

Review

Progress in Caking Mechanism and Regulation Technologies of Weakly Caking Coal

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Abstract

Efficient and clean utilization remains a pivotal development focus within the coal industry. Nevertheless, the application of weakly caking coal results in energy loss due to the caking property, thereby leading to a waste of resources. This paper, therefore, concentrates on the caking property, offering insights into the relevant caking mechanism, evaluation indexes, and regulation technologies associated with it. The caking mechanism delineates the transformation process of coal into coke. During pyrolysis, the active component generates the plastic mass in which gas, liquid, and solid phases coexist. With an increase in temperature, the liquid phase is diminished gradually, causing the inert components to bond. Based on the caking mechanism, evaluation indexes such as that characteristic of char residue, the caking index, and the maximal thickness of the plastic layer are proposed. These indexes are used to distinguish the strength of the caking property. However, they frequently exhibit a poor differentiation ability and high subjectivity. Additionally, some technologies have been demonstrated to regulate the caking property. Technologies such as rapid heating treatment and hydrogenation modification increase the amount of plastic mass generated, thereby improving the caking property. Meanwhile, technologies such as mechanical breaking and pre-oxidation reduce the caking property by destroying agglomerates or consuming plastic mass.

Keywords: weakly caking coal; caking property; caking mechanism; evaluation indexes; regulation technologies



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1. Introduction

Driven by the rapid depletion of fossil fuels and growing concerns over climate change, the global energy industry is actively advancing strategies for green and low-carbon energy transition. Global energy demand grew by 2.2% in 2024, outpacing the average growth rate over the past decade, with electricity demand surging by 4.3%, significantly exceeding the 3.2% growth of global GDP [1]. In 2024, the power generation from renewable energy accounted for 32% of global power generation [2]. Against this backdrop, China's energy system is undergoing a critical restructuring. While coal's dominance as the primary energy source is progressively diminishing, it remains indispensable for ensuring energy security during this transitional phase. China's unique energy mix and resource endowment dictate that coal will continue to underpin the national energy consumption framework for decades,

necessitating its dual role as both a transitional stabilizer and supply guarantor [3–5]. Therefore, the key direction of development is still to clarify the distribution of coal resources and master the clean and efficient utilization of coal [6]. This means that all links in the entire industrial chain of coal, including development, production, storage, transportation, and utilization, must achieve clean and efficient utilization, while focusing on efficiency improvement and control of traditional pollutants. Moreover, the integration of large-scale utilization with decarbonization and green development requirements is imperative. This necessitates a heightened focus on low-carbon initiatives and quality improvement to achieve clean, low-carbon utilization across all stages and components. As illustrated in Figure 1, the coal classification system in China is primarily predicated on the volatile matter content on a dry ash-free basis (V_{daf} , the volatile matter from proximate analysis), the caking index ($G_{R.I.}$, the ability of coal to bind inert additives when subjected to heat), and the maximal thickness of the plastic layer (Y_{max}) [7]. In addition, as coal is mainly utilized in the power, thermal, steel, and chemical industries, it can also be categorized into thermal coal and coking coal based on application scenarios [8,9].

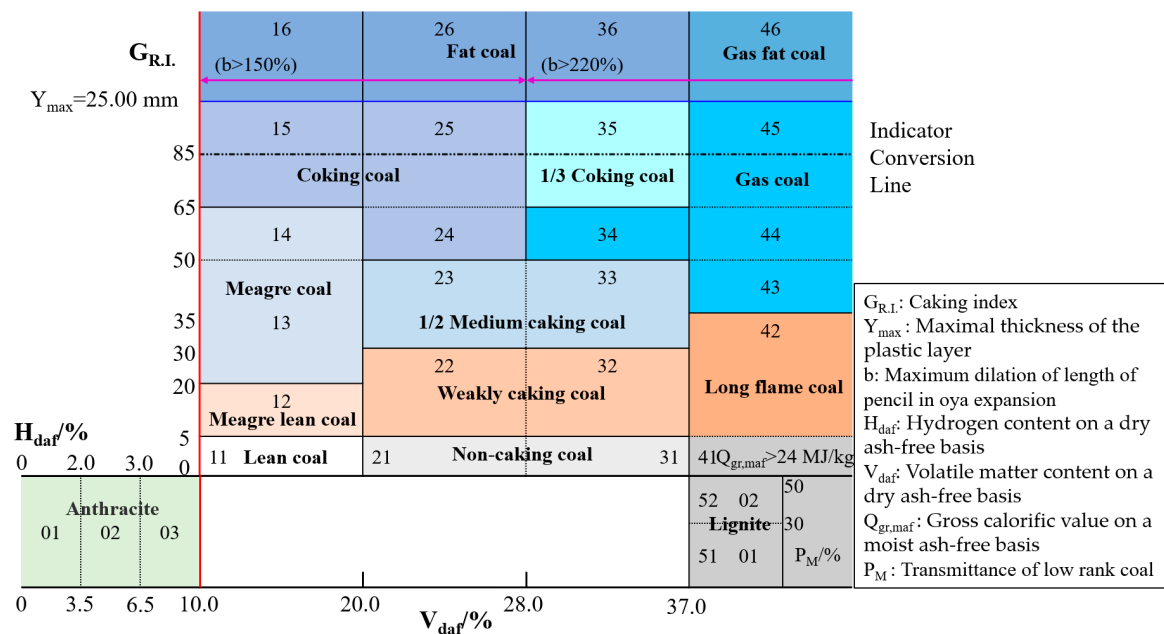


Figure 1. The coal classification system in China [7].

Currently, China's thermal coal is mainly utilized in power generation. With the promotion of energy transformation, it is clearly stated in the relevant policies that the role of coal-powered pockets of protection should be strengthened and the transformation and upgrading of coal-powered electricity should be actively promoted [10,11]. As one of the hosts of coal power units, coal-fired boilers are required to have good peak operation characteristics, while the emission of pollutants must meet national emission standards [12,13]. Consequently, the realization of clean and efficient coal utilization in thermal power generation remains a critical issue. Coking coal serves as both the fundamental energy source and primary raw material for the steel industry, contributing to approximately 80% of the total coal consumption within this sector [14]. It predominantly comprises gas coal, fat coal, lean coal, and so on. These coals possess a certain caking property, and during pyrolysis, can produce plastic masses which can bond inert components. Gas coal and fat coal, due to the ability to form coke with high compressive strength, are considered the optimal types of coal for coking. However, their limited reserves pose a significant conflict with the demands of actual industrial production. Consequently, a thorough examination of the caking property

and coal blending structures is fundamental to improving process efficiency and energy conservation within the coking industry.

In Figure 1, there is a weakly caking coal, which is a transitional coal type between thermal coal and caking coal. Its volatile content on a dry ash-free basis is 20% to 37%, while G_{RI} is generally 5 to 30, thus producing relatively few plastic masses during pyrolysis. Due to the weakly caking property and high content of inert components, weakly caking coal forms coke with a poor compressive strength during pyrolysis, precluding standalone coking applications. Moreover, its utilization in gasification and combustion processes additionally generates other issues. In a fixed bed gasifier, the weakly caking coal has a tendency to agglomerate or hang on the furnace wall. Meanwhile, in a fluidized bed gasifier, the formation of agglomerates within the chamber often leads to defluidization, as depicted in Figure 2 [15,16]. In addition, weakly caking coal tends to form porous light particles when heated. These particles are carried out by gas without complete combustion, which increases the amount of mechanically incomplete combustion [17,18]. Given the challenges, only a fraction of the weakly caking coal is utilized, while the majority of the coal ends up being stacked and stored, leading to a significant waste of resources [19]. Therefore, achieving clean and efficient utilization of weakly caking coal requires elucidating the caking mechanism and developing targeted regulation technologies.

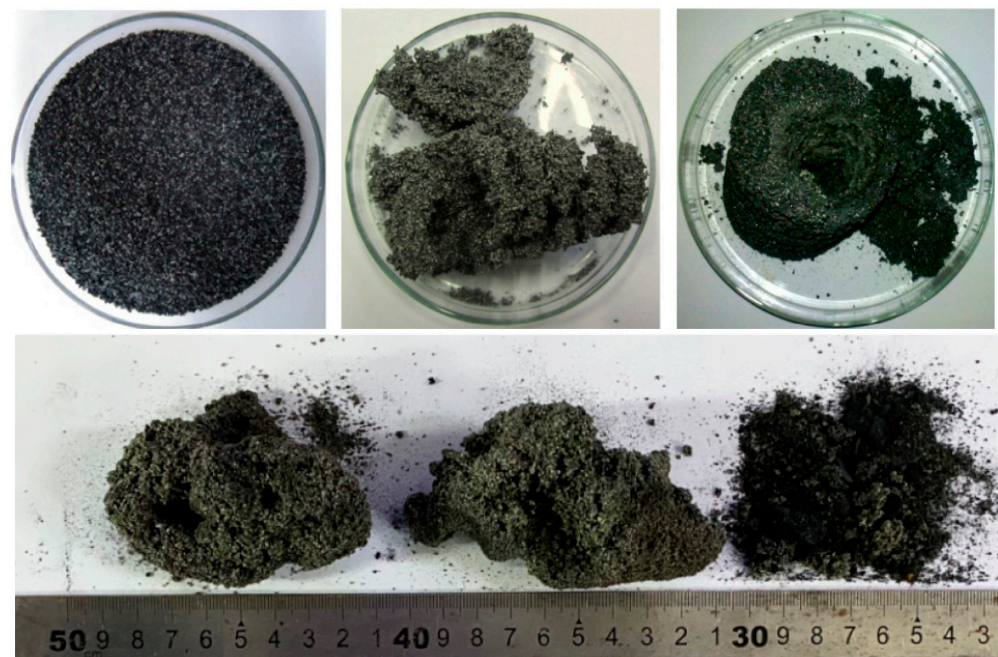


Figure 2. Agglomerates formed during gasification of weakly caking coal [15,16].

Considering the difficulty of utilizing weakly caking coal, both low-temperature rapid pyrolysis treatment [20] and hydrogenation modification [21,22] have been demonstrated to enhance the caking property, thereby improving the compressive strength of coke. To address agglomerate and energy loss caused by weakly caking coal, researchers have proposed technologies that can break agglomerates or reduce the caking property, such as mechanical breaking [23], blending with non-caking fuels [24], and pre-oxidation [25].

The regulation technology for the caking property has been fully developed, but existing research focuses on how to achieve regulation without paying much attention to its negative effects. Additionally, due to the complexity of the reactions that occur during pyrolysis, there is currently no consensus on the caking mechanism. Meanwhile, many evaluation indexes which have been proposed to evaluate the strength of the caking property

can only evaluate certain characteristics of the caking process. Therefore, a comprehensive and accurate evaluation index is lacking.

This paper provides a comprehensive summary of research on weakly caking coal, encompassing the caking mechanism, evaluation indexes for the caking property, and pertinent regulation technologies. Emphasis is also placed on the alterations in each component during the caking process, the intrinsic mechanism of technologies, and the current application status. Finally, the shortcomings of the existing evaluation indexes and regulation technologies are summarized, with a view to providing a reference for the clean and efficient utilization of weakly caking coal.

2. Caking Mechanism and Evaluation Indexes

2.1. Caking Mechanism

The caking mechanism is related to the pyrolysis of coal, so it is necessary to first understand the specific process of pyrolysis. During pyrolysis, a rise in temperature initiates a series of intricate physical and chemical reactions in the organic matter found in coal. This leads to the release of volatiles, leaving behind semi-coke or coke. The chemical reactions that occur during pyrolysis are extraordinarily complex, involving numerous intermediate pathways. These are generally classified into two primary categories: cracking and polycondensation. In the initial phase of pyrolysis, the process is primarily characterized by drying and degassing, with no external morphological changes observed. As the temperature escalates, the organic matter starts to decompose. Through cracking, coal produces a significant quantity of gas and tar. The gas primarily consists of gaseous hydrocarbons, CO, and CO₂. During this phase, the primary reactions include the breaking of bridge bonds, cleavage of aliphatic side chains, decomposition of oxygen-containing functional groups, and cracking of low-molecular-weight compounds. It is noteworthy that coal forms a plastic mass with coexisting gas, liquid, and solid phases at this stage. As the reaction progresses, coal gradually transforms into semi-coke. When the temperature reaches 550 °C, polycondensation reactions become predominant. Aromatic structures undergo dehydrogenative polycondensation, converting semi-coke into coke. Minimal tar is produced at this stage, and the gas primarily consists of hydrocarbon gases and hydrogen. In the context of coal's molecular structural theory, pyrolysis can be defined as a process in which thermally unstable components (such as side chains and functional groups surrounding the basic structural units) continually decompose to generate low-molecular-weight compounds. Concurrently, the condensed aromatic nuclei from the basic structural units form free radicals. These radicals then undergo polycondensation, leading to the formation of semi-coke or coke [26]. Figure 3 depicts the pyrolysis process of coal, involving macromolecular cleavage and condensation reactions.

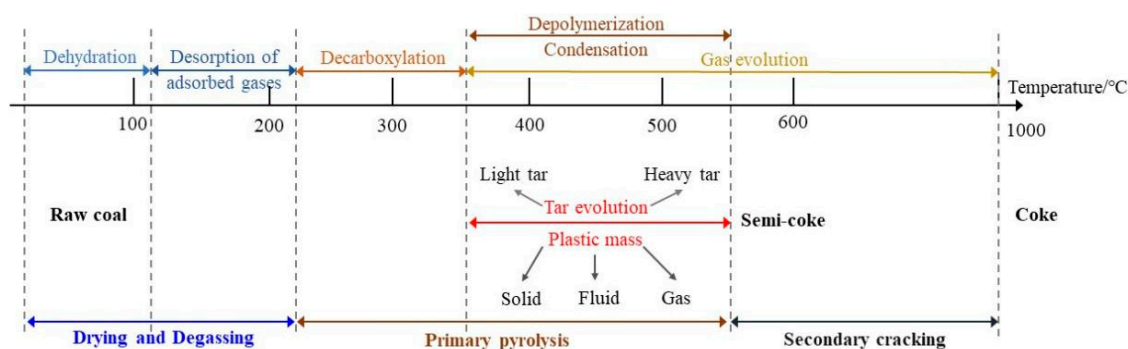


Figure 3. The pyrolysis process of coal.

Currently, several theories have been proposed regarding the caking mechanism, with the most influential being the plastic mechanism of coke formation and the mesophase mechanism of coke formation [27–29].

2.1.1. Plastic Mechanism of Coke Formation

The plastic mechanism of coke formation refers to the fact that when coal with the caking property is heated to a certain temperature, the active components will generate a mixture of gas, liquid, and solid phases coexisting together, which is known as the plastic mass. The plastic mass determines the caking property and therefore is the core of the caking mechanism [30].

Upon heating coal with the caking property to temperatures ranging from 350 °C to 500 °C, organic molecules within the coal undergo intense decomposition. This process entails the cleavage of side chains from condensed aromatic rings, prompting additional decomposition. The thermal decomposition products can be categorized based on relative molecular weights: those with small molecular weights are found in a gaseous state, whereas those with medium molecular weights exist in a liquid state. In contrast, condensed aromatic rings, now-deformed particles due to side-chain breakage, and other infusible components resulting from thermal decomposition maintain a solid state because of large relative molecular weights. Consequently, the coal forms a plastic mass comprising gaseous, liquid, and solid phases. When the temperature rises to between 450 °C and 550 °C, the decomposition rate of the plastic mass exceeds its formation rate. This results in some products being released as gas. The residual part binds with solid particles, undergoes thermal polycondensation, and subsequently solidifies to form semi-coke.



2.1.2. Mesophase Mechanism of Coke Formation

In fact, the mesophase mechanism is an additional observation about the phase behavior of the liquid phase closely related to caking progress, which researchers discovered during in-depth studies on the plastic mechanism [31]. The mesophase is perceived as an aromatic compound within the plastic mass, characterized by a high relative molecular mass and an extended carbon chain. The molecular structure in the mesophase notably exhibits both the mobility of liquid and the optical anisotropy of crystal. Essentially, mesophase is a liquid crystal which represents an intermediate phase that bridges the gap between liquid and solid. When the temperature exceeds the upper threshold of liquid crystal, it is transitioned to a liquid due to heat, resulting in the loss of optical anisotropy. Conversely, when the temperature falls below the lower threshold of liquid crystal, it is solidified into crystals, leading to the cessation of mobility. In the caking process, small spheroids are formed within the isotropic liquid via crystal nucleation. Subsequently, these spheroids are expanded, forming compound spheroids through bonding. Ultimately, they are solidified into an optical anisotropy organization within the coke, which is facilitated by an external force.

These two theories both posit that the caking property is decided by the plastic mass generated during pyrolysis. Consequently, extensive research has been conducted on the formation and properties of the plastic mass.

2.2. Plastic Mass

2.2.1. Formation of Plastic Mass

The results, which are summarized in Table 1, provide valuable insights into the formation and transformation of the plastic mass. Additionally, they emphasize that the caking property is closely associated with the production of hydrogen radicals, aliphatic compounds, aromatic compounds, and volatile components. The alterations in the associated components are illustrated in Figure 4.

It is currently posited that the liquid phase in plastic mass originates from four primary sources: (1) During low-temperature pyrolysis, a substantial quantity of free radicals is generated due to the cleavage of bridge bonds with small bond energies in the coal. Some of these free radicals are subsequently combined with active hydrogen to produce a stable liquid phase. (2) With increasing temperature, certain covalent bonds in aliphatic compounds are cleaved, yielding liquid small-molecule aliphatic hydrocarbons. (3) Upon further heating, the macromolecular structure undergoes breakdown and degradation, resulting in the formation of liquid small-molecule aromatic hydrocarbons. (4) Aromatic compounds, along with their hydrogenated counterparts, undergo a process of condensation polymerization, resulting in the formation of liquid small-molecule aromatic hydrocarbons.

Table 1. Research on plastic mass.

Authors	Contents of Research
Qiu [32]	The liquid phase is predominantly composed of alkyl-substituted monocyclic compounds and long-chain unbranched alkanes.
Li [33]	The caking property is predominantly influenced by the structure of aliphatic compounds. A shorter and more branched aliphatic chain typically results in a stronger caking property.
Qin [34]	The primary constituents influencing the caking property are the series of compounds, including benzene, naphthalene, anthracene, and phenanthrene, along with long-chain alkanes.
Wang [35]	The release of a substantial quantity of volatile gases and tar results in an increase in the quantity of aromatic hydrocarbons.
Lee [36,37]	Aliphatic compounds are pivotal in the formation process of plastic mass.
Chen [38]	The cleavage of aliphatic bridge bonds and hydrogen transfer mechanisms are identified as predominant factors governing the formation of plastic mass.
Ibara [39]	Aliphatic structures and oxygen-containing functional groups are gradually eliminated during pyrolysis, which is accompanied by a substantial increase in the concentration of aromatic hydrogen.
Lee [40]	Within the thermoplastic temperature range, the extensive cleavage of bridge bonds generates free radicals that are effectively stabilized through hydrogen transfer mechanisms, leading to enhanced formation of plastic mass.
Zhang [41]	Alkyl chains with reactive hydrogen sites enhance the supply of aliphatic hydrogen (AIH), which actively participates in the formation of plastic mass.
Cui [42]	Aliphatic and aromatic substituents are identified as the predominant factors governing the maximum fluidity temperature and re-solidification temperature during pyrolysis, which are critical process parameters for the caking property.

Table 1. Cont.

Authors	Contents of Research
Hammad [43]	The volatile compounds that are released from the vitrinite component of coal can be readily adsorbed by the porous structure of inertinite. This process leads to a reduction in the quantity of plastic mass, subsequently resulting in an increase in the caking property.
Chen [44]	Within the thermoplastic range, coal undergoes a series of chemical reactions—crosslinking, condensation, and re-polymerization—culminating in the depletion of oxygen. Consequently, this process facilitates the formation of condensed carbon-bearing crosslinking structures.
Soonho [45]	During early resolidification, structures of coking coal show a low degree of aromatic ring condensation and aromaticity but high CH_2/CH_3 .

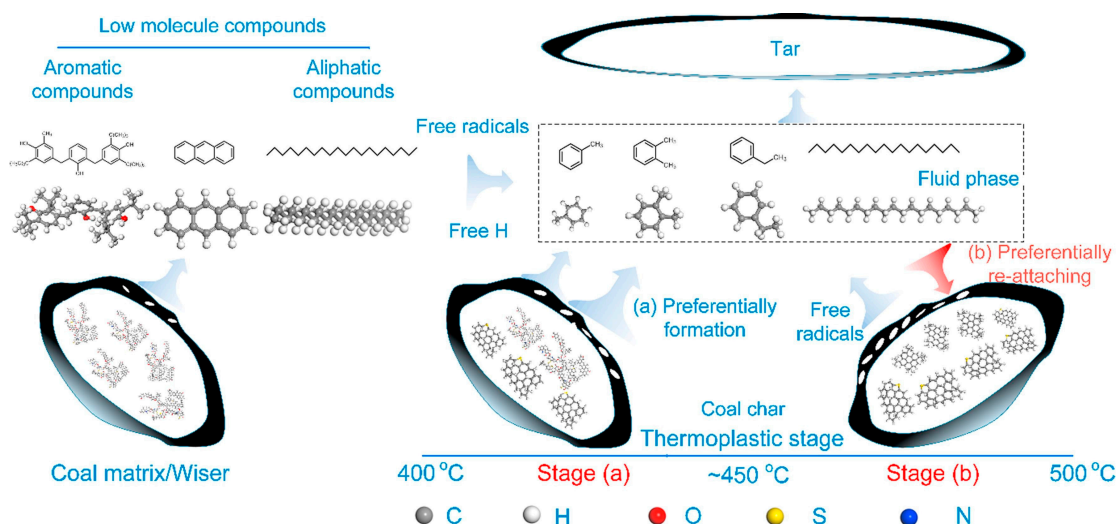


Figure 4. Mechanism of transformation of liquid in plastic mass [32].

2.2.2. Property of Plastic Mass

The main properties of plastic mass are thermal stability, permeability, fluidity, and expansibility [46,47]. (1) Thermal stability is typically quantified by the plastic temperature interval, which denotes the duration of stable existence for the liquid phase within the plastic mass. A broader plastic temperature interval correlates with prolonged stability of the plastic state, signifying enhanced thermal stability. Such improvement facilitates more extensive liquid-phase diffusion and ensures comprehensive interfacial contact among particles, thereby promoting caking formation. (2) Permeability relates to the resistance encountered by gases, produced during pyrolysis, as they attempt to escape through the plastic mass. Within a specified range, poorer permeability results in higher expansion pressure, thereby enhancing the likelihood of coal particles bonding with one another. (3) Fluidity is commonly quantified by $G_{R.I.}$, and elevated $G_{R.I.}$ values signify greater liquid-phase formation during the plastic state, which enhances fluidity and thereby optimizes interparticle void filling efficiency in coal blends. (4) Expansibility refers to the volumetric expansion resulting from gas evolution within the plastic mass. Typically, coals exhibiting high expansibility demonstrate a superior caking property.

The property of plastic mass is primarily influenced by the characteristics of coal, including the degree of coalification and macerals. Macerals encompass both organic and inorganic

components. The organic components predominantly originate from the organic matter of coal-forming plants, which can be further categorized into three distinct types: vitrinite, inertinite, and liptinite [48–50]. This study demonstrated that the volatile fraction yields, as well as the hydrogen, olefins, and alkane content of macerals, decreased in the sequence of liptinite, vitrinite, and inertinite [51–54]. Additionally, the carbon atoms in aromatic compounds are found to decline in the order of inertinite, vitrinite, and liptinite [55–57].

The pyrolytic property of macerals has a significant effect on the formation of coke [58,59]. This study demonstrated distinct pyrolysis reactivity among various components, decreasing in the order of liptinite, vitrinite, and inertinite [60,61]. Notably, the liptinite exhibited the highest de-volatilization reactivity, while the inertinite displayed the highest pyrolysis characteristic temperature. The vitrinite, which is the predominant component in coking coal, undergoes a transformation into the plastic mass during pyrolysis. Conversely, the liptinite, usually present in a lesser quantity, enables it to generate substantial volumes of tar and gas during the pyrolysis. The inertinite remains rigid throughout the pyrolysis and does not independently form coke, so its primary function is to serve as a structural framework. In conclusion, the vitrinite is pivotal in determining the properties of plastic mass [62,63].

The maceral components of coal have a significant impact on various properties of coal, and based on this, multiple evaluation methods have been developed. Among them, vitrinite reflectance (VR), which is defined as the percentage of incident light reflected from a polished vitrinite surface, is the most definitive maturation parameter for characterizing the maturation process of coal [64,65]. The mean maximum vitrinite reflectance (MMVR), one of the most important types of VR, is widely recognized as an important and effective means to evaluate the potential utility of coal in a range of applications [66]. It is worth noting that vitrinite is the main active component of coking coal, forming a non-volatile plastic layer during pyrolysis. The vitrinite has a higher thermoplastic property and contains more volatile matters, and it has a lower degree of shrinkage of aromatic compounds and a greater number of hydroxyl groups [67]. Therefore, researchers have attempted to use VR to characterize the caking property. Studies have found that VR and the caking property of coal show a parabolic trend. When the MMVR is around 1.1%, the coal exhibits the strongest caking property. The further the reflectance deviates from 1.1%, the weaker the caking property becomes, until it disappears entirely [68].

2.3. Evaluation Indexes of Caking Property

Researchers propose multiple evaluation indexes to assess the strength of the caking property in detail, focusing particularly on thermoplasticity and the coking property exhibited during the caking process.

1. **Thermoplasticity:** Thermoplasticity denotes the capacity to undergo flow deformation upon heating while retaining the shape post-cooling. Variations in this property directly affect characteristics of the plastic mass during pyrolysis, consequently differentiating pore–wall structures of coke formed through flow deformation and solidification. Based on this definition, evaluation indexes of thermoplasticity are divided into two categories. The first involves indirect determination through the shape and strength of coke, such as the crucible swelling number, Gray–King assay, and G_{RL} , and the second category directly quantifies the properties of plastic mass, such as Oya expansion, Gieseler fluidity, and Y_{max} [27,69,70].
2. **Coking property:** The coking property refers to the capability to form coke of a specific lump size and strength under coking or simulated coking conditions. There are two distinct perspectives on the measurement of the coking property. The first perspective suggests that the plastic mass, as measured under simulated industrial coking heating rates, can serve as an effective measurement. Conversely, the second perspective posits

that parameters such as the compressive strength of coke, obtained by simulating the coking process, can be utilized as a metric for measurement.

Commonly utilized evaluation indexes, as well as measuring methods, are summarized in Table 2. These indexes are measured to calculate parameters such as variations in plastic mass, shape, and the compressive strength of coke by simulating the caking process. The measuring methods of some indexes are efficient, which can realize the purpose of quickly determining the strength of the caking property. However, the ability to distinguish strongly caking coal from weakly caking coal is poor. Furthermore, some indexes are subjective and lack rigorous quantitative definitions. Collectively, these indexes pertain only to the specific evaluation of a single characteristic within the caking process. The interrelationships among them remain undetermined, precluding a comprehensive and precise evaluation of the caking property. To address this issue, researchers have undertaken studies examining the correlation between these indexes. Qin [71] found that both $G_{R.I.}$ and Y_{max} have a good linear relationship with the content of the medium component. The researchers employed binary linear regression analysis to derive the correlation equation between $G_{R.I.}$ and Y_{max} . The equations derived exhibit some inconsistencies in certain parameters, attributable to the differences in coal used [72]. However, it is noteworthy that the relationships between these parameters consistently exhibited positive correlations. Furthermore, the research revealed that Y_{max} exhibits a near-linear relationship with the maximum characteristic temperature, maximum shrinkage, and maximum Oya expansion. Nevertheless, the correlation of evaluation indexes was confined to a specific type of coal. Given the diversity of coal, accurately determining the correlation for each evaluation index remains elusive.

The existing indexes are insufficient to evaluate the weakly caking coal comprehensively. Therefore, forming an efficient method to accurately and comprehensively evaluate the caking property is a prerequisite for the clean and efficient utilization of weakly caking coal.

Table 2. Evaluation indexes utilized for caking property [27,69,70,73–76].

Evaluation Indexes	Measuring Methods	Contents of Evaluation	Advantages	Disadvantages
Characteristic of char residue (CRC)	After the determination of volatile matter, coal samples are transformed into coke and remain within the crucible. Subsequently, they are categorized based on the shape of the coke residue.	Ability of coal to bind itself	Operational simplicity and rapid experimentation	Lack of strict quantitative concept
Crucible swelling number	Place a specified mass of coal samples in a specialized crucible and subject them to rapid heating (400 °C/min) to 800 °C. The resulting coke is then compared with standard coke to determine its crucible swelling number.	Expansibility and caking property of coal	Operational simplicity and rapid experimentation	Highly subjective and poorly able to discriminate between strongly caking coal

Table 2. Cont.

Evaluation Indexes	Measuring Methods	Contents of Evaluation	Advantages	Disadvantages
Gray–King assay	Coal samples are subjected to a heating process up to 600 °C in a high-temperature-resistant tube, with a rate of temperature increase maintained at 5 °C/min, in isolation from air, and held for a duration of 15 min. Subsequently, the coke residue preserved within the tube is evaluated against a standard coke type to ascertain its classification.	Expansibility and coking property of coal	Rapid experimentation	Complexity of measuring method
Roga index	A mixture of 1 g of bituminous coal and 5 g of anthracite with a particle size of 0.3–0.4 mm is rapidly heated to produce coke. The strength of the resulting coke is evaluated using a drum of defined specifications. Subsequently, the index is determined using a pre-established formula.	Ability of bituminous coal to bind inert additives (anthracite) when subjected to heat	Operational simplicity and rapid experimentation	Inaccurate results for strongly caking coal and weakly caking coal
G _{R.I.}	A mixture of 3 g of bituminous coal and 3 g of anthracite with a particle size of 0.1–0.2 mm is rapidly heated to produce coke. The strength of the resulting coke is evaluated using a drum of defined specifications. Subsequently, the index is determined using a pre-established formula.	Ability of bituminous coal to bind inert additives (anthracite) when subjected to heat	Expanded the application range of the Roga index and reduced errors	Insufficient ability to differentiate between strongly caking coal
Oya expansion (Audibert–Arnu method)	Coal samples are shaped into coal pencils and positioned within expansion tubes, to which expansion rods are attached, then heated to 500–550 °C with a steady rate of 3 °C/min in a furnace preheated to 330 °C. Subsequent calculations of expansion and shrinkage are based on the maximum rise distance of the expansion rod.	Permeability and expansibility of coal	Distinguishes between coals of medium caking and above	Inaccurate results for strongly caking coal
Y _{max}	The coal sample is positioned within a coal cup and subsequently placed in a heating furnace, then heated at a steady rate of 3 °C/min. The thickness of the gelatinous layer, observed between the softening and curing points, is measured using a probe to determine the maximal plastic-layer thickness.	Quantity of plastic mass generated by coal	Visualizing the quantity of plastic mass	Highly subjective and unable to measure the property of plastic mass

Table 2. Cont.

Evaluation Indexes	Measuring Methods	Contents of Evaluation	Advantages	Disadvantages
Gieseler fluidity	Coal sample with a particle size of 0~0.43 mm is placed into a crucible. The stirring paddle is then rotated using a consistent torque (100 g·cm), while the crucible is heated at a steady rate of 3 °C/min. As the temperature escalated, the fluidity of the plastic mass altered, necessitating adjustments in the rotational speed of the stirring paddle, which is utilized to calculate the Gieseler fluidity.	Thermal stability, permeability, fluidity, and expansibility of plastic mass	Better ability to differentiate between different coals	Poor reproducibility and high costs
Swelling pressure	Depending on coal type, preparation method, and heating conditions, each coal develops a certain swelling pressure. Listed here is a measurement method for reference: Rapidly heat 2 g coal sample compressed at 218 MPa and constant 500 °C. Then, determine the swelling pressure dynamics in the context of 2 MPa initial external load.	Ability of coal to exert pressure within the limiting surface when heated in the fixed volume	Highly valuable for industrial applications	Complexity of measuring method

3. Regulation Technologies for Weakly Caking Coal

Through the utilization of rapid heating treatment [20], hydrogenation modification [21,22], the additive method [77], and other advanced technologies, the caking property can be significantly enhanced, resulting in the production of superior-quality coke. Furthermore, blending with non-caking fuels [24], pre-oxidation [15], and other technologies can reduce the caking property, which can solve problems in applications, such as defluidization in a fluidized bed.

3.1. Enhanced Caking Property

3.1.1. Rapid Heating Treatment

During the 1970s, it was ascertained that rapid heating treatment could enhance the caking property of coal. Yoshida [78,79] heated the coal to the thermoplastic temperature (400~500 °C) with a heating rate greater than 100 °C/min and found that the caking property was significantly enhanced. Research [80] involved conducting heat treatment on coals with varying caking properties at different heating rates. The results suggested that an increase in the heating rate was linked to an enhancement in the caking property. Furthermore, under equal treatment settings, the enhancement in the caking property of weakly caking coal was more significant than that of strongly caking coal. Saito [81] introduced a theory pertaining to the depolymerization of coal molecules, positing that an increase in the heating rate could expedite the cleavage of crosslinked bonds and thereby foster macromolecular depolymerization. Matsuura [82] further explored the alterations in coal's molecular structure at elevated heating rates, utilizing Nuclear Magnetic Resonance techniques. The findings revealed an enhancement in the fluidity of the molecular structure, concurrently with a relaxation in the aggregation structure. Zhang [41] comparatively ana-

lyzed caking property changes at different heating rates and proposed new interpretations for the mechanism underlying rapid heating's influence on the caking property, which is shown in Figure 5. Rapid preheating-induced depolymerization ruptured non-covalent bonds within coal macromolecules, reducing the crosslinking density and loosening the structure while generating additional high-mobility components. Substantial quantities of aliphatic chains on aromatic rings were cleaved, particularly alkyl chains containing hydrogen active sites. This cleavage resulted in an increased presence of AIHs, which allows for a greater participation in the formation of the bonding phase. The synergistic impact of the aforementioned reactions results in an increased quantity of plastic mass with improved fluidity, thereby enhancing the caking property.

Research had indicated a correlation between the caking property and the content of oxygen-containing functional groups (OCFGs). Building on this, Cui and his team [83] devised a low-temperature rapid pyrolysis (LTRP) treatment aimed at enhancing the caking property. This was achieved through a reduction in the content of OCFGs. The study demonstrated that the content of volatile matter and OCFGs was diminished as the temperature increased under an N₂ atmosphere. Concurrently, the pore volume exhibited a decreasing trend, followed by a slight increase with rising temperature. Furthermore, G_{R.I.} peaked at 410 °C before subsequently decreasing. Liu [20] employed the LTRP treatment on non-caking sub-bituminous coal, utilizing a heating rate of approximately 80 °C/min and selecting N₂ as the atmosphere. The findings revealed that G_{R.I.} rose progressively with an increase in temperature, peaking at 450 °C. This revealed that the LTRP treatment had the potential to enhance the caking property, and additionally, there was an optimal temperature for this process. The modification process of LTRP treatment proposed based on the aforesaid research content is displayed in Figure 6. Volatiles were released when a portion of OCFGs on the coal detached during LTRP treatment. Simultaneously, certain AIHs binding to the free radicals were generated by macromolecular splitting, thereby preventing a significant reduction in the number of free radicals. The caking property was enhanced by the synergistic effect of these processes.

3.1.2. Hydrogenation Modification

The property of the plastic mass is strongly correlated with hydrogen. As a result, researchers have implemented water vapor and hydrogen to thermally treat coal, thereby achieving hydrogenation modification and enhancing the caking property [84–86]. Shui [21] injected water vapor at different temperatures into the reactor at a controlled rate of 5 mL/min to subject sub-bituminous coal to heat treatment. The related parameters changed during this process are detailed in Table 3. After one hour of treatment, G_{R.I.} exhibited an initial increase followed by a decrease as temperature rose. Moreover, it reached a maximum value of 42.4 at 150 °C, significantly exceeding the baseline measurement of 34.6 for raw coal. Coking experiments conducted on the treated coal demonstrated an improvement in the strength of coke. The removal of OCFGs from coal molecules was facilitated by hydrogenation modification. Furthermore, this process facilitated the degradation of macromolecules, which in turn allowed the coal to generate an increased quantity of hydrocarbons.

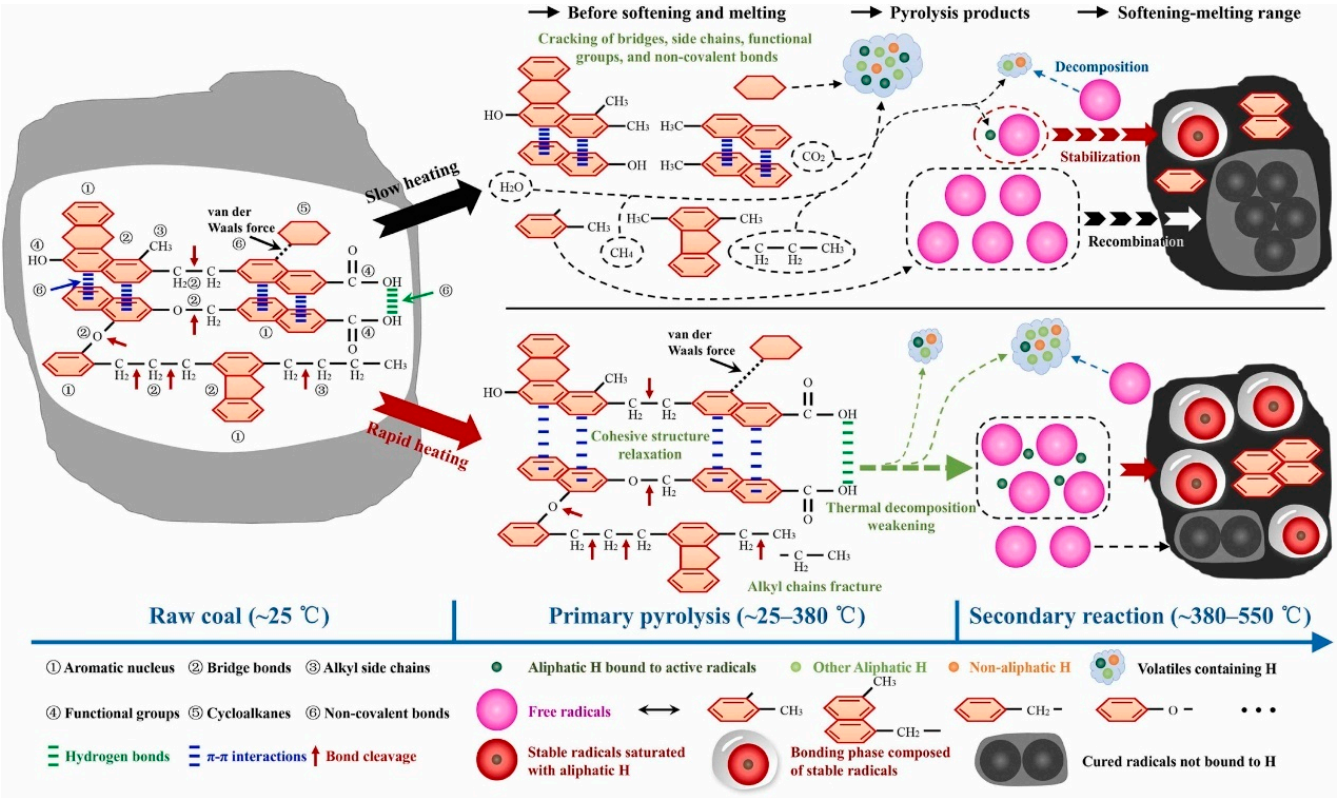


Figure 5. Mechanism of rapid heating enhancing the caking property of coal [41].

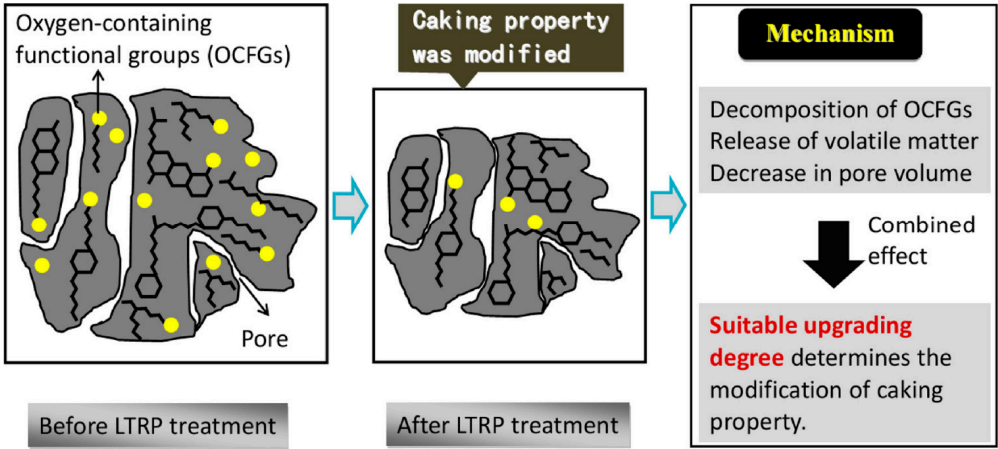


Figure 6. Modification mechanism of LTRP treatment [20].

Table 3. Related parameters changed during hydrogenation modification [21].

Samples	Temperature (°C)	G _{R.I.} ¹	Extraction Yield _{daf} (wt.%)	V _{daf} (wt.%)
Raw coal	/	34.6	4.8	38.3
1#	100	38.4	10.3	36.5
2#	150	42.4	15.2	31.4
3#	200	41.2	16.0	30.2
4#	250	39.2	15.6	28.7

¹ 1:1 by mass ratio blending with a standard rich coal (G_{R.I.} is 98).

Zhao [22] discovered that the hydrogenation modification of lignite within a subcritical water–CO system had the potential to disrupt covalent and hydrogen bonds. This

disruption promoted the rearrangement of aromatic rings, resulting in the formation of larger aromatic free radicals that subsequently reacted with hydrogen to form the plastic mass.

3.2. Reduced Caking Property

Although weakly caking coal can produce coke with a higher compressive strength after its caking property is enhanced, strongly caking coal still has much greater value for practical application in the coking sector. However, from the perspective of reserves and price, weakly caking coal, which is more abundant and cheaper, is more suitable for gasification and combustion. Yet during gasification, weakly caking coal tends to cause agglomeration. For this reason, addressing agglomeration by reducing the caking property not only expands the raw material sources for gasification technologies but also broadens high-value utilization pathways for weakly caking coal. Ultimately, this promotes the efficient and rational utilization of coal resources.

3.2.1. Mechanical Breaking

The agglomerates will be produced during the gasification of weakly caking coal in a fixed bed. This not only affects the reaction process but also hinders the gasifier's ability to discharge slag efficiently. Mechanical breaking has been suggested as a solution to this issue. The researchers employ a probe or a stirring device that is affixed at the bottom of the gasifier to physically disassemble the resulting coke lumps [24]. Mechanical breaking is appropriate for coal varieties with a $G_{R.I.}$ of less than 50 [23]. Although mechanical breaking is an uncomplicated process, the structural design restricts its applicability to a fixed bed. Additionally, there is the challenge of attaining processing capacities that are sufficient to satisfy the demands of industrial production.

3.2.2. Pre-Oxidation

The primary objective of pre-oxidation is to reduce the caking property of coal by pre-treating it with oxygenated gas at a specific temperature. Table 4 provides a comprehensive overview of a few investigations on pre-oxidation. The reduction in caking property can be influenced by parameters such as the content of oxygen, temperature, and duration.

Table 4. Advances in pre-oxidation research.

Authors	Contents of Research
Forney [87]	When strongly caking coals were heated to 120~250 °C in air and kept for a certain time, the caking property decreased significantly with increasing temperature and time.
Gasior [88]	The caking property could be drastically reduced by using an inert gas with 1% oxygen by volume, maintaining the coal at the softening temperature for 1~3 h, and then slowly heating it to the plastic temperature range.
Forney [89]	The pre-oxidation of coal using an inert gas containing 0.2% oxygen by volume, conducted at temperatures between ~400 and 425 °C, demonstrated a significant reduction in the caking property.
Ren [90]	A lower oxygen concentration delays the heat flow curve, raises the characteristic temperature, and slows the oxidation reaction. In contrast, smaller coal particle sizes increase heat release intensity.
Zhao [25]	The temperature, gas flow rate, and oxygen volume fraction of pre-oxidation had a more pronounced effect on the caking property.
Zhao [19]	The jetting pre-oxidation fluidized bed gasification technology could be applied to achieve stable gasification of coal with a $G_{R.I.}$ of 20.

Throughout the process of pre-oxidation, the concentration of hydrogen radicals within the coal steadily diminishes, while the number of OCFGs gradually increases. Orchin and

Sanchez [91,92] proposed that the formation of oxygen-containing linkages during the pre-oxidation influenced the fluidity of plastic mass. Ignasiak [93] likewise proposed that OCFGs formed during pre-oxidation constituted the primary factor reducing the caking property. However, there were different views on the main functional groups that influence the caking property. Rhoads [94] proposed that the reduction in AIHs was responsible for the decrease in the caking property, while Painter [95] suggested that the ether groups generated therein were the main influencing factor. Liotta [96] also found that a large number of crosslinked structures caused by ether groups were generated in the coal after pre-oxidation. Conversely, Larsen [97] deduced that the emergence of ether groups did not correlate with a reduction in the caking property. Wang's experimental results [98] proposed that this reduction should be the outcome of a combined effect of various factors within the structure. Furthermore, Nakagawa [99] employed mass spectrometry and in situ infrared spectroscopy to investigate the alterations in distinct functional groups during pre-oxidation. The findings revealed that aliphatic groups underwent selective oxidation to form aldehydes, which were subsequently oxidized to carboxyl, carbonyl, and ester groups.

In addition, some researchers targeted the variations in the pore structure and pyrolysis property. Ruiz [100] conducted a pre-oxidation of the coal at 270 °C, followed by an examination of the pore structure. The results indicated that the coal samples underwent a transformation into semi-coke, which was distinguished by its porous structure. Moreover, there was a noticeable increase in the number of micropores corresponding to an extended duration of treatment. Zhao [25] conducted a study on the pre-oxidation of coal using a fixed bed and performed pyrolysis tests on the treated samples. The results suggested that the proportion of heavy oil in the tar decreased, while the proportion of light oil increased. This may be attributed to the fragmentation of the aliphatic branched chain resulting from its reaction with oxygen during pre-oxidation. Furthermore, pre-oxidation improved the pore structure and decreased the release time of volatiles, which led to an increased gas yield. Overall, the aromatic structure is generally relatively stable during pre-oxidation, whereas the aliphatic branched chains and bridge bonds endure a breakdown in response to oxygen. This process leads to a decrease in AIHs and an increase in OCFGs. Concurrently, the degree of crosslinking increases, resulting in the formation of larger molecular structures by connecting small and medium-sized molecules.

In addition to the intrinsic mechanism, researchers have also designed pre-oxidation processes that can be utilized for industrial production. Among them, the decaking of coal in free fall [101] and the jetting pre-oxidation fluidized bed gasification (JPFBG) technology [15,19,102] are representative. The decaking of coal in free fall entails exposing coal to water vapor infused with 5.5% to 12.7% oxygen, at a temperature range of 560 to 580 °C, for a duration of 2 s. Subsequent to this treatment, the sample is cooled utilizing an inert gas, resulting in a product devoid of the caking property. The JPFBG technology decouples the gasification process into two sub-processes: pre-oxidation and semi-coke gasification. A schematic diagram of JPFBG technology is illustrated in Figure 7a. In this process, quantitative air transports the pulverized coal into the pre-oxidation zone of the fluidized bed, where a high temperature and oxygen-containing atmosphere are utilized to achieve pre-oxidation. This not only transforms the coal into semi-coke but also reduces the caking property. Upon falling into the gasification zone, semi-coke is contacted with and reacted to the gasification agent, a process that generates high-temperature gas. This gas subsequently provides energy for the pre-oxidation zone. Importantly, the spatial separation of pyrolysis and gasification ensures that the inhibitory effects of pyrolysis gas on gasification are effectively mitigated, thereby enhancing the overall efficiency of gasification.

Previous research systematically investigated JPFBG technology's impact on decaking, focusing on the reaction temperature, excess air ratio (ER), and O₂ concentration in the

pre-oxidation zone [15,19,101]. The operational conditions for fully decaking the tested coal were a temperature above 950 °C and ER above 0.1. Based on this, a 150 kg/h pilot JPFBG system successfully achieved efficient gasification and utilization of weakly caking coal, with $G_{R.I.}$ values of 12 and 20. These results indicate that the JPFBG technology enables the efficient gasification application of weakly caking coal. However, the oxygen in the pre-oxidation zone, while providing pre-oxidation effects for coal, burns part of the combustible gases in the produced gas, reducing both the carbon conversion efficiency and calorific value of gas. Therefore, more in-depth research should be conducted on this issue.

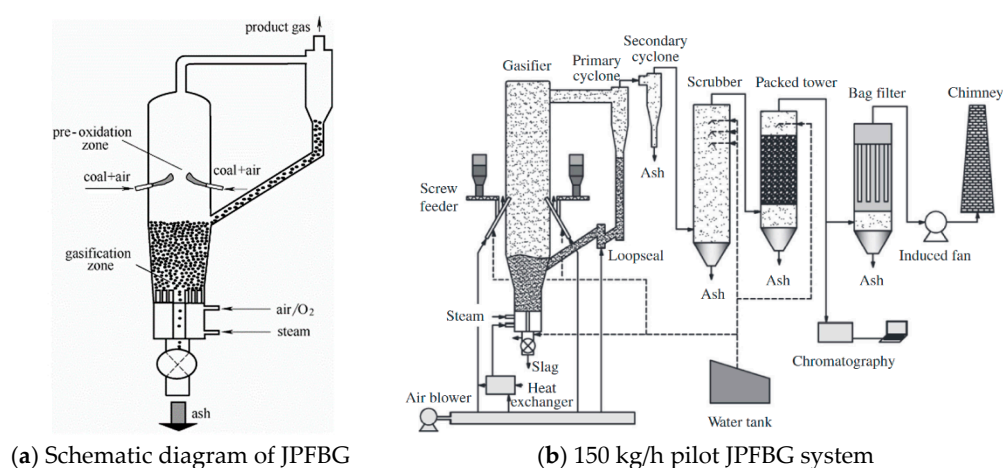


Figure 7. Schematic diagram and test platform of JPFBG technology [15].

3.2.3. Other Technologies of Decaking

In addition to regulation technologies such as mechanical breaking and pre-oxidation, other technologies available for the reduction in the caking property are listed in Table 5.

Table 5. Introduction to technologies of decaking.

Technologies	Introduction	Evaluate
Blending with non-caking fuels [24]	Blending the weakly caking coal with non-caking fuels in specific proportions to change the caking property.	The caking property changes nonlinearly after blending and this method is less economical.
Additive method [103]	- Additives are added during weakly caking coal gasification or combustion to promote oxidation reactions for decaking. - Cellulose used as an additive negatively affects plastic layer formation, above all quantitatively. Adding cellulose and replacing the coal portion in the load increase the release of OCFGs in pyrolysis [74].	Due to the poor effect of decaking when the additive is used alone, it needs to be used in conjunction with other technologies.
Extraction [71]	Components with caking property can be extracted from coal by organic solvents (CS_2 -NMP).	The extraction process significantly impacts the structure of residual organic components. Moreover, extractants present issues including high costs and environmental pollution.

Table 5. Cont.

Technologies	Introduction	Evaluate
Weathering [93]	The oxidation of weakly caking coal at ambient temperature with natural air can effectively reduce the caking property.	While this method is cost-effective and straightforward to implement, it necessitates a more extended processing time.
Low-temperature pyrolysis treatment (LTPT) [104]	When coal is heated to a specified temperature at a slow heating rate within an inert atmosphere, the aliphatic ester compounds and long-chain aliphatic are effectively reduced. This process subsequently minimizes the formation of plastic mass.	LTPT consumes organic components and has a certain amount of energy consumption, which makes it less economical.

3.3. Shortcomings in Regulation Technologies

All of the above technologies can realize the regulation of the caking property but still have the following shortcomings:

1. On the one hand, existing technologies require energy consumption to regulate the caking property, such as heating to a specific temperature. On the other hand, they will also decrease the volumetric weight and volatile matter content of coal.
2. Prior research has mostly focused on the variations in coal components, such bridge bonds and functional groups associated with the plastic mass. The impact of pretreatment on coal kinetics and activity, however, has received very little attention.
3. Research in this field has primarily focused on the effects of parameters such as the temperature, heating rate, and atmosphere on the caking property. However, the influence of a scale effect, specifically the particle size of coal, has seldom been examined.
4. Partial regulation technologies exhibit a significant impact on both strongly caking coal and non-caking coal. However, this effect becomes less pronounced when applied to weakly caking coal.

4. Conclusions and Prospects

4.1. Conclusions

This paper provides a comprehensive examination of the caking mechanism and evaluation indexes, followed by a thorough review and critical analysis of regulation technologies. Main conclusions and prospects are presented as follows:

1. The caking mechanism primarily outlines the specific process involved in the transformation of coal into coke. During pyrolysis, the active component generates the plastic mass, in which gas, liquid, and solid phases coexist. With an increase in temperature, the liquid phase is diminished gradually, causing the inert components to bond. Therefore, the strength of the caking property is mainly determined by the plastic mass.
2. Evaluation indexes such as CRC, $G_{R.I.}$, and Y_{max} can be utilized to distinguish the strength of the caking property and clarify the type of coal. However, due to the complexity of the caking mechanism and measuring conditions, the existing evaluation indexes can only be utilized to assess the caking property under specific circumstances, and they cannot perform an accurate assessment in actual applications.
3. Technologies such as rapid heating treatment and hydrogenation modification can increase the amount of plastic mass generated, thereby improving the caking property. Technologies such as mechanical breaking and pre-oxidation reduce the caking property by destroying agglomerates or consuming plastic mass.

4.2. Future Work

1. Regarding research on the mechanism of coal caking, future efforts should focus on breakthroughs in the visualization of the caking process and the accurate identification of key substances. Through dynamic characterization methods such as in situ thermal stage microscopy and real-time infrared imaging, the entire process from the onset of caking to the agglomeration of particles can be tracked. Combined with analytical methods such as thermogravimetric-mass spectrometry (TG-MS), caking-related substances can be accurately extracted and their chemical composition, microstructure, and formation path can be clarified.
2. Given that existing evaluation indexes mostly describe the caking property at the macro level, lacking micro-level mechanisms and quantitative characterization, follow-up research is needed to construct a multi-dimensional evaluation system covering basic coal quality parameters, reaction characteristics, and caking processes to achieve an accurate classification and prediction of the caking property.
3. In terms of the development of regulation technologies, on the one hand, energy loss caused by the pretreatment process can be reduced by optimizing the parameters of existing technologies. On the other hand, based on an in-depth analysis of the caking mechanism, low-energy and high-efficiency technologies should be developed for specific links in the production of key materials.

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Abbreviations

The following abbreviations are used in this manuscript:

V_{daf}	Dry ash-free basis
$G_{R.I.}$	Caking index
Y_{max}	Maximal thickness of plastic layer
CRC	Characteristic of char residue
OCFGs	Oxygen-containing functional groups
LTRP	Low-temperature rapid pyrolysis
JPFBG	Jetting pre-oxidation fluidized bed gasification
LTPT	Low-temperature pyrolysis treatment
AIH	Aliphatic hydrogen

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