Application Characteristics and Industrial Development Countermeasures of Shenmu Semi-coke

Ning Wei¹, Lidan Wang², Bo Zhao¹, Qingcong Yan³

¹ Shaanxi Energy Quality Supervision and Inspection Institute, Xi’an, Shaanxi, 710054, China
² China National Accreditation Service for Conformity Assessment, Beijing, 100062, China
³ Shenmu Semi-coke Industrial Service Centre, Yulin, 719300, China

*Corresponding author’s e-mail: wlyxb@sxnys.com

Abstract. The quality index of Shenmu semi-coke is investigated to study its application characteristics, combined with the quality index of Shenmu raw coal and anthracite. Through the analysis of semi-coke products and the environmental protection characteristics in the production process, the ideas for cleaner production are provided. The industrial development countermeasures are put forward based on the development and future demand of Shenmu semi-coke industry.

1. Introduction

With 1017.6 billion tons of ascertained storage and 4552.1 billion tons of predicted storage, there are abundant coal resources in China. In general, coal accounts for 94%, oil accounts for 5.4% and natural gas accounts for 0.6% of the proven energy reserves in China, showing an apparent energy structure of "rich coal, lack of oil and less gas". Coal, as the only primary energy with the advantages of energy resources and self-sufficiency, will still be an essential source of energy and organic chemical raw materials in the future in China. Therefore, the development of the modern coal chemical industry model based on coal retorting is conducive to China's energy security.

China is rich in low-rank coal resources, with proven reserves accounting for 55% of coal resources and output accounting for about 40% of the total coal production, which is an essential part of China's coal energy production and supply[1]. With the main coal-producing area moving westward, the output of low-rank coal will increase year by year in the future. The structure and physicochemical characteristics of low-rank coal determine that it is suitable for cascade utilization with medium and low-temperature pyrolysis as the target. It can be divided into gas (coal gas), liquid (coal tar), solid (semi-coke) three energy states. The above three states can be further transformed into high value-added products such as oil, gas, chemical, electricity and clean fuel.

The proven reserves of low-rank coal in the Shenmu area reach 56 billion tons, accounting for 1/4 of the total resources of Shenu-Dongsheng Coalfield and 1/12 of the whole country. Shenmu is a vital energy and chemical base of the country. Shenmu low-rank coal has the characteristics of low ash, low sulfur, low phosphorus, high volatile and high reactivity, which is very suitable to be used according to different grades and different substances.
2. Quality index characteristics and application characteristics of Shenmu semi-coke

2.1. Quality index range of Shenmu semi-coke

Semi-coke is a solid carbon product with low volatile matter obtained by distillation and pyrolysis of high volatile bituminous coal at medium and low temperature [2]. Shenmu semi-coke has the characteristics of high fixed carbon, high calorific value, high reaction activity, high specific resistance, low ash content, low sulphur content, low phosphorus content and low aluminium content. It is widely used in calcium carbide, ferroalloy, fertilizer gasification, blast furnace injection, fuel and other fields. It is an indispensable intermediate industry to undertake raw coal, calcium carbide, and metallurgy. The range of main quality index of Shenmu semi-coke is shown in Table 1.

Table 1. The range of main quality index of Shenmu semi-coke (d-dry basis; daf-dry ash free)

| Project       | Symbol | Unit  | Range of main quality indicators |
|---------------|--------|-------|----------------------------------|
| Ash           | A_d    | %     | 6.0-10.0                         |
| Heat          | Q_net  | MJ/kg | >25.0                            |
| Total Sulfur  | ST_d   | %     | <0.4                             |
| Total moisture| M_d    | %     | ≤13.0                            |
| Volatile      | V_daf  | %     | 6.0-10.0                         |
| Lower limit rate | R_d    | %     | ≤10.0                            |
| Chlorine      | Cl_d   | %     | ≤0.050                           |
| Phosphorus    | P_d    | %     | ≤0.01                            |
| Arsenic       | As_d   | μg/g  | ≤10                              |
| HG            | Hg_d   | μg/g  | ≤0.01                            |
| Fluorine      | F_d    | μg/g  | ≤100                             |
| Resistivity   | ρ      | 10⁻⁶Ω.m | >15000                           |

2.2. Quality index analysis and application characteristics of Shenmu semi-coke

Shenmu semi-coke (LT), Shenmu raw coal (BN) and anthracite (WY) samples were selected to analyze the fundamental indexes and primary process performance indexes. Through data comparison and analysis of different industrial application requirements, the industrial application characteristics of Shenmu semi-coke were obtained. The coal quality indexes of the three samples contained the fundamental coal quality indexes in Table 2, the specific surface area and coal ash characteristic indexes in Table 3, and other process performance indexes in Table 4.

Table 2. Basic coal quality indicators

| Sample | M_d/% | A_d/% | V_d/% | Q_net,ar/MJ/kg | S_d,d/% | C_d/% | H_d/% | N_d/% | P_d/% | Cl_d/% | As_d/μg/g | Hg_d/μg/g | F_d/μg/g | ρ/10⁻⁶Ω.m |
|--------|-------|-------|-------|----------------|---------|-------|-------|-------|-------|--------|-----------|-----------|----------|-----------|
| LT     | 9.8   | 7.65  | 7.57  | 26.96          | 0.33    | 85.47 | 2.55  | 0.80  | 0.002 |
| BN     | 15.2  | 8.85  | 37.25 | 25.83          | 0.46    | 81.25 | 5.02  | 0.92  | 0.013 |
| WY     | 3.82  | 9.72  | 6.75  | 27.89          | 0.65    | 83.18 | 2.32  | 1.01  | 0.025 |

Table 3. Specific surface area and coal ash characteristic index

| Sample | Specific surface area, m²/g | Ash melting, °C | Coal ash composition analysis, % |
|--------|-----------------------------|-----------------|----------------------------------|
|        | DT | ST | HT | FT | CaO | Fe₂O₃ | K₂O | Na₂O | Al₂O₃ |
| LT     | 17.98 | 1160 | 1180 | 1180 | 1190 | 29.34 | 10.68 | 0.48 | 0.62 | 11.83 |
| BN     | 4.60  | 1120 | 1170 | 1180 | 1190 | - | - | - | - | - |
| WY     | 6.32  | 1260 | 1500 | 1500 | 1500 | 4.28 | 3.96 | 0.62 | 1.02 | 36.24 |

Table 4. Other process performance indicators

| Sample | HGI | AI | Ignition temperature, °C | Burnout temperature, °C |
|--------|-----|----|--------------------------|-------------------------|
| LT     | 51  | 68 | 480                      | 705                     |
From the data in Table 2, it can be found that Shenmu semi-coke has the characteristics of low volatile matter, low ash content, high carbon content and high calorific value. The sulfur content, nitrogen content and phosphorus content of Shenmu semi-coke are lower than those of Shenmu raw coal and anthracite, indicating that Shenmu semi-coke has higher combustion performance. The data in Table 3 show that Shenmu semi-coke has a large specific surface area and high CaO content in ash, which can react with the SO$_2$ generated from combustion, and be conducive to the self-desulfurization reaction to reduce SO$_2$ emission. Shenmu semi-coke has the characteristics of high quality and clean fuel.

The data in Table 3 shows that the pore structure of Shenmu semi-coke is more developed than that of Shenmu raw coal. The specific surface area is more than three times of raw coal, indicating that the burning rate of semi-coke after ignition is faster than that of raw coal. The content of Al$_2$O$_3$ in ash is low, but the content of Fe$_2$O$_3$ and CaO is high, and the total percentage of potassium and sodium is only 0.066%. Shenmu semi-coke has low volatile matter, no explosive or low explosive property, and no apparent flame return is found in the most semi-cokes. The relationship between semi-coke flame return length and the volatile matter is shown in Figure 1, which indicates that semi-coke is safe for blast furnace injection. Shenmu semi-coke is suitable for blast furnace injection in combustion characteristics, chemical composition characteristics and safety characteristics.

Figure 1. The relationship between the flame return length of blue charcoal and volatile matter$^{[3]}$

The injection of pulverized coal is used to replace coke in the blast furnace, which plays a role of heating and reduction, to reduce the coke ratio of blast furnace and smelting cost. High-rank coal such as lean coal and anthracite are often used in traditional blast furnace injection. The characteristic indexes of Shenmu semi-coke are compared with the technical requirements of anthracite listed in GB/T 18512-2008 "technical conditions of coal for blast furnace injection". The ash content ($A_d$), phosphorus content ($P_d$), total potassium and sodium ($\omega(k) + \omega(Na)$) meet the grade I technical requirements. The total sulfur ($S_d$), Hardgrove grindability index (HGI) and total moisture ($M_t$) meet the grade II technical requirements. It can be seen that all indexes of Shenmu semi-coke fully meet the requirement of the coal injection standard for blast furnace, and its combustion performance is better than anthracite. It can replace anthracite for blast furnace injection, to make rational use of coal resources, reduce the production cost of ironmaking, and achieve the effect of low carbon and environmental protection.

According to table 2 and 3, the softening temperature (ST) in the fusibility of Shenmu semi-coke ash is 1180 °C, which belongs to the lower softening temperature. Therefore, attention should be paid to the risk of slagging during high proportion injection. HGI 51 and AI 68 show that Shenmu semi-coke is hard to be ground and has strong wear performance, indicating that attention should be
paid to the abrasion of pipelines, such as conveying the main pipe, a connecting hose and coal lance. The grind ability can be improved by selecting suitable coal and reducing the retorting temperature to increase the volatile.

3. Environmental performance characteristics of Shenmu semi-coke

3.1. Environmental performance characteristics of Shenmu semi-coke products

In the production process of Shenmu semi-coke, sulfur, chlorine, phosphorus, mercury and other harmful components have been removed. The results show that 60% of sulfur, 28% of nitrogen and 95% of polycyclic aromatic hydrocarbons (PAHs) can be effectively removed from raw coal by low-temperature distillation. Compared with bituminous coal, PM$_{2.5}$ decreased by 86.76%, organic carbon emissions decreased by 83.51%, and elemental carbon emissions decreased by 94.61%. Sulfur and nitrogen emissions have incomparable effects of bituminous coal, which has significant advantages in reducing pollution and emission reduction.

Semi-coke entered the civil clean fuel market in 2014, and it is an alternative raw material for bulk coal recommended by the Ministry of environmental protection, energy administration and national standards committee. It is a clean fuel in the process of coal to electricity and coal to gas.

3.2. Environmental performance characteristics of semi-coke production process

In the low-temperature pyrolysis process of low-rank coal, particulate matter, industrial wastewater and volatile organic compounds (VOCs), such as non-methane hydrocarbons, benzopyrene and other pollutants, will be produced. From 2018 to 2020, with the development of low-rank coal pyrolysis technology and semi-coke industry, as well as the limitation of wet quenching, the pollution of low-rank coal pyrolysis, semi-coke wastewater and volatile organic compounds (VOCs) has gradually attracted attention.

The composition of difficult-to-biodegradable substances in coal pyrolysis and semi-coke wastewater is shown in Table 5.

| Pollutants                      | Proportion (%) | Pollutants                      | Proportion (%) | Pollutants                      | Proportion (%) |
|--------------------------------|----------------|--------------------------------|----------------|--------------------------------|----------------|
| Nitrogen-containing heterocycles | 18.19          | Trimethylsilvaleric acid        | 1.54           | Butyric acid                    | 4.62           |
| Phenol                         | 7.05           | 2,6-bis(1,1-dimethyl)naphtalene | 3.71           | (N-)tetracosane                 | 0.42           |
| Quinol                         | 5.00           | 5,5-Dimethylhydantoin          | 0.63           | Octadecane                      | 0.46           |
| Resorcinol                     | 3.72           | 3-methyl 2 (3H) benzofuranone   | 2.68           | Heptadecane                     | 0.28           |
| P-methylphenol                 | 9.08           | 1-(2-furan)-1-heptanone        | 0.32           | Hexadecane                      | 0.28           |
| 2,3-Dimethylphenol             | 3.41           | Trimethylsilyl hexanoic acid    | 3.40           | Tridecane                       | 0.32           |
| 3,4-Dimethylphenol             | 2.31           | 4,6 dimethyl 2,3-2H-benzofuranone | 1.28            | Eicosan                         | 0.21           |
| 3,5-Dimethylphenol             | 5.94           | 2,5-Diformyl furan              | 1.51           | Eicosan                         | 0.37           |
| 4,5-Dimethyl-hydroquinone      | 2.32           | Enanthate                      | 2.15           | Dodecamethylcyclohexasiloxane   | 0.18           |
| 2-Methyl-hydroquinone          | 3.76           | Caproic acid                   | 4.85           |                                |                |

In recent years, air pollution in China is regional composite air pollution characterized by fine particles and ozone. Large amounts of volatile organic compounds (VOCs) are the crucial precursors of PM$_{2.5}$ and ozone. With the wide application of the technology of coal classification and cascade utilization, the production and emission of volatile organic compounds (VOCs) in the process of semi-coke production cannot be underestimated. The generation and emission of volatile organic
compounds (VOCs) will corrode production equipment, endanger human health, cause environmental pollution, cause waste of resources, and also have adverse effects on safety production.

Most of the semi-coke industry has less investment in environmental protection, lower pollution control level and equipment level, and there is still a gap with modern coal chemical enterprises. Significant efforts need to be made in environmental protection to solve these problems. The semi-coke industry should continuously improve product process design, adopt advanced technology and equipment, improve production management and environmental protection management level, and improve resource utilization efficiency from source reduction, process control and end treatment. Wastewater treatment and volatile organic compounds (VOCs) treatment should be coupled with the production process to reduce the production and emission of pollutants in the production process. Reduce or eliminate the hazards to the production process equipment, human health and environment, and finally form cleaner production.

4. Development status and countermeasures of Shenmu semi-coke industry

4.1. Development status of Shenmu semi-coke industry

Since 1978, the semi-coke industry has been greatly developed for 40 years, especially after the large-scale furnace type, steam quenching and wastewater treatment in 2015. The semi-coke production technology level has been improved, the product application market has been gradually expanded, and the coal tar deep-processing level has been improved. Large amounts of high-quality low-rank coal and semi-coke products at a low price significantly promote the development of the semi-coke industry. At present, Shenmu has four semi coke industrial zones, forming several circular industrial chains. 49 semi-coke production enterprises with an annual output of 600000 tons and above have been established, with an annual total capacity of 34.55 million tons. The full scale of the semi-coke industry in China is about 100 million tons, and Shenmu semi coke accounts for about 1/3.

The semi-coke industry is an economical and efficient low-rank coal classification utilization mode, and also an essential part of the green and efficient utilization of national coal. In 2014, the Ministry of industry and information technology issued the coking product access policy. In October 2016, the semi-coke was officially listed as clean energy by the Ministry of environmental protection of the people's Republic of China. Since then, semi-coke has been used in steel mills, calcium carbide plants, smelters, power plants, chemical fertilizer plants and other industrial fields. In terms of civil use, the State encourages semi-coke to replace the seriously polluted bulk coal. These policies promote the utilization of semi-coke and provide long-term policy guarantees for the long-term development of semi-coke.

At present, the semi-coke industry is facing new industrial policies and market opportunities. For example, some critical regional governments have issued policies to limit the energy consumption and coal consumption of enterprises, and restrict the direct use of coal as a fuel for civil and small and medium-sized boilers. Semi coke does not occupy the coal consumption index. In these areas, the purchase of semi-coke instead of coal is increased for blast furnace injection, civil fuel, boiler fuel. Policy incentives have expanded the use of semi-coke. However, with the gradual expansion of the application scope and use area of semi-coke, and the increasing pressure of environmental protection, the semi-coke industry still faces many problems. The main issues are that the overall planning of semi-coke comprehensive utilization is not vital, the construction of industrial park needs to be improved, the technical level needs to be improved, the environmental protection level is uneven, the industrial chain is not developed enough, and the adaptability of raw coal needs to be improved.

4.2. Development strategy of Shenmu semi-coke industry

Semi-coke production technology is an effective way for efficient and clean utilization of low-rank coal. With the support of relevant national industrial policies, the semi-coke industry should take the large-scale, clean and efficient road to build an industrial chain and lay the foundation for industrial survival and sustainable development. During the 14th Five Year Plan period, water resource was
comprehensively controlled, energy consumption was held, and ultra-low atmospheric emissions were fully implemented. It is an inevitable trend to strengthen the policies of VOCs and solid waste treatment and increase investment in environmental protection and safety in the semi-coke industry.

The development orientation of Shenmu semi-coke industry should be planned as a whole to guide efficient and orderly development. From the pursuit of development quantity to the pursuit of development quality, the industrial competitiveness can be improved. Industrial-scale and industrial park development is imperative. It is necessary to strengthen the combination of strong enterprises, build large-scale and super sizeable comprehensive utilization energy enterprises through market-oriented enterprise merger and acquisition, and enhance the core competitiveness of leading enterprises.

Shenmu semi-coke industry should increase investment in technology and environmental protection, and strengthen joint research with universities and scientific research departments, to upgrade equipment level, enhance the scale of a single unit, clean production level and reduce energy consumption. The industry should improve environmental protection facilities, centralized disposal of three wastes, solve decentralized emission, reduce ecological protection costs, improve overall energy efficiency, and solve the pollution problems as soon as possible.

It is necessary to play an essential role in replacing bulk coal with semi-coke and expand its application in various industries. By extending the semi-coke industry chain and matching different application scenarios, the customized production of semi-coke products is realized to meet the needs of other users and finally expand the application field. At the same time, the relevant standards of the semi-coke industry should be improved. At present, there are only 4 national standards for semi-coke and 1 local standard for Shaanxi Province. It is necessary to speed up the formulation and improvement of semi-coke production standards and industrial chain standards, to promote standardization to lead the industrial development.

5. Conclusion

Shenmu semi-coke is of good quality and widely used. From the data, it can be found that Shenmu semi-coke is suitable for blast furnace injection in combustion characteristics, chemical composition characteristics and safety characteristics. The development prospect of blast furnace injection is good. But Shenmu semi-coke has lower softening temperature, hard to be ground and strong wear performance. Therefore, attention should be paid to the risk of slagging during high proportion injection, and the grind ability can be improved by selecting suitable coal and reducing the retorting temperature to increase the volatile.

In the production process of Shenmu semi-coke, sulfur, chlorine, phosphorus, mercury and other harmful components have been removed. It has significant advantages in reducing pollution and emission reduction. The wastewater and volatile organic compounds (VOCs) of semi-coke production process has gradually attracted attention. Significant efforts need to be made in environmental protection to solve these problems.

At present, the semi-coke industry is facing new industrial policies and market opportunities. The development orientation of Shenmu semi-coke industry should be planned as a whole to guide efficient and orderly development. Shenmu semi-coke industry should increase investment in technology and environmental protection. It is necessary to play an essential role in replacing bulk coal with semi-coke and expand its application in various industries.

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