

Review

Heat Recovery from High Temperature Slags: A Review of Chemical Methods

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Abstract: Waste heat recovery from high temperature slags represents the latest potential way to remarkably reduce the energy consumption and CO₂ emissions of the steel industry. The molten slags, in the temperature range of 1723–1923 K, carry large amounts of high quality energy. However, the heat recovery from slags faces several fundamental challenges, including their low thermal conductivity, inside crystallization, and discontinuous availability. During past decades, various chemical methods have been exploited and performed including methane reforming, coal and biomass gasification, and direct compositional modification and utilization of slags. These methods effectively meet the challenges mentioned before and help integrate the steel industry with other industrial sectors. During the heat recovery using chemical methods, slags can act as not only heat carriers but also as catalysts and reactants, which expands the field of utilization of slags. Fuel gas production using the waste heat accounts for the main R&D trend, through which the thermal heat in the slag could be transformed into high quality chemical energy in the fuel gas. Moreover, these chemical methods should be extended to an industrial scale to realize their commercial application, which is the only way by which the substantial energy in the slags could be extracted, *i.e.*, amounting to 16 million tons of standard coal in China.

Keywords: high temperature slag; waste heat recovery; chemical methods; fuel gas production

1. Introduction

The steel industry is an energy-intensive and CO₂-intensive industry, consuming around 9% of total anthropogenic energy [1] and emitting one quarter of all industrial CO₂ into the atmosphere in the World [2]. Although numerous advanced technologies have been implemented, steel industry still faces a serious challenge of meeting the CO₂ targets when global emissions are cut to less than 50% of 2000 levels by 2050 [3]. The greenhouse gases (GHG) footprint and the material flows of steel industry have been mapped by several studies [2,4,5] and it has been pointed out that the present iron and steel sector is not environmentally sustainable. Fruehan *et al.* [6] have estimated the potential energy savings in the steel industry and found that there is an opportunity to further reduce the energy consumption by ~25%. The iron and steel sector could do a lot to contribute to sustainable development, and as reported by Bisio [7] and Barati *et al.* [8], high temperature (1723–1923 K) slags, which carry a substantial amount of high quality thermal energy, represent the largest undeveloped energy source in the steel industry.

At present, China remains the World's largest steel producer, and the output of pig iron and crude steel in China amounted to 660 million tons and 720 million tons, respectively, in 2012 [9]. For typical iron ore grades (60% to 66% iron), a blast furnace normally produces about 0.30 ton of blast furnace slag (BFS) per ton of pig iron produced and a steel furnace typically produces 0.10-0.15 ton of steel slag (SS) per ton of crude steel [10]. Using these ratios and data, it can be estimated that China's production of BFS and SS in 2012 was around 200 million tons and 110 million tons, respectively. These slags are exhausted in the temperature range of 1723-1923 K and accordingly, the total waste heat of these slags is more than 4.96×10^{19} J with the slag enthalpy of ~1.6 GJ per ton of slag [8,11], corresponding to around 16.5 million tons of standard coal. However, Cai *et al.* [12] have reported that in China the waste heat recovery ratio of high temperature slags is less than 2%, so there is a great potential for waste heat recovery.

Nowadays extensive traditional and advanced methods have been exploited and investigated to extract the waste heat of high temperature slags, which can mainly be divided into physical methods, chemical methods and direct electricity generation methods. As a traditional method, physical methods concentrate on the development of various granulation technologies through which the molten slags are granulated into small particles and the thermal heat in the slag is exchanged with a heat transfer medium (air, steam and phase change materials (PCM)). Many granulation methods have been exploited including the rotary cup atomizer (RCA) [13–16], rotary cylinder atomizer (RCLA) [17,18], air blasts [7,8,19] and so on. However, heat recovery by physical methods has not been realized in industrial applications [12,19], because of the fundamental constraints of heat recovery, *i.e.*, low thermal conductivity, a trend to easy crystallization, and the temperature-time discontinuity, which will be discussed in detail in this paper. Meanwhile, the method of direct electricity generation combined with heat recovery from slags has been proposed recently [8], through which the thermal energy could be exchanged and stored in the PCM [8,20] and utilized for electricity generation using the Seebeck effect.

On the other hand, heat recovery through chemical methods, which is reviewed and analyzed in this paper, shows some specific advantages to meet the constraints and has been an R&D hot spot lately. Conventionally, there were two kinds of chemical methods for heat recovery from hot slags. First, the traditional chemical reaction for syngas production was combined with the heat recovery from hot slags and a high value syngas containing CO, H₂ and CH₄ was obtained, which was especially significant with the declining fossil fuel supplies [1–3]. Second, the chemical compositions of the slags were modified by various additives and the material resources were directly recycled for extraction of valuable elements or slag wool production [19]. These foregoing chemical methods provided various possibilities of heat recovery from hot slags. The object of this paper is not only to summarize the fundamental constraints of heat recovery from high temperature slags and review these chemical methods exploited during past decades especially from viewpoint of thermodynamics possibility and kinetic mechanism but also to forecast possible promising routes in the future.

2. Challenges for Heat Recovery

As mentioned above, there are several constraints on heat recovery from slags, especially for BFS, *i.e.*, low thermal conductivity, their trend of easy crystallization, and temperature-time discontinuity, which make up the main challenges that restrict the industrial application of heat recovery from high temperature slags, as summarized in Table 1.

2.1. Low Thermal Conductivity

It is generally believed that the first challenge of heat recovery is the low thermal conductivity, especially of liquid slags, which increases the difficulty of extracting the heat from slags. Nishioka et al. [21] and Li et al. [22] have measured the thermal conductivity of solid slags using square-wave pulse heat method and hot strip method separately over 296–1196 K and they found that the thermal conductivity slightly increased from 1 to 3 W/(m K) with increasing temperature. The hot wire method has been proved a useful method to measure the thermal conductivity of liquid slags and Kang et al. [23] and Nagata et al. [24] have reported that thermal conductivity in slag melts ranges from 0.1 to 0.5 W/(m K). To explore the heat transfer modes, Yoshinaga et al. [25,26] have measured the temperature distribution inside the slags and it has been found that the temperature difference between the core and surface of a slag particle of 5 mm in diameter could exceed 473 K. Recently, Meng et al. [27] and Sun et al. [28] have computerized the temperature gradients of slags using numerical simulations and they found the similar results. The large temperature difference indicates that the temperature inside the slags falls slowly compared with that on the surface, thus leading to other problems, for example, inside crystallization phenomena, which accounts for another serious challenge in slag heat recovery. Because of the low thermal conductivity, the slags should be granulated into small particles with diameters of 3-5 mm [7,8] to extract the thermal heat and meanwhile the heat transfer medium should flowed through with a larger rate; thus the temperature of the medium could not reach a high level and subsequently this explains the low waste heat recovery efficiency achieved through physical methods [7,8,19].

Constraints	Details	Solutions	References				
Low thermal conductivity	1 W/(m K) for solid slags;	Dry granulation into	[7 9 21 26]				
	0.1 W/(m K) for liquid slags small particles/dr		[7,8,21-20]				
Easy crystallization trend	Large temperature difference \rightarrow	Small particles;	[7,8,29,30]				
	Easy inside crystallization trend	Water quenching					

Chemical methods:

Phase change materials

Table 1. Summary of the fundamental constraints of heat recovery.

Temperature discontinuity;

Production discontinuity

2.2. Crystallization Behaviors

Discontinuous availability

If the temperature of slags cannot fall rapidly, especially when the real cooling rate is smaller than the critical cooling rate, R_c , crystals will form in the slag melts and the value of slags will be reduced. R_c is a cooling rate larger than which crystallization does not occur and the least cooling rate to form pure glassy phases. Ryu *et al.* [29] and Kashiwaya *et al.* [30] have studied the crystallization behaviors of BFS and they found the critical cooling rate could be more than 10 K/s. Recently, Sun *et al.* [28] identified that the increasing Al₂O₃ content in the slags caused by the degradation of the iron core resulted in a larger critical cooling rate is hard to achieve and as a result, crystals could precipitate. As for the BFS, once crystals are formed in the slags, the obtained solid slags would show inherently weak hydraulic cementitious properties [10] and therefore are not useful raw materials for the cement industry. To confirm the effective conversion of thermal energy, the slag should be granulated into small droplets to increase the heat transfer surface area through various methods [7,8,19]. It is generally believed that slag granulation is the first step to extract sufficient waste heat from slags [7,8].

2.3. Discontinuous Availability

In addition to the basic properties of slags, such as low thermal conductivity and inside crystallization behaviors, the availability of heat from slags is discontinuous, from the point of view of temperature and time. From high temperature to low temperature, the thermal conductivity greatly changes [7,8,31], and as a result, the difficulties of heat recovery vary, which makes up the first discontinuity. Furthermore, if the liquid slag follows a cooling path with a small cooling rate, crystals could form inside the slag and therefore the physical properties of the slag including the thermal conductivity and viscosity would change greatly; accordingly the cooling path of the slag could be divided into at least three regions, *i.e.*, liquid region, crystallization region and solid region [32], which made up a great discontinuity of the heat recovery from slags. Besides, the molten slags are produced from steel factories intermittently [20] and if physical methods are used to generate electricity, the obtained electricity is not continuous, which will impact the power grid and accounts for another discontinuity of heat extraction, so the transformation from intermittently emitted heat of slags to a stable heat source is a significant challenge for heat recovery from molten slags, from the viewpoint of which, a chemical method is reasonable.

[7.8.20.31.32]

3. Chemical Reactions in Detail

In the past decade, numerous advanced chemical methods have been exploited to recover the waste heat of high temperature slags, amongst which the production of fuel gas has attracted increasing attention because of the rapid depletion of fossil fuel together with the substantial emissions of GHG. It was estimated that the decomposition of limestone, reforming of methane and gasification of carbon are the most promising ways based on thermodynamic calculations [33]. Furthermore, other chemical methods have been proposed and applied, including production of slag wool and selective crystallization and phase separation (SCPS). These methods could be chosen and employed depending on the individual purposes.

3.1. Fuel Gases Production

3.1.1. Methane Decomposing Reactions

The methane steam reforming reaction (MSR) is widely employed for hydrogen production and Ni-base catalysts are generally applied in this reaction [34,35]. The waste heat in the hot slags could be used to supply the heat for MSR and the hot slags could even act as effective catalysts for MSR, the concept of which was first proposed by Kasai *et al.* [36] in 1997, as shown in Figure 1. The waste heat of the hot slag was recovered by means of Equation (1) in the steam reformer; then the produced hot gases are cooled down to atmospheric temperature; after that heat was released through the reversible Equation (1) for steam production and the CH4 was meanwhile regenerated. After the concept was proposed, a series of MSR experiments were performed to verify the concept at 1473–1823 K [36,37]. The results indicated that the hot slags acted as not only a heat carrier but also an effective catalyst for MSR, similar to the Ni catalyst [38]. In addition, it was found that an increasing temperature and a high basicity (CaO/SiO₂) enhanced the MSR while the presence of sulfur and FeO in the slags gives rise to a higher reaction rate. Actually, sulfur and FeO are common components of BFS [39,40] and therefore the content of these components should be effectively controlled to confirm the efficiency of MSR:

$$CH_4 + H_2O = CO + 3H_2 \tag{1}$$

Then, a combined system was proposed and the economic feasibility was estimated in a further study [41], which consisted of a MSR system and a RCA system, as shown in Figure 2. Molten slag was first granulated using a RCA [13,14] and then a packed bed made up of granulated slag was used to conduct the MSR [36,37]. Heat recovery using the methane-steam reforming system required only 52 kg of medium per ton of crude steel. The reduction of carbon dioxide emission was about 25 kg per ton of crude steel. In addition, it was calculated that the cost benefits based on the steam reforming reaction amount to total US\$ 1945 million per year for discharged slag; in other words, this proposed system was economically feasible. Beside steam, CO₂ could be used as reforming agent of methane by means of Equation (2) [42,43], which was especially important from the viewpoint of carbon capture and storage (CCS) and meeting emission target. In 2006, Purwanto *et al.* [44] designed an experiment to investigate the possibility of decomposing methane-CO₂ mixture (biogas) at 973–1273 K. The slags

were first granulated into small particles using RCA and then used to perform the experiments in a packed bed. The results showed that substantially more H_2 was produced than CO and meanwhile the largest methane conversion achieved could be up to ~96% at 1173 K; most importantly, the catalytic effect of the BFS was identified because the obtained rate parameter and activation energy by kinetic calculations was similar to those seen when using Ni-base and metallic catalysts [43].



 $CH_4 + CO_2 = CO + 2H_2 \tag{2}$

Figure 1. Schematic diagram of the concept for methane-steam reforming reaction. Reprinted with permission from [36], copyright 1997 The Iron and Steel Institute of Japan.



Figure 2. Proposed heat recovery concept comprising RCA system and MSR system. Reprinted with permission from [41], copyright 2004 The Iron and Steel Institute of Japan.

3.1.2. Pyrolysis and Gasification of Coal

Like methane reforming, coal gasification is a common industrial reaction for CO and H₂ production [45,46] and the obtained syngas could be further applied as a material for the chemical engineering industry. The thermal heat required for gasification was supplied by partial combustion of the feed coal, from the point of which the coal gasification reaction could be combined with the recovery of sensible heat of BFS. In 2004, Liu et al. [47] promoted this concept; similar to MSR [41], this system was mainly composed of a RCA system and a coal gasification system. To explore this concept, Li et al. [48–50] performed a series of experiments using the agent CO₂. It was found that this method was effective because of the wide adaptability on coal samples and granularities and the catalytic effect of hot slags was also demonstrated because of the decreasing activation energy. Moreover, the coal/CO₂ gasification followed various Avrami-Erofeev models and the added slags changed the specific kinetic models. The CO₂ used in coal gasification could be replaced by the waste gas generated from the steel industry [51], which was expected to show special advantage of CCS and emission reduction in the steel industry. Additionally, a synergistic system was proposed, which involved five operational processes including a molten slag gasifier, RCA apparatus, granules slag gasifier, boiler and heat exchanger. Meanwhile, steam was also generally used as the gasifying agent for coal gasification [46,52], and in a further study, Duan et al. [53] calculated the thermodynamics of coal steam gasification using hot slags through a HSC chemistry software based on the Gibbs free energy minimization approach. They found that the optimum temperature was 1048 K, and atmospheric pressure and increasing basicity showed a positive effect on hydrogen production.

Recently, other coal treatment methods including coal pyrolysis have been further exploited. Shatokha et al. [54] developed a heat treatment method using brown and sub-bituminous coals mixed with BFS to generate char. The more porous chars were obtained by charring in contact with slag; additionally, the combustion tests indicated that the char with slag showed a higher volatile ignition temperature. This study proved that the slags could not only act as good heat carrier but also change the properties of the expected product, which should be considered for a real industrial process. It is generally believed that the pyrolysis process included the volatile release, tar decomposition and char formation [55,56]. Cabyono et al. [57] investigated the effect of SS on tar reforming during coal pyrolysis at 773–1173 K and they found that slag has a good activity for decomposing tar into the gas phase because of the oxides (CaO, FeO and Al₂O₃) in the slag. The metal oxides in the slags could prevent the formation of stable chemical structures in hydrocarbons and speed up hydrocarbon degradation. In addition, an integrated industrial system was proposed where the saved energy was used in the steel industry. The produced char or coke was used in the blast furnace process and meanwhile the high carbon content of SS could be utilized as a supplementary fuel to reduce coke-breeze usage. It was calculated that this proposed system offered an energy-saving benefit of 103 MJ/ton steel and a 6% mass reduction in coke-breeze usage in the steelmaking industry.

3.1.3. Pyrolysis and Gasification of Solid Wastes

With the continuous urbanization in China, large amounts of solid wastes are discharged, the timely and efficient disposal of which has become a serious environmental issue [58,59]. The feasibility of

municipal solid waste (MSW) gasification using hot slag was explored at 873–1173 K [60] and it was found that the BFS acted as the catalyst and the heat carrier, which promoted the gasification reactivity of MSW. Qin *et al.* proposed a new technique to recover the heat of slags for treatment of an individual waste namely waste printed circuit boards (PCB) [61]. This method combined a rotary multi-nozzle cup atomizer (RMCA) system and a PCB pyrolysis system to form combustible gas, as displayed in Figure 3. The pyrolysis reaction occurred in the temperature range of 873–1173 K and the main gaseous products were CO, H₂, C_mH_n, and CH₄. In addition, the residues after pyrolysis were used for cement production and precious metal recovery. However, the highest heat recovery ratio achieved was 12% because the contact between the hot slag and the PCB powder was poor and



Figure 3. Schematic of PCB pyrolysis using hot slags. Reprinted with permission from [61], copyright 2012 Springer Science + Business Media.

3.1.4. Pyrolysis and Gasification of Biomass

Biomass is a kind of CO₂-neutral resource, the gasification and pyrolysis of which have been widely used for syngas production [62,63]. The sensible heat could be utilized to supply the heat for the thermal chemical processes of biomass. In 2012, Luo *et al.* proposed a method for hydrogen-rich gas production from biomass catalytic gasification using hot BFS at 1073–1473 K [64]. A moving-bed reactor was designed and the results showed that BFS demonstrated good catalytic performance in improving tar cracking, enhancing char gasification and reforming of hydrocarbons; higher BFS temperature and smaller particles size can produce more light gases, less char and condensate. Using a similar experimental system, biomass pyrolysis using hot slags for bio-oil production was investigated at 773–1023 K [65]. It was found that an increase in slag particle size and biomass particle size decreased the production of bio-oil because of the change of heat transfer between slag particle and biomass particles. Therefore, the particle size should be reasonably controlled with a view to optimizing heat transfer. As the gasification temperature was 1473 K, the gas yield and H₂ content achieved could be up to 1.28 N m³/kg and 46.54%, respectively. However, from the viewpoint of material recycling of slags, the gasification should be less than 1173 K [32], and therefore, recently

Sun *et al.* proposed an integrated method to use the waste heat of BFS, *i.e.*, low temperature biomass gasification (523–773 K) [66]. They found that the kinetic mechanism of biomass gasification changed from an Avrami-Erofeev model to a three-dimensional diffusion model because of the addition of slag. Most importantly, an industrial prototype plant was proposed comprising multiple systems including the steel industry, the cement industry and the agriculture, through which the potential of energy saving and emission reduction were 19.1 million tons of standard coal and 69.9 million tons of CO₂, respectively.

3.1.5. Reduction of the Slag Compositions

In addition with heat carrier and catalyst, high temperature slags could act as reactants in some chemical reactions to produce syngas due to the individual components in the slags. Syngas indeed is the product of reduction reactions where H₂O or CO₂ are reduced by different agents, CH₄, carbon (coal), or the effective components in the slags. The latter is discussed in this section. The steam-iron process is one of the traditional methods of producing hydrogen [67], during which the main reaction was that FeO or Fe was oxidized by steam to form magnetite and hydrogen. Matsuura et al. [68] have calculated the generation of H₂ gas by reaction between FeO in SS and steam by means of Equation (3) and it was found that an increase in introduced gas temperature, basicity and FeO content in slag could improve the amount of H₂ production. In 2012, Sato et al. [69] designed an experimental apparatus to realize this reaction. The reaction at 1723 K indicated that an increase of FeO content and basicity enhanced the production of H₂, which was consistent with the calculated results [37]. In 2013, Malvoisin *et al.* even designed a pioneering experiment to produce high-purity H₂ gas from the reaction between SS and water at 473–673 K and 50 MPa by means of Equation (4) [70]. It was found that at 623 K, approximately 5 NL of H₂ were produced and meanwhile 0.142 kg of CO₂ was captured per kg of SS. In other words, the SS could show multiple roles of both H₂ production and CO₂ capture, while these effects should be balanced for different purposes:

$$2FeO+H_2O=Fe_2O_3+H_2$$
(3)

$$3FeO+H_2O=Fe_3O_4+H_2$$
(4)

Beside FeO in the slag, another effective component in the slag is V₂O₃, which can reduce H₂O and CO₂ into fuel gas, *i.e.*, H₂ and CO. Nakano *et al.* [71] designed a reaction to convert CO₂ and H₂O gas into CO and H₂ using a mixture of molten CaO-rich metallurgical slag and V₂O₃-rich gasifier slag and they found that 97% of CO₂ was transformed to CO in the temperature range of 1678–1733 K. Equations (5) and (6) present the reaction process, in which CaO exhibits a strong thermodynamic affinity for V₂O₃, resulting in the formation of calcium orthovanadate in a highly exothermic reaction. In addition, the potential of this method was evaluated and the results showed that a steel plant producing 7680 t steel per day would convert 970 t CO₂ into 620 t CO, corresponding to an extra 12,000 MWh/day worth of power.

$$3CaO + V_2O_3 + 2CO_2 = (CaO)_3(V_2O_5) + 2CO$$
 (5)

$$3CaO + V_2O_3 + 2H_2O = (CaO)_3(V_2O_5) + 2H_2$$
 (6)

3.2. Other Chemical Methods

3.2.1. Production of Slag Wool

In addition to fuel gas production, there exist some other methods related to chemical reactions to recover the high temperature waste heat. Among them, production of slag wool is an economically reasonable alternative, in which hot BFS is directly utilized as the raw material. The properties of molten slag, such as viscosity, acidity, and liquidus temperature are modified using additives and then these molten slags are drawn, blown, or refined to form slag wool, the schematic diagram of which is shown in Figure 4. Yang *et al.* [72] proposed a one-step slag wool production method to directly use the sensible heat of slag and it has been estimated that the recovery efficiency was more than 80%. Slag wool can be widely applied in industry and civil engineering because of its combined advantages of excellent thermal insulation ability and fire resistance properties [73]. Recently, Zhao *et al.* [74] and Li *et al.* [75] separately reported the slag wool production using BFS, in which the molten BFS was combined with coal ash and the viscosity and acidity were effectively modified. It was also estimated that this novel method showed an energy consumption reduction of ~70% and a waste smoke reduction of ~90% compared to the traditional methods. These methods expand the utilization field of slag and recovery of waste heat, especially in view of the strong ability of slag treatment.



Figure 4. Process of the production of slag wool.

3.2.2. Selective Crystallization and Phase Separation

Similar to the process of slag wool production, the SCPS method is widely used to extract valuable elements and partially recover waste heat from the molten slags. For some special kinds of slags, the chemical compositions have been modified by additives to use the tapped high quality thermal energy during the process of melting and holding of additives, as shown in Figure 5.



Figure 5. Process of SCPS method.

In vanadium-bearing SS, the effect of SiO₂ and Al₂O₃ on the enrichment of vanadium has been investigated [76] and it was found that when the slag is modified by SiO₂ and Al₂O₃ to lower the basicity, the vanadium can be mainly concentrated in the solid solution of Ca₃[(V, P, Si)O₄]₂ containing more than 45 wt% V₂O₅. For recovery of phosphorus from P-bearing SS, it was found that SiO₂, Al₂O₃ and TiO₂ have a positive influence on the P recovery ratio, which proved good additives [77]. Sui et al. [78] studied the precipitation behavior of boron-bearing slags and it was found that suanite (2 MgO B₂O₃) existed as the main crystalline phase by changing chemical composition, holding temperature and additions. As for the Ti extraction, the influence of SiO₂ and TiO₂ on the extraction of Ti element from Ti-bearing BFS was investigated by Li et al. [79,80] and it has been proved that SiO₂ is a good modifier to change the basicity of slags under C/CO equilibrated atmospheres and enhance the growth of anosovite. The extraction of valuable elements from the slags expands the field of utilization of waste heat recovery and provides new integrated ways of using these residual wastes. Through the process of slag wool production and SCPS, the chemical composition of the slag was directly modified and the sensible heat was used to melt the additives. Then the high value slag wool was produced or the valuable elements were extracted after a series of industrial operations. Although these two methods were quite different from those of syngas production, they are also classified as chemical methods. In addition, these methods provided a distinct possibility of waste heat recovery from high temperature slags because of the substantial amount of treatment compared with that of fuel gases production.

4. Analysis of These Chemical Methods

After the introduction of these chemical methods, it is necessary to induce the characteristics of these methods and identify whether these methods effectively address the aforementioned fundamental challenges of heat recovery. Table 2 summarizes these methods and accordingly, several characteristics could be deduced. First, the reaction temperatures are distributed in the range of 473–1973 K, found in almost the whole cooling path of slags, which suggests that the sensible heat of slags at different levels should be recovered using different methods. For example, the sensible heat of BFS at high temperatures could be used for MSR, while that at relative low temperatures it could be used for biomass gasification. However, the further utilization of the slags after heat recovery should be

considered, which was an important issue required to be addressed. For the heat recovery of BFS, if the reaction temperature of the chemical methods was higher than 900 $^{\circ}$ C and the slags could not be cooled not rapidly enough, the obtained slags could not be used as raw materials for cement production because of the inside crystallization of the slags; on the contrary, the collected slags could be utilized in the cement industry if the slags was first rapidly cooled to form glassy state and the chemical reaction occurred below 900 $^{\circ}$ C. As for the SS, the solid slags after treatment could be used for road construction and landfilling.

Reaction Type	Reaction Equation	Temperature (K)	Agent	Slag Type	Reaction Role of Slag	References
Methane-steam gasification	$CH_4 + H_2O = CO + 3H_2$	1473–1823	H ₂ O(g)	Blast furnace slag	Heat carrier, catalyst	[33,36,37,41]
Methane-CO ₂ decomposition	$CH_4+CO_2=2CO+2H_2$	973–1273	CO ₂	Blast furnace slag	Heat carrier, catalyst	[44]
Coal pyrolysis	$Tar \rightarrow H_2 + CO + CO_2 + other$ light hydrocarbon + C	773–1173		Blast furnace slag, steel slag	Heat carrier, catalyst	[54,57]
Coal-steam gasification	$C + H_2O = CO + H_2$	1048	H ₂ O(g)	Blast furnace slag	Heat carrier	[53]
Coal-CO ₂ gasification	$C + CO_2 = 2CO$	1223–1423, 1573–1773	CO ₂	Blast furnace slag	Heat carrier, catalyst	[47–51]
Gasification of municipal solid waste	-	873–1173	N2, air, steam	Blast furnace slag	Heat carrier, catalyst	[60]
Pyrolysis of printed circuit boards	$\label{eq:cmHnO} \begin{split} C_m H_n O &\rightarrow C_a H_b O_c + CO + H_2 \\ &+ C H_4 + CO_2 \end{split}$	873–1173	-	Blast furnace slag	Heat carrier	[61]
Biomass pyrolysis	$\begin{split} C_m H_n O_x & \rightarrow a CO_2 + b H_2 O + \\ c C O + d C H_4 + f C_{2+} \end{split}$	773–1023	-	Blast furnace slag	Heat carrier	[65]
Biomass gasification	$\label{eq:cmHnOx} \begin{split} C_m H_n O_x + H_2 O &\rightarrow a C O_2 + \\ b H_2 O + c C O + d C H_4 + f C_{2+} \end{split}$	1073–1473, 523–773	H2O(g), H2O(g)- O2	Blast furnace slag	Heat carrier, catalyst	[64,66]
FeO reduction	$2FeO + H_2O = Fe_2O_3 + H_2$ $3FeO + H_2O = Fe_3O_4 + H_2$	1723, 1873–1973, 473–673	H ₂ O(g)	Steel slag	Heat carrier, reactant	[68–70]
V ₂ O ₃ reduction	$3CaO + V_2O_3 + 2CO_2 =$ $(CaO)_3(V_2O_5) + 2CO$ $3CaO + V_2O_3 + 2H_2O =$ $(CaO)_3(V_2O_5) + 2H_2$	1678–1733	CO2, H2O(g)	CaO-rich metallurgical slag; V2O3-rich gasifier slag	Heat carrier, reactant	[71]

Second, numerous studies including methane reforming [36,37], coal gasification [47–50], PCB pyrolysis [61] and biomass gasification [64–66] indicate that the recovery process should be at least divided into two steps. The liquid slags should be first granulated into small droplets and rapidly quenched to glassy phases and then the heat transfer of chemical reactions is conducted. Indeed, a two-step heat recovery process has been forecasted by Barati *et al.* [8] based on operational processes; moreover, based on the inherent crystallization properties of slags [28,32], the heat recovery



Figure 6. Schematic diagram of the multi-stage control of waste heat recovery [32].

Third, it can be seen that the slags can act as good catalysts in addition to heat carriers. However, it should be pointed that the catalytic effect of vitreous phase is weak [81,82], except that crystal forms in the slags, which is opposite to the purpose of BFS utilization, *i.e.*, making raw materials for the cement industry. Thus both the heat recovery and the material recycling should be considered in an actual industrial process. For the individual slags, specific component in the slag, such as FeO and V_2O_3 , could be used to reduce CO_2 and H_2O into CO and H_2 , which has expanded the field of utilization of slags. In other words, the hot slags could act in three types of roles in the chemical process, *i.e.*, heat carrier, catalyst, and reactant; these roles should be reasonably selected considering the subsequent utilization of the solid slags. Fourth, the present studies are concentered on fuel gas production, which combines the steel industry to the chemical engineering industry and energy industry. The combustion of produced fuel gas can create high temperatures, which improves the quality of energy. On the other hand, the fuel gas can be directly used in the steel industry and reduce the metal from minerals. Thus an integrated system should be designed in advance comprising various industrial sectors. Fifth, the present investigations are on a lab scale and their commercial application has not been realized. Because of their low thermal conductivity, the slags should be granulated into small particles to avoid crystallization inside the slags. Through chemical methods, especially those of fuel gas production, the discontinuous waste heat can be transferred into continuous and stable chemical energy.

Furthermore, the industrial achievement of these chemical methods not only requires optimum design in view of the technological process but also requires a reasonable energy policy including the cooperation of different industrial, urban and agricultural sectors and the necessary policy supports [83–85]. Overall, only after solving these fundamental challenges, will the real scientific heat recovery from high temperature slags come to be used in the modern steel industry in the context of pursuit of sustainable development.

5. Conclusions

In summary, nowadays there is a large potential to reduce energy consumption in the steel industry through heat recovery from hot slags. Many methods have been exploited to extract the waste heat, including physical methods and chemical methods, among which chemical methods can meet well the challenges that restrict the extraction of the waste heat. This paper reviews these chemical reactions used in the heat recovery and characterizes them as follows.

- (1) The basic challenges that restrict the waste heat recovery from molten slags are the low thermal conductivity, the inside crystallization, and the discontinuous time-temperature availability;
- (2) Many chemical reactions have been utilized in the waste heat recovery, including fuel gas production and direct modification of slag compositions to generate high value products;
- (3) Fuel gas production is the main R&D trend because of the strong demand for alternative and renewable fuels in modern society, such as the production of combustible gas by coal gasification, biomass gasification and methane reforming;
- (4) The role of slags in these chemical reactions can be that of heat carrier, catalyst and reactant, and especially that the latter two roles expand the field of utilization of molten slags;
- (5) Direct utilization of the waste heat and material resources of the slags has also been developed in the past decades, such as the slag wool production by compositional modification and mineral extraction by the SCPS method;
- (6) Dry granulation of slags into small droplets can effectively address the issue of the low thermal conductivity of slags and avoid crystallization inside slags; while chemical methods can address the problem of the discontinuous availability and create high quality fuel gas; therefore a combination of dry granulation and chemical reactions to make up an integrated system is the main direction of heat recovery from slags, as summarized in Figure 7.



Figure 7. A promising integrated system of dry granulation and chemical methods.

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Author Contributions

The work presented here was carried out in collaboration between all authors. Zuotai Zhang and Yongqi Sun conceived and designed the study. Yongqi Sun wrote the paper and Zuotai Zhang edited the manuscript. Lili Liu and Xidong Wang discussed about this review. All authors read and approved the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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