific process and calculation formula are consistent with the study of

Li *et al.* (2022). Figure 5 shows the recovery efficiency of waste heat in the process of heat transfer between spherical heat carrier and biomass ash under different parameters. The results show that the recovery rate of waste heat can reach 46% under the optimal working conditions. Generally, the ash discharge temperature of ash is far higher than 300 °C. If suitable phase-change material is selected to recover the heat above 300 °C, it is possible to obtain a higher recovery of waste heat. In addition, the heat storage time of phase-change materials is generally within 10 h, which provides the possibility of long-distance heat transfer. After the heat carrier recovers the heat energy of the ash, it can be transported to the cold end for heat release, such as drying. Because the heat source used is almost cost-free waste heat, this can effectively solve the high energy consumption problem existing in the drying process of biomass, sludge, and other substances (Deng *et al.* 2021). Moreover, the direct contact heating of the cold source using heat carrier can also ensure the efficient use of thermal energy.



Fig. 4. The system of recovering heat energy by phase-change heat carrier

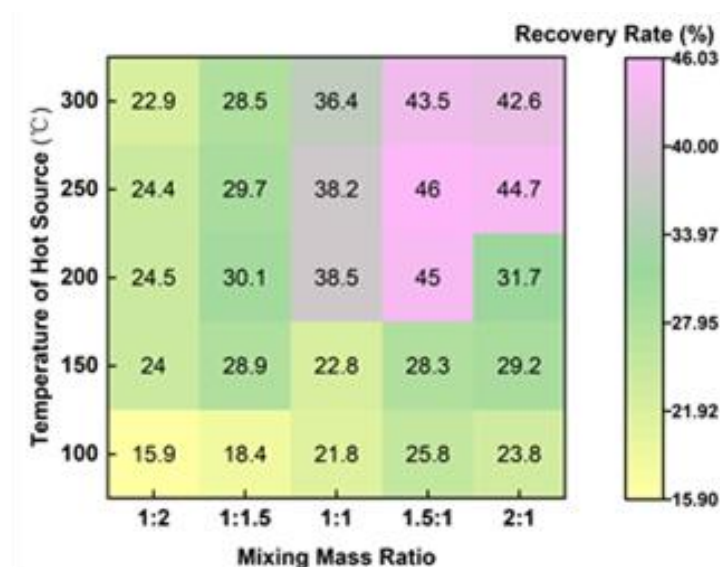


Fig. 5. Waste heat recovery rate under different parameters

CONCLUSIONS

As a high-temperature waste heat resource, the recycling of thermal energy of high-temperature ash (TEHA) can produce high economic and environmental benefits, and it is an important technical way to achieve the goal of reducing peak carbon dioxide emissions.

1. According to Carnot's theorem, the recovery of TEHA of China from the coal industry alone is expected to save 4.65×10^8 GJ of energy per year nationwide, which is equivalent to 15.87 Mt of standard coal.
2. At present, TEHA recovery methods are mainly divided into two types: direct utilization method and indirect utilization method. The thermal efficiency of direct utilization method is between 12% and 92%, while the thermal efficiency of indirect utilization method is between 41% and 59%. From the perspective of energy recovery rate, the direct utilization method has more application value than the indirect utilization method.
3. Although the existing direct utilization method generally has higher thermal efficiency, it has strong limitations and suffers from the phenomenon that the heat carrier is easily polluted by the ash. While the indirect utilization method can effectively solve the pollution phenomenon, the heat loss is serious. Therefore, a simple and efficient TEUHA directly process combining the advantages of the existing direct and indirect utilization methods has become an urgent need.
4. After determining the matching relationship between the phase-change temperature of the phase-change material and the working temperature, the corresponding material is encapsulated as a phase-change heat carrier and directly mixed with high temperature solid ash. This approach not only can avoid the pollution of the heat carrier by the ash, but it also can increase the energy recovery efficiency. In addition, due to the excellent thermal insulation ability of phase-change materials, it is not only feasible to use heat carriers to recover ash heat energy and then dry biomass, but also possible to achieve efficient utilization of heat energy.

REFERENCES CITED

- Agrela, F., Cabrera, M., Morales, M. M., Zamorano, M., and Alshaaer, M. (2019). "Biomass fly ash and biomass bottom ash," in: *New Trends in Eco-Efficient and Recycled Concrete*, Woodhead Publishing, Sawston, UK, pp. 23-58.
- Akram, N., Moazzam, U., Ali, M., Ajaz, A., Saleem, A., Kilic, M., and Mobeen, A. (2018). "Improved waste heat recovery through surface of kiln using phase-change material," *Thermal Science* 22(2), 1089-1098. DOI: 10.2298/tsci170611301a
- Al-Kutti, W., Saiful Islam, A. B. M., and Nasir, M. (2019). "Potential use of date palm ash in cement-based materials," *Journal of King Saud University - Engineering Sciences* 31(1), 26-31. DOI: 10.1016/j.jksues.2017.01.004
- Anagnostopoulos, A., Navarro, M. E., Stefanidou, M., Ding, Y., and Gaidajis, G. (2021). "Red mud-molten salt composites for medium-high temperature thermal energy storage and waste heat recovery applications," *Journal of Hazardous Materials* 413, Article ID 125407. DOI: 10.1016/j.jhazmat.2021.125407

- Barati, M., Esfahani, S., and Utigard, T. A. (2011). "Energy recovery from high temperature slags," *Energy* 36(9), 5440-5449. DOI: 10.1016/j.energy.2011.07.007
- Barati, M., and Jahanshahi, S. (2019). "Granulation and heat recovery from metallurgical slags," *Journal of Sustainable Metallurgy* 6(2), 191-206. DOI: 10.1007/s40831-019-00256-4
- Berra, M., Mangialardi, T., and Paolini, A. E. (2015). "Reuse of woody biomass fly ash in cement-based materials," *Construction and Building Materials* 76, 286-296. DOI: 10.1016/j.conbuildmat.2014.11.052
- Chen, Z., Cao, L., Shan, F., and Fang, G.Y. (2013). "Preparation and characteristics of microencapsulated stearic acid as composite thermal energy storage material in buildings," *Energy & Buildings* 2013, 62: 469-474. DOI: 10.1016/j.enbuild.2013.03.025
- Cui, Y., and Wang, D. M. (2019). "Effects of water on pore structure and thermal conductivity of fly ash-based foam geopolymers," *Advances in Materials Science and Engineering* 2019, 1-10. DOI: 10.1155/2019/3202794
- Dai, X., Qi, Y., and Zhang, C. (2008). "Development of molten slag dry granulation and heat recovery in steel industry," *Journal of Iron and Steel Research* 20(7), 1-6. DOI: 10.13228/j.boyuan.issn1001-0963.2008.07.011 (In Chinese)
- Dal Magro, F., Savino, S., Meneghetti, A., and Nardin, G. (2017). "Coupling waste heat extraction by phase-change materials with superheated steam generation in the steel industry," *Energy* 137, 1107-1118. DOI: 10.1016/j.energy.2017.04.051
- Das, B., Prakash, S., Reddy, P. S. R., and Misra, V. N. (2007). "An overview of utilization of slag and sludge from steel industries," *Resources, Conservation and Recycling* 50(1), 40-57. DOI: 10.1016/j.resconrec.2006.05.008
- Duan, W. J., Li, P., Lei, W., Chen, W., Yu, Q. B., Wang, K., and Qin, Q. (2015). "Thermodynamic analysis of blast furnace slag waste heat-recovery system integrated with coal gasification," *JOM* 67(5), 1079-1085. DOI: 10.1007/s11837-015-1389-5
- Fan, Y. M., and Wang, J. F. (2019). "Numerical analysis on dynamics and heat transfer progress of a granulated molten slag particle by gas," *The Chinese Journal of Process Engineering* 19(4), 685-692. DOI: 10.12034/j.issn.1009-606X.218292
- Feng, Y. H., Zhang, Z., Qiu, L., and Zhang, X. X. (2019). "Heat recovery process modelling of semi-molten blast furnace slag in a moving bed using XDEM," *Energy* 186, Article ID 115876. DOI: 10.1016/j.energy.2019.115876
- Hu, X., Yuan, X., Wang, J., and Luo, S. (2018). "Experimental research on pyrolysis of scrapped tires by heat in blast furnace slag means of waste," *Modern Chemical Industry* 38(1), 162-164. DOI: 10.16606/j.cnki.issn0253-4320.2018.01.038 (In Chinese)
- Ishaq, H., Dincer, I., and Naterer, G. F. (2019). "Exergy and cost analyses of waste heat recovery from furnace cement slag for clean hydrogen production," *Energy* 172, 1243-1253. DOI: 10.1016/j.energy.2019.02.026
- Kasai, E., Kitajima, T., and Akiyama, T. (1997). "Rate of methane-steam reforming reaction on the surface of molten BF slag: For heat recovery from molten slag by using a chemical reaction," *ISIJ International* 37(10), 1031-1036. DOI: 10.2355/isijinternational.37.1031
- Kawaguchi, T., Sakai, H., Sheng, N., Kurniawan, A., and Nomura, T. (2020). "Microencapsulation of Zn-Al alloy as a new phase-change material for middle-high-temperature thermal energy storage applications," *Applied Energy* 276, Article ID 115487. DOI: 10.1016/j.apenergy.2020.115487.

- Khoo, Y. C., Johari, I., and Ahmad, Z. A. (2013). "Influence of rice husk ash on the engineering properties of fired-clay brick," *Advanced Materials Research* 795, 14-18. DOI: 10.4028/www.scientific.net/amr.795.14
- Li, Q., Ma, X., Zhang, X., Ma, J., Liu, J., Hu, X., and Lan, Y. (2021). "Preparation and properties of Al/Al₂O₃ core-shell microencapsulated phase-change material," *Journal of Alloys and Compounds* 888, Article ID 161606. DOI: 10.1016/j.jallcom.2021.161606
- Liao, G., Liu, L., Zhang, F., Jiaqiang, E., and Chen, J. (2019). "A novel combined cooling-heating and power (CCHP) system integrated organic Rankine cycle for waste heat recovery of bottom slag in coal-fired plants," *Energy Conversion and Management* 186, 380-392. DOI: 10.1016/j.enconman.2019.02.072
- Luo, S., and Feng, Y. (2016). "The production of hydrogen-rich gas by wet sludge pyrolysis using waste heat from blast-furnace slag," *Energy* 113, 845-851. DOI: 10.1016/j.energy.2016.07.130
- Luo, S., Zhou, Y., and Yi, C. (2012). "Hydrogen-rich gas production from biomass catalytic gasification using hot blast furnace slag as heat carrier and catalyst in moving-bed reactor," *International Journal of Hydrogen Energy* 37(20), 15081-15085. DOI: 10.1016/j.ijhydene.2012.07.105
- Mahian, O., Ghafarian, S., Sarrafha, H., Kasaeian, A., Yousefi, H., and Yan, W. M. (2021). "Phase-change materials in solar photovoltaics applied in buildings: An overview," *Solar Energy* 224, 569-592. DOI: 10.1016/j.solener.2021.06.010
- Mao, Y., Qv, Y., and Wang, Z. (2013). "Review of blast furnace molten slag treatment and sensible heat recovery technologies," *Shanghai Metals* 35(3), 45-50. DOI: 10.3969/j.issn.1001-7208.201 (In Chinese)
- Men, Y. Y., Liu, X. H., Zhang, T., Xu, X., and Jiang, Y. (2019). "Novel flue gas waste heat recovery system equipped with enthalpy wheel," *Energy Conversion and Management* 196, 649-663. DOI: 10.1016/j.enconman.2019.06.026
- Mizuochi, T., Akiyama, T., Shimada, T., Kasai, E., and Yagi, J. (2001). "Feasibility of rotary cup atomizer for slag granulation," *ISIJ International* 41(12), 1423-1428. DOI: 10.2355/isijinternational.41.142
- National Bureau of Statistics (2021). "Statistical Communiqué of the People's Republic of China on the 2020 National Economic and Social Development," (http://www.stats.gov.cn/tjsj/zxfb/202102/t20210227_1814154.html), Accessed 21 March 2022.
- National Energy Information Platform (2020). "The development status and trend analysis of China's coal industry in 2019 De-capacity has become a trend," (<https://baijiahao.baidu.com/s?id=1672898123040020115&wfr=spider&for=pc>), Accessed 21 March 2022.
- Nazir, H., Batool, M., Bolivar Osorio, F. J., Isaza-Ruiz, M., Xu, X., Vignarooban, K., Phelan, P., Inamuddin, and Kannan, A. M. (2019). "Recent developments in phase-change materials for energy storage applications: A review," *International Journal of Heat and Mass Transfer* 129, 491-523. DOI: 10.1016/j.ijheatmasstransfer.2018
- Ouyang, T. C., Xu, J. S., Qin, P. J., and Chen, L. (2022). "Utilizing flue gas low-grade waste heat and furnace excess heat to produce syngas and sulfuric acid recovery in coal-fired power plant," *Energy* 258, Article ID 124825. DOI: 10.1016/j.energy.2022.124825

- Purwanto, H., and Akiyama, T. (2006). "Hydrogen production from biogas using hot slag," *International Journal of Hydrogen Energy* 31(4), 491-495. DOI: 10.1016/j.ijhydene.2005.04.021
- Qi, X., Song, G., Song, W., Yang, S., and Lu, Q. (2016). "Effects of wall temperature on slagging and ash deposition of Zhundong coal during circulating fluidized bed gasification," *Applied Thermal Engineering* 106, 1127-1135. DOI: 10.1016/j.applthermaleng.2016.06
- Qi, Y., Gan, L., Wang, H., Zhang, X., and Yan, D. (2012). "Development process and trend of the waste heat recovery technique of the molten blast furnace slab," *Iron Steel* 47(4), 1-8. DOI: 10.13228/j.boyuan.issn0449-749x.2012.04.012 (In Chinese)
- Qin, Y., Lv, X., Bai, C., Qiu, G., and Chen, P. (2012). "Waste heat recovery from blast furnace slag by chemical reactions," *JOM* 64(8), 997-1001. DOI: 10.1007/s11837-012-0392-3
- Qiu, L., Sang, D., Feng, Y., Gong, Y., and Zhang, X. (2019). "Optimization analysis of waste heat recovery in blast furnaceslag fluidized bed," *Journal of Engineering Thermophysics* 40(5), 1086-1094. (In Chinese)
- Qudoos, A., Kim, H. G., Atta Ur, R., Jeon, I. K., and Ryou, J.-S. (2019). "Influence of the particle size of wheat straw ash on the microstructure of the interfacial transition zone," *Powder Technology* 352, 453-461. DOI: 10.1016/j.powtec.2019.05.005
- Soni, V., Kumar, A., and Jain, V. K. (2018). "Performance evaluation of nano-enhanced phase-change materials during discharge stage in waste heat recovery," *Renewable Energy* 127, 587-601. DOI: 10.1016/j.renene.2018.05.009
- Sun, Y., Zhang, Z., Liu, L., and Wang, X. (2015). "Heat recovery from high temperature slags: A review of chemical methods," *Energies* 8(3), 1917-1935. DOI: 10.3390/en8031917
- Sun, Y., Zhang, Z., Liu, L., and Wang, X. (2015). "Two-stage high temperature sludge gasification using the waste heat from hot blast furnace slags," *Bioresource Technology* 198, 364-371. DOI: 10.1016/j.biortech.2015.09.051
- Tan, Y., Wang, H., Zhu, X., Lv, Y. W., Ding, Y. D., and Liao, Q. (2020). "Film fragmentation mode: The most suitable way for centrifugal granulation of large flow rate molten blast slag towards high-efficiency waste heat recovery for industrialization," *Applied Energy* 276, Article ID 115454. DOI: 10.1016/j.apenergy.2020.115454
- Tan, Y., Zhu, X., He, X. Y., Ding, B., Wang, H., Liao, Q., and Li, H. (2018). "Granulation characteristics of molten blast furnace slag by hybrid centrifugal-air blast technique," *Powder Technology* 323, 176-185. DOI: 10.1016/j.powtec.2017.09.040
- Thomas, B. S., Yang, J., Mo, K. H., Abdalla, J. A., Hawileh, R. A., and Ariyachandra, E. (2021). "Biomass ashes from agricultural wastes as supplementary cementitious materials or aggregate replacement in cement/geopolymer concrete: A comprehensive review," *Journal of Building Engineering* 40, Article ID 102332. DOI: 10.1016/j.jobe.2021.102332
- Thy, P., Jenkins, B., Grundvig, S., Shiraki, R., and Lesher, C. (2006). "High temperature elemental losses and mineralogical changes in common biomass ashes," *Fuel* 85(5-6), 783-795. DOI: 10.1016/j.fuel.2005.08.020
- Umamaheswaran, K., and Batra, V. S. (2008). "Physico-chemical characterisation of Indian biomass ashes," *Fuel* 87(6), 628-638. DOI: 10.1016/j.fuel.2007.05.045

- Valenti, G., Bonacina, C. N., and Bamoshmoosh, A. (2020). "Optimal cascade phase-change regenerator for waste heat recovery in a batch industrial dryer," *Case Studies in Thermal Engineering* 22, Article ID 100734. DOI: 10.1016/j.csite.2020.100734
- Vassilev, S. V., Baxterm, D., Andersen, L. K., and Vassileva, C. G. (2013). "An overview of the composition and application of biomass ash," *Fuel* 105, 19-39. DOI: 10.1016/j.fuel.2012.10.001
- Wang, B., Wang, X., Yuan, Y., and Zhou, Q. (2014). "Advances in the study of the blast furnace slag waste heat recovery technologies," *Journal of Engineering for Thermal Energy and Power* 29(2), 113-120. DOI: 10.16146/j.cnki.rndlgc.2014.02.001 (In Chinese)
- Wang, C., He, B., Yan, L., Pei, X., and Chen, S. (2014). "Thermodynamic analysis of a low-pressure economizer based waste heat recovery system for a coal-fired power plant," *Energy* 65, 80-90. DOI: 10.1016/j.energy.2013.11.084
- Wang, H., Wu, J. J., Zhu, X., Liao, Q., and Zhao, L. (2016). "Energy–environment–economy evaluations of commercial scale systems for blast furnace slag treatment: Dry slag granulation vs. water quenching," *Applied Energy* 171, 314-324. DOI: 10.1016/j.apenergy.2016.03.079
- Wang, K., Zhang, T., Wang, T., Xu, C., Ye, F., and Liao, Z. (2022). "Microencapsulation of high temperature metallic phase-change materials with SiCN shell," *Chemical Engineering Journal* 436, article ID 135054. DOI: 10.1016/j.cej.2022.135054
- Wang, L. L., Zhang, Y. Z., Long, Y., and Ke, H. B. (2020). "Simulation of primary breakup of molten slag in the gas quenching dry granulation process," *Applied Thermal Engineering* 181, Article ID 115850. DOI: 10.1016/j.applthermaleng.2020.115850
- Wang, W., Liu, X., and Zheng, Y. (2014). "Quantitative chemical composition determination and thermal analysis for typical biomass ashes in China," *Asia-Pacific Journal of Chemical Engineering* 9(5), 751-758. DOI: 10.1002/apj.1821
- Wu, J., Liu, Y., Zhang, X., Chen, R., and He, Q. (2020). "Experimental research on thermal conductivity of coal-fired boiler ash in thermal power plant," *Power & Energy* 41(5), 632-635. DOI: 10.11973/dlyny202005023 (In Chinese)
- Xiao, R., Chen, X., Wang, F., and Yu, G. (2011). "The physicochemical properties of different biomass ash," *Acta Energetica Solaris Sinica* 32(3), 364-369. DOI: 10.19912/j.0254-0096.2011.03.014 (In Chinese)
- Xie, H., Li, R., Wang, Z., Yao, X., and Yu, Q. (2019). "Hydrogen production of bio-oil steam reforming combining heat recovery of blast furnace slag: Thermodynamic analysis," *International Journal of Hydrogen Energy* 44(47), 25514-25523. DOI: 10.1016/j.ijhydene.2019.08.014
- Yao, X., Yu, Q., Xie, H., Duan, W., Han, Z., Liu, S., and Qin, Q. (2017). "The production of hydrogen through steam reforming of bio-oil model compounds recovering waste heat from blast furnace slag," *Journal of Thermal Analysis and Calorimetry* 131(3), 2951-2962. DOI: 10.1007/s10973-017-6804-4
- Zhang, H., Wang, H., Zhu, X., Qin, Y. J., Li, K., Chen, R., and Liao, Q. (2013). "A review of waste heat recovery technologies towards molten slag in steel industry," *Applied Energy* 112, 956-966. DOI: 10.1016/j.apenergy.2013.02.019
- Zhang, S., Wu, W., and Wang, S. (2017). "Integration highly concentrated photovoltaic module exhaust heat recovery system with adsorption air-conditioning module via phase-change materials," *Energy* 118, 1187-1197. DOI: 10.1016/j.energy.2016.10.139

- Zhao, L., Wang, H., Qing, S., and Liu, H. (2010). "Characteristics of gaseous product from municipal solid waste gasification with hot blast furnace slag," *Journal of Natural Gas Chemistry* 19(4), 403-408. DOI: 10.1016/s1003-9953(09)60087-6
- Zhao, Y., Zhao, C. Y., Markides, C. N., Wang, H., and Li, W. (2020). "Medium- and high-temperature latent and thermochemical heat storage using metals and metallic compounds as heat storage media: A technical review," *Applied Energy* 280, article ID 115950. DOI: 10.1016/j.apenergy.2020.115950
- Zhong, Z. Q., Chen, Y. Q., Fu, M. Y., Li, M. Z., Yang, K. S., Zeng, L. P., Liang, J., Ma, R. P., and Xie, Q. (2023). "Role of CO₂ geological storage in China's pledge to carbon peak by 2030 and carbon neutrality by 2060," *Energy* 272, article 127165. DOI: 10.1016/J.ENERGY.2023.127165

Article submitted: February 9, 2023; Peer review completed: April 8, 2023; Revised version received: May 18, 2023; Accepted: May 20, 2023; Published: May 24, 2023. DOI: 10.15376/biores.18.3.4866-4883