Highly Efficient Use Technology of The By-Product Gas in Iron and Steel Making Process

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Abstract. BOF gas, with an annual output of more than 100 billion standard cubic meters, is one of the primary by-product energy resources in the steelmaking process. However, the up to 34.7% abandoned rate of BOF gas in China has caused a lot of carbon emissions and energy resources waste. The abandoned BOF gas, with a high temperature of 1773~1873K and 20~40%(vol.%) CO and 20~30%(vol.%) CO₂ has a vast physical sensible heat and chemical latent heat. There are predictable recyclable values and comprehensive utilization prospects to achieve the ultra-low carbon emissions and energy conversion in ironmaking and steelmaking. The paper has carried out a detailed calculation of the energy value of abandoned BOF gas, and the feasibility analysis and program design of the overall resource recycling and energy utilization in ironmaking and steelmaking, including blast furnace smelting of vanadia-titania magnetite, combined blowing in BOF and vanadium-extracting converter, co-production of steel-chemicals industry.

Keywords: Abandoned BOF Gas; Vanadia-Titania Magnetite; V-Extracting Converter; Co-production of Steel-Chemicals industry; By-product Recycling.

1. Introduction

About 70% of the total energy used in the steel industry will be converted into secondary energy (including by-product gas), but about 30% of the secondary energy is not fully recycled. At present, the sensible heat recovery rate of products, flue gas, cooling water, and slag in China are 50.4%, 14.92%, 1.9%, and 1.59%, respectively, and the waste heat recovery rate of the steel industry is 25.8%.

At present, most steel industries in China have a low average gas recovery rate, large energy consumption, and serious carbon emissions. For the single-slag converter steelmaking process, the gas recovery can generally reach 100~110 Nm³/t·s. However, the calorific value is low (generally about 1700×4.186 KJ/Nm³), which is one of the reasons why the energy consumption on key processes per ton of steel in China's steel industry is higher than advanced developed countries in the world. According to Table 1, the CO concentration and calorific value of the basic oxygen furnace gas (BOFG) are both high. However, release rate of BOFG is also higher than blast furnace gas (BFG) and coke oven gas (COG), which caused great loss of physical sensible heat and chemical latent heat every year. [1-2]

There is about 16~17 min of by-product gas generation in the BOF blowing process, in which the front-stage is about 3 min, and the end-stage is about 2 min. At present, the recovery standard of the by-product gas is generally started when the CO concentration reaches 40%, and the recovery is reduced to
35%, which generated in the middle stage of blowing. The recovery conditions for BOFG in steel companies in China are shown in Table 2. The CO concentration of recovered BOF gas (RBOFG) in the middle stage is about 50–70%, and the total CO content in the begin and end stages is about 20–40%. Besides, the by-product gas in begin and end stages is called abandoned BOF gas (ABOFG), which is ignited and discharged after used for simple waste heat recovery and dust removal only at present.

Table 1. Current status of by-product gas release in steel companies of China

| Statistical Indicators | BFG | COG | BOFG |
|------------------------|-----|-----|------|
| Volume of Abandoned Gas / \times 10^8 Nm³ | 167.4 | 7.5 | 381.3 |
| Abandoned Rate / % | 7.23 | 4.59 | 34 |

Table 2. Recycling conditions for BOFG in steel companies of China

| Enterprise & BOF level | Start-CO ≥ /% | Start-O₂ ≤ /% | Termination-CO ≥ /% |
|------------------------|--------------|--------------|-------------------|
| BAOWU Steel-300 t      | 40           | 1            | 35                |
| SGJT Steel-300 t       | 38           | -            | 40                |
| MA Steel-300 t         | 35           | 1.5          | 35                |
| PAN Steel-120 t        | 35           | -            | 30                |
| BAYI Steel-120 t       | 35           | 0.9          | 30                |
| LAIWU Steel-120 t      | 35           | -            | 35                |

According to Table 2, the qualifying BOF gas is recovered in the middle stage of the BOF blowing that the CO concentration is high (average 40%), and the O₂ concentration is lower (average less than 1%). However, the unqualified BOG gas is abandoned without any handing properly. According to the data provided by the by-product gas system in BAOWU Steel, the specific volume of ABOFG (20–30% CO content) is estimated to be 12500 Nm³/furnace, and the recoverable volume is about 10000 Nm³/furnace. According to the actual production situation of Baosteel, the number of blown furnaces per day is 128 furnaces, the working time is 365 days, the average converter operation rate is 95%, and the average converter tapping capacity is 300 t/furnace. According to the statistics from the China National Bureau of Statistics and the World Iron and Steel Association, China's BOF crude steel output in 2018 is 928.26 million tons (90% by BOF). So, the volume of ABOFG and the volume of recoverable ABOFG (ABOFG-R) are calculated, as shown in Table 3.

Table 3. Recycling conditions for BOFG in steel companies of China

| Gas Volume | ABOFG | ABOFG-R |
|------------|-------|---------|
| A Furnace / \times 10^4 Nm³ | 1.25 | 1.0 |
| A tonne of steel / Nm³ | 41.67 | 33.33 |
| Annual total output / \times 10^8 Nm³ | 328.78 | 262.98 |

The calorific value of ABOFG is mainly composed of physical sensible heat and chemical latent heat. According to the literature and the actual steelmaking process, the composition and average content (vol.%) of the ABOFG are shown in Table 4. The physical sensible heat value of the furnace gas discharged from the 1500 °C to 70 °C is \( q_1 \), wherein the constant heat capacity is \( C_v \). According to the chemical thermodynamics database, the isotherm specific heat of the main compounds in the furnace gas is shown in Table 5.

Table 4. The composition and content of ABOFG

| Composition | CO | CO₂ | H₂ | O₂ | N₂ | H₂O |
|-------------|----|-----|----|----|----|-----|
| Content / vol.% | 20–40 | 20–30 | 1–2 | 0.1–0.5 | 50–55 | Sat. |

Table 5 Isovolumetric specific heat capacity of major compounds in ABOFG (\( C_{v1} = 0.8 C_{v2} \))
As shown in Eqs. (1), the mixed equal volume heat capacity $C_v$ of the ABOFG is the sum of the multiplications of the volumetric heat capacity $C_{vi}$ of each component in the ABOFG and its volume fraction $\omega_i$ respectively, and the calculated result of $C_v$ is 1.3954 KJ/Nm$^3 \cdot ^\circ C$. According to Eqs. (2), the calculated result of the physical calorific value $q_a$ of ABOFG is 1995.5 KJ/Nm$^3$. In addition, it is also known that the calorific value $q_{b}$ of the standard coal is 7000×4.186 KJ/Kg, and the calorific value $q_{c}$ of the coke is 6800×4.186 KJ/Kg. So, the physical heat $Q$ of the ABOFG and standard coal quantity and coke quantity converted from $Q$ are calculated with Eqs. (3).

$$C_v = \sum C_{vi}\omega_i \text{ (i}=\text{CO, CO}_2, \text{H}_2, \text{N}_2, \text{O}_2, \text{H}_2\text{O}) \quad (1)$$

$$q_a = C_v\Delta T = C_v(T_2-T_1) \quad (2)$$

$$Q_{a/r} = q_a V_{a/r} \quad (3)$$

$C_v$: Mixed isometric heat capacity of ABOFG, KJ/Nm$^3 \cdot ^\circ C$;

$C_{vi}$: Isovolumetric specific heat capacity of each compound in ABOFG, KJ/Nm$^3 \cdot ^\circ C$;

$\omega_i$: Volume fraction of each compound in ABOFG, %;

$q_a$: Physical calorific value of ABOFG, KJ/Nm$^3$;

$Q_a$: Physical heat value of ABOFG, KJ;

$Q_r$: Physical heat value of ABOFG-R, KJ;

$\Delta T$: Temperature difference before and after heat exchange of furnace gas, °C;

$T_2$: The ABOFG temperature before the heat exchange (1500 °C), °C;

$T_1$: The ABOFG temperature after the heat exchange (70 °C), °C;

The main combustion-exothermic reactions in the ABOFG are involved in CO, H$_2$, and a small number of alkane compounds. The exothermic reactions are shown in Eqs. (4) and Eqs. (5). The chemical latent heat released by the chemical reaction of CO and H$_2$ under constant pressure is calculated in the paper, which showed as the reaction enthalpy change $\Delta r H$. And the standard molar formation enthalpy $\Delta H_m^\Theta$ of each compound in ABOFG can be seen by the Inorganic Thermodynamic Data Manual, as shown in Table 6.

$CO + \frac{1}{2}O_2 \rightleftharpoons CO_2, \Delta r H_{TK}^\Theta = \Delta r H_{TK,CO_2}^\Theta - \Delta r H_{TK,CO}^\Theta \quad (4)$

$H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O, \Delta r H_{TK}^\Theta = \Delta r H_{TK,H_2O}^\Theta \quad (5)$

Table 6. Standard molar formation of CO, CO$_2$, and H$_2$O at different temperatures $\Delta H_m^\Theta$/KJ·mol$^{-1}$

| Composition | CO       | CO$_2$   | H$_2$O  |
|-------------|----------|----------|---------|
| $\Delta H_m^\Theta$ (298K) | -110.527 | -393.522 | -285.83 |
| $\Delta H_m^\Theta$ (1800K) | -117.384 | -396.311 | -251.138 |

According to the above calculations, the total heat of the ABOFG is about 1.54×10$^8$ GJ, which equivalent to standard coal and coke up to 5.254 million tons and 5.406 million tons, respectively. That means the annual heat loss of the ABOFG is $388.2 million in China. In other word, if the heat energy of the ABOFG-R is fully recycled, the annual loss can be reduced by $305.2 million.

2. Prospective comprehensive utilization of abandoned BOF gas

As a kind of energy that can be recycled, BOF gas has tremendous economic benefits and recovery value. In recent years, with the gradual depletion of primary energy such as oil and coal and the strict control of the country's environmental issues, we have increasingly focused on improving the efficiency.
of the use of existing resources. However, at present, most of the domestic steel companies' BOF gas has not been fully recovered, and most of the recovered BOF gas is directly put into the gas-fired boiler for power generation, which has not been fully utilized. This has caused economic losses and added environmental pressure. Nowadays, there is an urgent need for energy utilization, and we should increase efforts to develop the comprehensive utilization of ABOFG. Specifically, there are three aspects.

2.1. Application of Abandoned BOF Gas to Ironmaking
Vanadium-titanium magnetite is a polymetallic element symbiotic magnetic iron ore containing iron (Fe), vanadium (V), titanium (Ti), cobalt (Co), nickel (Ni), chromium (Cr), niobium (Sc), gallium (Ga). The experimental research in China began in the late 1950s. Through laboratory research and small blast furnace smelting experiments, it is considered that the higher the content of TiO2 in the slag is, the more difficult it is to smelt, which is easy to cause blast furnace hearth accumulation, poor slag iron separation, high sulfur content of pig iron, high coke ratio and low production efficiency. [3]

When the TiO2 content in the smelting slag is less than 25%, the iron output from the slag is uneven, and the slag iron is not sticky. When the furnace temperature is high, slag iron "great diarrhea" may occur, although the phenomenon of furnace accumulation occurs, but Adjusting the furnace temperature, appropriately reducing the [Si] content, blowing the concentrate into the slag mouth, adding manganese ore and other measures, the blast furnace is basically antegrade. However, when the slag in the smelting slag is in the 30% stage, the slag is severely thickened and difficult to flow. The furnace is accumulating, and even the slag iron cannot be discharged. After the slag port is continuously sprayed and the silicon content is reduced by a significant amount, the problem of slagging and balanced slagging and tapping is solved, but the molten iron can still be severe and slag Iron hooks and other problems. [3]

At present, the biggest difference between China's ironmaking indicators and the advanced international level is that the hot air temperature is low. In recent years, the hot air temperature of key steel enterprises is decreasing, with a difference of 100~150°C. The hot air temperature is increased by 100°C, and the defocus ratio is 10 to 15 kg/t. Cancel the current blast furnace smelting with 10%~15% natural rich ore, increase the TiO2 in the slag to 25%~28%. In industrial tests in which TiO2 content in the past slag reached 30% to 35%, there was a high iron loss (7% to 10%), hot metal cans, and even foam slag in the 1000 m³ blast furnace test. Therefore, in order to solve the foaming slag and reduce the iron loss, measures should be taken to suppress the reduction of TiO2 to form TiC, TiN, and Ti (C, N), and the wind temperature is not less than 1000 °C. [3-4]

The mechanism for the formation of titanium carbonitride is mainly divided into a Slag-Coke reaction and a Slag-Iron reaction. [3-6]

(1) Slag-Coke Reaction ("Adsorption-Dissociation-Desorption" Kinetic Model)

\[
(TiO_2) + 3C = TiC + 2CO, \Delta G^\circ = 524130 - 333.55T
\]  

(6)

The TiO2 in the slag first moves to the surface of the coke, and the adsorption reaction is carried out at the slag coke interface. Then, the TiO2 adsorbed on the surface of the coke dissociates and dissociates into Ti and oxygen atoms at the active point of the coke surface, and oxygen atoms and coke. C reacts to form CO, and Ti reacts with C in coke to form TiC. Since P N2 in the gas phase is high, the N atom after high-temperature dissociation is smaller than Si atom. As TiC is continuously formed, N atom continuously flows to TiC. Diffusion, the formation of Ti (C, N), as the Ti (C, N) particles continue to grow, the C at the center of the particle diffuses outward through the Ti (C, N) layer and the N atoms of the outer layer diffuse inward. Thus, a concentration changes of C, N is formed on the cross-section of the Ti (C, N) particles, resulting in a situation where the center C is high N and low, and the edge C is low N high. The concentration gradient of C and N increases with time. The smaller the size, the better the formation of Ti (C, N), which stabilizes the C and N ratios. As the reduction reaction time increases, Ti (C, N) will increase, and a dense Ti (C, N) layer will gradually form, but in the blast furnace production, the scouring of the gas stream and the slag iron makes the Ti(C,N) layer very It is easy to peel off from the coke, so that the TiO2 in the slag will continue to adsorb on the surface of the coke to form Ti (C, N).
(2) Slag-Iron Reaction

\[(\text{TiO}_2) + 2[C]_{\text{sat.}} = [\text{Ti}] + 2\text{CO}, \Delta G^\circ = 679900 - 391.74T\]  
(7)

\[[\text{Ti}] + [C]_{\text{sat.}} = \text{TiC}, \Delta G^\circ = -127600 + 55.65T\]  
(8)

In the slag iron reaction, TiO₂ is first reduced by C in Fe to Ti dissolved in molten iron. When [Ti] and [C] reach a certain concentration value, TiC and Ti (C, N) solid solution particles are precipitated. When the temperature is constant, [Ti] increases with the increase of TiO₂ activity in the slag. As the temperature increases, [Ti] also increases rapidly, but due to the precipitation reaction of Ti (C, N), it is limited. The increase in [Ti]. In the slag iron reaction, the Ti (C, N) phase equilibrium [Ti] is lower than the TiC phase equilibrium [Ti], therefore, the C and Ti in the pig iron are precipitated as Ti (C, N) solid solution, compared with It is much easier to precipitate in the form of pure TiC. Moreover, as long as solid C is present, it is impossible to precipitate TiN, and only Ti (C, N) can be precipitated. The lower the P₁₂ in the gas phase, the less TiN in the precipitated Ti (C, N), and the corresponding in the pig iron. The amount of Ti is also higher. The reduction of Ti and the formation of Ti (C, N) are largely carried out at the slag-iron interface. The C in the pig iron is close to saturation. At the slag-iron interface, the activity of C is 1, and due to the slag coverage, it is not directly in contact with the gas in the furnace, the N₂ in the gas can only be dissolved in the slag, and the slag layer reaches the slag-iron interface, which reduces the precipitation of Ti (C, N) and increases the [Ti] in the molten iron, which is beneficial to suppress Ti (C, N) Effect on the fluidity of slag iron.

In summary, when C is present, it is inevitable that Ti (C, N) is formed after reduction of TiO₂ at high temperature, but the key is to inhibit its formation and finally oxidize and decompose these carbonitrides. The CO₂ in the sprayed ABOFG has an effect on the presence of titanium carbonitride in the vanadium-titanium blast furnace. The main thermodynamic analysis is as follows.

\[3(\text{TiO}_2) + 7C + N_2 = 2\text{TiN} + \text{TiC} + 6\text{CO}, \Delta G^\circ = 1263266 - 852.7T\]  
(9)

\[\text{TiC}(s) + \text{TiN}(s) + 3O_2 = 2(\text{TiO}_2) + 1/2N_2 + CO_2, \Delta G^\circ = -1361700 + 244.33T\]  
(10)

\[2\text{CO} + O_2 = 2\text{CO}_2, \Delta G^\circ = -133400 + 40.17T\]  
(11)

If the equilibrium oxygen potential at the slag-iron interface is calculated by the gas partial pressure of the reducing gas in the blast furnace, it is significantly higher than the reducing oxygen potential of the titanium oxide, and the oxidizing oxygen potential of the titanium carbonitride during the reduction process, indicating the presence of carbon dioxide. It can inhibit the reduction of titanium and promote the oxidation of titanium carbonitride. However, in the actual reduction process, since the molten iron is covered by the slag, the oxygen potential at the interface of the actual slag iron is much smaller than the value calculated by thermodynamics, so the inhibition is only The effect of inhibition, or even oxidative decomposition can be exerted when the oxidizing atmosphere is maintained at a high level.

As the proportion of carbon dioxide increases, the oxygen potential at the slag-iron interface increases significantly, while the reduced oxygen potential of titanium dioxide and the oxidation-oxygen potential of titanium carbonitride decrease, indicating that N₂ is limited as the concentration of carbon dioxide increases. The transfer to the slag-iron interface reduces the P₂₅ at the slag-iron interface, thereby reducing the amount of TiN produced and inhibiting the precipitation of Ti (C, N), while the carbon dioxide and coke compaction layer (dead pile) undergoes gasification endotherm The reaction, on the one hand, has the effect of controlling the furnace temperature, and at the same time increases the partial pressure of the PCO and the total pressure in the hearth, which is beneficial to reduce the formation of TiN and increase the criticality of aTiO₃, thereby inhibiting the formation of titanium carbide.

As shown in Figure 1, the flow progress of ABOFG utilization of the vanadia-titania magnetite blast furnace was designed. ABOFG can also play the role of "physical heat, chemical cold," which helps to accelerate the carburization of molten iron and contributes to the separation of slag and iron. Otherwise, it also can increase the oxygen potential in the dead zone of the tuyere, optimize the gas distribution in the furnace, and reduce the position of the melting-dripping zone.
2.2. Application of Abandoned BOF Gas to Steelmaking

During the steelmaking process, CO₂ in ABOFG can participate in the following reactions.

| Reactions | ΔG°(J) | ΔG°1773K(J) | ΔH°(KJ) |
|-----------|--------|-------------|--------|
| CO₂(g) + [C] = 2CO(g) | 137890 - 126.52T | -86.43 | 175.52 |
| CO₂(g) + Fe(ℓ) = (FeO) + CO(g) | 48980 - 40.62T | -23.04 | 40.37 |
| 2CO₂(g) + [Si] = (SiO₂) + 2CO(g) | -247940 + 41.18T | -174.93 | -344.36 |
| CO₂(g) + [Mn] = (MnO) + CO(g) | -133760 + 42.51T | -58.39 | -101.91 |
| 3/2CO₂(g) + [V] = 1/2(V₂O₃) + 3/2CO(g) | -161990 + 31.935T | -105.37 | -190.74 |

The above reaction produces more CO gas and strengthens the agitation. The endothermic reaction of CO₂ with Fe and C plays a role in temperature regulation, while O₂ reacts with C and Fe, Si, Mn, V, and other elements. Therefore, it is considered whether a small amount of CO₂ can be incorporated into oxygen to lower the fire point temperature and help to oxidize the carbon in molten iron. [7-8]

As shown in Figure 2, a duplex BOF system with self- CO₂ recycling and self-CO enriching properties was designed. In the circulation system, it is possible to achieve a zero abandoning gas production. The duplex BOF system includes a steelmaking BOF and a vanadium-refining BOF. The BOF gas produced by the steelmaking BOF and the vanadium-extracting BOF is recovered and enriched. After preliminary dust removal and slight temperature reduction treatment, the gas is divided into ABOFG and recoverable BOF gas (RBOFG) by component detection. Then, the ABOFG is sprayed from the bottom of the BOF through a spray gun to realize the functions of carbon removal and heat preservation, enrichment of CO, full agitation, and vanadium extracting. The CO in the multi-cycle ABOFG is recovered after being enriched to the RBFGF standard. The CO in ABOFG is recovered after several cycles of enrichment to the standard.

The resource application of CO₂ in the metallurgical industry, the stirring effect of CO₂, the temperature control effect and the dilution effect on blast furnace ironmaking, converter steelmaking, electric furnace steelmaking, refining and continuous casting protection, and ladle baking furnace, rolling steel heating furnace, circulating combustion of rotary hearth furnaces, rotary kiln and applications in industries such as nonferrous metals. At present, China has carried out practical production applications for CO₂ in BOF production. [9-10]

At present, the application of CO₂ in steelmaking mainly has three aspects. CO₂ is used as a reaction gas mainly in BOF steelmaking, stainless steel production, and steel slag carbonation; CO₂ is used as a stirring gas mainly for converter bottom blowing, ladle mixing, and LF furnace refining; CO₂ is used as shielding gas mainly in tapping, tundish, and continuous casting processes. The use of CO₂ for steel production has the advantages of low cost, good thermodynamic conditions, high density, strong mixing ability, and utilization of CO₂ resources.
2.3. Application of Abandoned BOF Gas to Co-production of Metallurgical-Chemical Industry

The utilization of by-product gas in China's major steel companies is shown in Table 8.

| Enterprise       | Volume$/\times10^8$ m$^3$ | Utilization                                      |
|------------------|-----------------------------|--------------------------------------------------|
| BAOWU Steel      | 59                          | Fermentation to ethanol; Coal to ethylene glycol  |
| HEGANG           | 39.7                        | DMTE to ethanol; Charge                           |
| SHAGANG          | 34.5                        | Charge                                           |
| ANSHAN Steel     | 30.8                        | Charge                                           |
| SHOUGANG         | 24.9                        | Charge                                           |
| SHANXI LIHENG    | 18                          | Coking and co-production of ethylene glycol LNG   |

From the table, it can be found that by-product gas is currently mainly used for power generation, but steel gas power generation is not the only option. Chemical grade CO extracted from blast furnace gas, and converter gas can produce a variety of chemical products. Currently, there are methanol, ethanol, ethylene glycol, butanol, formic acid, acetic acid, oxalic acid, DMF, phosgene (polycarbonate, TDI, MDI). Its advantage lies in:

a) 40% cheaper. Steel gas is associated with gas, the price is decoupled from coal price, and the cost of raw material gas is 40% cheaper;

b) Save 30%. There is no need to build large-scale facilities such as gas-making furnaces, air separation plants, and coal yards, and the investment can save more than 30%;

c) Earn 40% more. For example, the cost of ethylene glycol is 3,500 yuan/ton for tempering and 5,000 yuan/ton for the coal chemical industry.

The by-product gas and coal gas in the steel process contain CO, H$_2$, CH$_4$, and CO$_2$, and the content is not low, while the steel gas is associated with gas, the N$_2$ is very high, and the pressure of coal gasification becomes higher than before. Therefore, steel gas power generation is not the only option, and it is better to choose to temper. The advantages of steel gas tempering and co-production are considerable and more promising than the coal chemical industry.

The by-product gas produced by the steel process is used to burn electricity. There is no hedging of steel revenue and power generation revenue, but it causes problems such as rising carbon emissions and smoke emissions. That is to say, gas combustion power generation is no problem, but it is not the best. The way of utilization is not the most rational solution for resource utilization. [11-17]

(1) Transformation of ethanol by microbial fermentation with abandoned BOF gas
The converter gas is pressurized by the compressor and sent to the TSA tower and the desulfurization tower to remove harmful substances such as aromatic hydrocarbons, and then sent to the fermentation after deoxidation. The main fermentation reaction of industrial gas with CO as an active ingredient can be expressed as:

$$6\text{CO} + 3\text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_5\text{OH} + 4\text{CO}_2 + \text{Heat}$$ (12)

That is, carbon monoxide with water is bio-fermented to produce fuel ethanol and carbon dioxide, and one ton of CO is bio-fermented by the bacteria to produce 0.274 tons of ethanol. Fermentation uses water as a carrier to add trace elements necessary for microorganisms and vitamins to maintain life activities. In the fermenter, the cells convert CO to produce ethanol mash, and the residual CO of the fermentation tail gas is sent to RTO (regenerative incinerator) to recover heat. Steam is produced for distillation, and ethanol is sent to the distillation to produce 99.5% of the finished ethanol product.

(2) Ammonia preparation by atmospheric pressure oxidation with abandoned BOF gas

The atmospheric pressure non-catalytic partial oxidation conversion process is adopted, and the coke oven gas does not need to be purified, and the organic matter brought by the coke oven gas (tar, naphthalene, phenol) can be directly converted under normal pressure at a temperature of 1300 to 1400 °C. And organic sulfur compounds) are all cracked and converted, and the organic sulfur is converted into inorganic sulfur, which reduces the difficulty and cost of desulfurization. The content of CO in the abandoned BOF gas is 20%-40%, the gas is relatively clean, and it can be directly used as a supplement to the synthesis gas feed gas without further purification, and it can supplement the carbon for the post-process methanol synthesis. It can play a role in regulating the hydrogen to nitrogen ratio for ammonia production. The ratio of abandoned BOF gas and coke oven gas can be flexibly adjusted between 0 and 50%. The cost of abandoned BOF gas is only 5~10% of coke oven gas, and the price is low. If used fully, the gas cost of syngas can be reduced by 50%. The coke oven gas atmospheric pressure non-catalytic conversion plus BOF gas synthesis gas process has the characteristics of low investment, good efficiency, safety, and environmental friendliness.

(3) Ethylene glycol preparation with abandoned BOF gas

At present, China's technology in coal processing and utilization has ranked in the forefront of the world. Among them, coal-based gas, coal-to-liquids, coal-to-olefins, coal-based aromatics, coal-based ethylene glycol, and coal-to-ethanol have formed scale industries. Coal to ethylene glycol reaction:

$$2\text{CO} + 1/2\text{O}_2 + 4\text{H}_2 \rightarrow (\text{CH}_2\text{OH})_2 + \text{H}_2\text{O}$$ (13)

The abandoned BOF gas from the steel plant enters the converter gas cabinet for buffering and is sent to the abandoned BOF gas compressor for compression (the final outlet pressure is 1.2 MPa). The compressed gas passes through dephosphorization, arsenic removal, defluorination, deoxidation, and hydrogenation. In the desulfurization process, the purified gas and the desulfurized gas are decarburized by MDEA and sent to the PSA decarbonization process, and the qualified CO is compressed to 0.6 MPa by the CO compressor and sent to the oxalate synthesis process. At present, the gap in domestic ethylene glycol is still relatively large. Compared with coal and natural gas to ethylene glycol, abandoned BOF gas as a raw material for ethylene glycol has the advantages of low comprehensive energy consumption and low cost, which can not only fill domestic glycol. The gap in demand and the ability to create good economic benefits for many steel plants.

(4) Methanol preparation with abandoned BOF gas and COG

As an important basic organic chemical raw material, methanol is mainly used for coal and coke oven gas. In the process of producing methanol from coke oven gas, the ideal hydrogen/carbon ratio of synthesis gas is 2.05, and the actual hydrogen to carbon ratio is 2.9~3.5. The excess hydrogen increases the circulation of the system and increases the power consumption by 30%. In view of the problem of excess hydrogen in the methanol process of coke oven gas, the carbon is purified by using converter gas to be used as a carbon source for methanol production. To optimize the use of resources, while increasing methanol production and increasing the added value of methanol gas. [18-21]
The use of abandoned BOF gas to synthetic chemical products not only reduce the pressure on the environment caused by the steel industry but also bring higher economic benefits. The comprehensive utilization of abandoned BOF gas is a useful exploration path to achieve energy conservation and emission reduction and resource recycling.

3. Conclusions
(1) The total heat of the ABOFG is about $1.54 \times 10^8$ GJ, which equivalent to standard coal and coke up to 5.254 million tons and 5.406 million tons, respectively. That means the annual heat loss of the ABOFG is $388.2$ million in China. In another words, if the heat energy of the ABOFG-R is fully recycled, the annual loss can be reduced by $305.2$ million.

(2) ABOFG can also play the role of "physical heat, chemical cold", which helps accelerate the carburization of molten iron and contributes to the separation of slag and iron. Increase the oxygen potential in the dead zone of the tuyere, reduce the coke ratio, optimize the gas distribution in the furnace, and improve the gas utilization rate. Reducing the position of the melting-dripping zone, increasing the melting temperature and dripping temperature will help the smoothing of the vanadium blast furnace production.

(3) The use of CO$_2$ for steel production has the advantages of low cost, good thermodynamic conditions, high density, strong mixing ability, and utilization of CO$_2$ resources. The self-recycling of CO$_2$ in ABOFG can not only achieve the above effects, but also reduce carbon emissions and heat loss, and also enrich CO in BOF gas to improve the quality of converter gas.

(4) The abandoned BOF gas can be used in transformation of ethanol by microbial fermentation, ammonia preparation, ethylene glycol preparation, and methanol preparation. The use of abandoned BOF gas to synthetic chemical products not only reduce the pressure on the environment caused by the steel industry but also bring higher economic benefits. The comprehensive utilization of abandoned BOF gas is a useful exploration path to achieve energy conservation and emission reduction and resource recycling.

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