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Study of hydrogen production from coal gasification in supercritical water

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Abstract. The coal supercritical water gasification technology is a new technology that directly converts coal into hydrogen, with advantages such as cleanliness, high efficiency, and low cost. With the global trend towards hydrogen energy development, the coal supercritical water gasification technology has broad application prospects. Research on this technology is significant for providing a new path for China's clean energy development, promoting sustainable development in the energy field, and contributing to global emission reduction and climate change response. This article analyzes the current development status of coal gasification technology, summarizes the related categories in four aspects: raw material selection, catalysts, reactors, and heating methods, and analyzes the unique advantages of each method. Based on this, a relatively efficient hydrogen production scheme is briefly selected. In addition, the future development trend of this technology is discussed. This article may provide a reference for clean energy development and the efficient utilization of coal resources.

Keywords: coal gasification, supercritical water, hydrogen production.

1. Introduction

As one of the most abundant energy resources in China, coal consumption accounts for 50% of the world's total in 2019, making China the largest coal-consuming country in the world. The consumption of coal results in a significant amount of carbon dioxide emissions, representing 29% of global emissions. High pollution, high emissions, and low efficiency present significant challenges to environmental protection and economic development. With the continuous growth of energy demand and increasingly severe environmental problems, hydrogen is gradually attracting attention as a clean and efficient energy source. As an important hydrogen production technology, the supercritical water gasification process can reduce CO_2 emissions by more than 90% and decrease SO_2 emissions by more than 99%. This hydrogen production technology is widely considered as an effective means to address the challenges of high pollution and emissions from coal and has significant implications for promoting the development of the hydrogen economy. The purpose of this paper is to analyze the reaction steps of the coal supercritical water gasification technology and summarize the relatively efficient scheme. This paper will delve into a comprehensive analysis of the coal supercritical water gasification technology in terms of four steps. From the perspectives of physical and chemical properties, impurities, raw material properties, and reactant requirements, this article analyzes the advantages and disadvantages of reaction materials in various applications. In terms of catalyst types, the benefits of metal catalysts, oxide

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catalysts, carbon material catalysts, phosphate catalysts, and composite catalysts are compared. Additionally, different types of reactors, such as spray bed reactors, circulating bed reactors, microwave heating reactors, and rotating bed reactors, are examined in regards to their corresponding production needs. Furthermore, four types of heating methods, including electric heating, microwave heating, fuel combustion heating, and heat exchange heating, are evaluated based on energy consumption and their compatibility with the reaction process. A comprehensive analysis of the coal supercritical water gasification technology is presented, summarizing existing research findings and development trends, and providing a reference for further research and application in order to promote the development of the hydrogen economy.

2. Reaction principle

Supercritical water gasification of coal is a technology that reacts coal and other carbonaceous resources with water under high temperature and pressure to produce hydrogen gas [1]. Supercritical water refers to a series of characteristics, such as a significant decrease in density, a remarkable reduction in viscosity, and a significant decrease in dielectric constant, under high temperature and high pressure. It has higher solubility and reactivity than conventional water, as well as high heat transfer efficiency, high speed, no need for expensive catalysts, and mild reaction conditions. It can accelerate the gasification reaction of coal.

Using the special properties of supercritical water (temperature >374.1 ℃, pressure >22.1 MPa), such as low dielectric constant and high solubility, supercritical water is used as the reaction medium, and coal undergoes fast and efficient homogeneous gasification reaction in supercritical water. The carbon and hydrogen elements in coal are directly gasified and converted into CO_2 and H_2, while some of the supercritical water is also hydrolyzed to H_2. Elements such as N, S, and heavy metals in coal are mineralized and deposited in the solid residue at the bottom of the reactor.

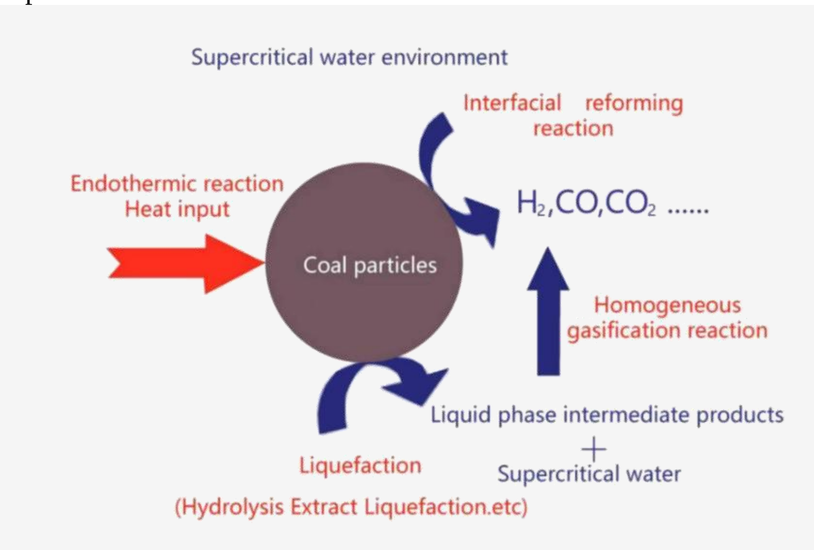

Figure 1. Complex homogeneous and heterogeneous process [2].

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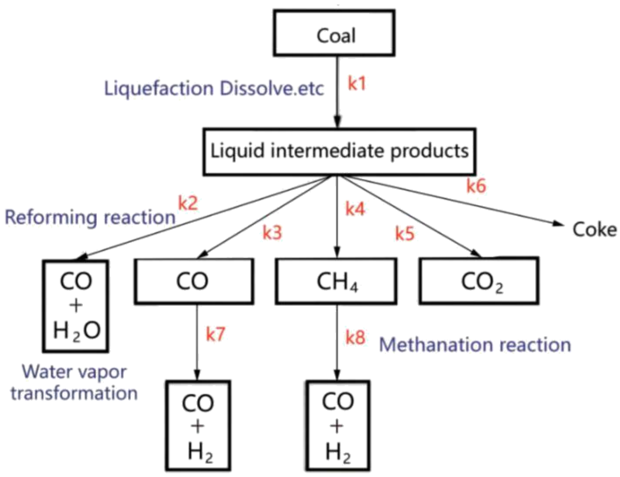

Figure 2. Hydrogen production from coal supercritical water gasification. Total parameter model [2].

Supercritical water refers to a series of characteristics, such as a significant decrease in density, a remarkable reduction in viscosity, and a significant decrease in dielectric constant, under high temperature and high pressure. It has higher solubility and reactivity than conventional water, as well as high heat transfer efficiency, high speed, no need for expensive catalysts, and mild reaction conditions. It can accelerate the gasification reaction of coal [3].

The main processes of coal supercritical water gasification for hydrogen production include four steps.

The first step is coal pyrolysis: Under high temperature and high pressure of supercritical water, coal undergoes pyrolysis reaction, producing a large amount of gas products, including methane, carbon monoxide, carbon dioxide, etc.

The second step is coal gasification: The carbonaceous part in coal reacts with water vapor to generate carbon monoxide and hydrogen gas, with the following reaction equation:

$$\mathrm{C(solid) + H_2O(gas) \rightarrow CO(gas) + H_2(gas)} \tag{1}$$

The third step is coal reduction: The non-carbonaceous part in coal undergoes reduction reaction in supercritical water to generate hydrogen gas, with the following reaction equation:

$$\mathrm{FeO(solid) + H_2O(gas) \rightarrow Fe(solid) + H_2(gas)} \tag{2}$$

The last step is the liquid product treatment: During the reaction process, some high molecular compounds and impurities are contained in the liquid products produced by coal, which need to be treated subsequently.

Through coal supercritical water gasification for hydrogen production, clean conversion and efficient utilization of coal can be achieved, which also has some advantages such as high reaction efficiency, mild reaction conditions, and high product purity. However, this technology also faces some challenges, such as the stability and purity of reaction products, optimization of reaction conditions, etc., which require further research and development.

3. Reaction steps

The supercritical water gasification of coal is a technology including four aspects: selection of raw coal, catalyst, reactor and heating methods [4]. The reaction process is mainly composed of four parts, and each step affects the purity of reaction gas and the production of final product. The different reaction products will affect the types of co-production methods with their own significance. Therefore, each step of these four parts is crucial for the overall reaction process.

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3.1. Selection of raw coal

3.1.1. The nature of the physical chemistry. The physical and chemical properties of the raw material coal, such as coal quality structure, moisture content, ash content, volatile matter, and fixed carbon content, directly affect the quality of the reactants and the composition of the products in the gasification process [5]. Higher moisture content leads to higher reaction temperature and more difficult control of coal drying, which may result in excessive water content in the products and reduce hydrogen production. Higher ash content leads to higher ash content in the products, which may cause catalyst deactivation and slow down the reaction rate. Pre-treatment methods such as drying can be used to reduce the moisture content of high moisture coal for better gasification reaction. Therefore, when selecting raw material coal, it is necessary to consider its physical and chemical properties, choose coal with low moisture content, low ash content, and high volatile matter.

3.1.2. Impurity elements Impurities in raw material coal, such as sulfur, nitrogen, and oxygen elements, have an important impact on the quality and yield of reaction products in the gasification process. Sulfur elements increase the content of hydrogen sulfide and sulfur dioxide in the products, which not only harm the environment but also damage the stability of catalysts. Nitrogen elements react with hydrogen to generate ammonia gas during the reaction process, which reduces the yield of hydrogen. Oxygen elements increase the content of carbon dioxide in the products, which reduces the yield of hydrogen. Therefore, when selecting raw material coal, impurities should be minimized as much as possible, and some sulfur-containing coal may need desulfurization treatment before the reaction to reduce the content of hydrogen sulfide and sulfur dioxide in the reaction products. For coal with high nitrogen and oxygen elements, pre-treatment with nitrogen and hydrogen gases is required to reduce the interference of nitrogen elements on the reaction.

3.1.3. Nature of raw materials. The type, quality, and source of raw material coal also affect the quality and yield of reaction products in gasification. Different types of coal may have different product compositions and yields during the reaction. The gas yield and energy yield of hard coal and brown coal are also different during the gasification reaction. Brown coal can undergo gasification reaction at lower temperatures, but the gas yield in its products is lower. In contrast, hard coal can undergo the reaction at higher temperatures, but requires higher reaction pressure and longer reaction time. In addition, the quality and properties of coal in different regions and mines also vary, so the selection of raw material coal needs to be based on the actual situation.

3.1.4. Reactant requirements. In the gasification process, in addition to raw material coal, some reactants such as water and catalysts need to be added. The requirements of these reactants also affect the selection of raw material coal. The purity of water affects the efficiency of the reaction and the quality of the products, so high-purity water needs to be used. The type and quality of catalysts also affect the efficiency of the reaction and the quality of the products, so suitable catalysts need to be selected.

The raw material coal has a significant impact on the quality and yield of reaction products in gasification. To achieve higher reaction efficiency and better product quality, it is necessary to consider the physical and chemical properties, impurities, characteristics, and requirements of reactants when selecting raw material coal.

3.2. Catalyst

The role of catalysts in coal supercritical water gasification for hydrogen production is to reduce the activation energy of the reaction, accelerate the reaction rate, and increase the conversion rate of the reaction [6, 7]. There are various types of catalysts available, and different catalysts may have different effects on the reaction. The following are some possible types of catalysts used in the reaction:

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3.2.1. Metal catalysts. Metal catalysts such as copper, iron, nickel, and other metals are commonly used catalysts in coal supercritical water gasification for hydrogen production.These metal catalysts can promote the gasification reaction,increase reaction rates,and hydrogen yield.In the coal supercritical water gasification reaction, metal catalysts can activate water and coal at reaction temperature, breaking their molecular bonds and transforming them into gaseous products, such as hydrogen and carbon monoxide. Additionally, metal catalysts can alter the kinetics and thermodynamic properties of the reaction to favor hydrogen production. However, metal catalysts may suffer from corrosion, carbon deposition, and other problems that need to be considered in practical applications.

3.2.2. Oxide catalysts. Oxide catalysts such as titanium, zirconium, aluminum, and other oxides can promote reaction rates, reduce activation energy, and improve reaction efficiency. In coal supercritical water gasification, oxide catalysts can act as oxidants to facilitate the reduction reaction during the reaction. Additionally, oxide catalysts can provide specific catalytic sites to facilitate reaction. Different types of oxide catalysts have different physicochemical properties and catalytic activity, which need to be selected based on reaction conditions and target products.

3.2.3. Carbon material catalysts. Carbon material catalysts such as graphene, carbon nanotubes, and other carbon materials can suppress coking reactions, improve reactor life [8]. In coal supercritical water gasification, carbon material catalysts can adsorb and catalyze species produced during the reaction, reduce species accumulation in the reactor, and avoid coke formation. Additionally, carbon material catalysts exhibit high chemical stability and heat resistance, making them suitable for high-temperature and high-pressure reaction conditions. However, carbon material catalysts also have some issues, such as low catalytic activity and large particle size, which require reasonable design and preparation to optimize catalyst performance.

3.2.4. Phosphate catalysts. Phosphate catalysts such as trihydroxymethyl aminomethane, aluminum hydroxide phosphate, and other phosphates can promote coal cracking, alter coal structure and composition [9]. In coal supercritical water gasification, phosphate catalysts can act as acid catalysts to accelerate coal cracking and gasification processes. Additionally, phosphate catalysts can alter the chemical properties of reactants, such as increasing the nucleophilicity of reactants, promoting their reaction. Different types of phosphate catalysts have different acidity and catalytic activity, which need to be selected based on reaction conditions and target products.

3.2.5. Composite catalysts. Composite catalysts such as Ni-Mo/γ-Al2O3, Ru/C, Co-Ni/Al2O3, and other composite catalysts have efficient and stable catalytic activity, which can improve reaction efficiency and hydrogen yield. In coal supercritical water gasification, composite catalysts can exert multiple catalyst effects, making the reaction more efficient and stable.

Different catalysts have different effects on the reaction. The selection of a catalyst requires comprehensive consideration of factors such as reaction conditions, target products, and catalyst properties, as well as evaluation and selection. At the same time, attention should be paid to potential issues during catalyst preparation and use, such as catalyst deactivation, coking, catalyst performance, and service life.

3.3. Reactor

In the coal supercritical water gasification process for hydrogen production, the reactor plays a crucial role in providing a reaction environment, controlling reaction parameters, and stabilizing the reaction process. Supercritical water is the reaction medium in the reactor, carrying coal and catalysts as reactants. By adjusting parameters such as temperature, pressure, and flow rate, the reactor can achieve the goals of mixing and transforming reactants, as well as separating and collecting products. Thus, the reactor is of paramount importance in the reaction process.

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3.3.1. Spray bed reactor. This reactor mainly utilizes the high temperature and high pressure of supercritical water and its excellent mass transfer performance to spray coal into supercritical water, and uses the action of oxidants to promote the coal oxidation-reduction reaction and generate hydrogen gas. The reactor has the characteristics of high reaction efficiency and fast reaction speed, but the spray technology requirements are high, and the reactor has strict requirements on the size and shape of coal particles.

3.3.2. Circulating fluidized bed reactor. This reactor consists of gas, liquid, and solid three-phase components[10]. After coal gasification reaction in supercritical water, the produced gas forms an internal circulation in the reactor, further promoting the coal gasification reaction. The reactor has high reaction temperature and pressure, fast reaction speed, but also has problems such as reactor blockage and poor equipment stability.

3.3.3. Microwave heating reactor. This reactor uses microwave heating to heat coal and supercritical water to promote gasification reaction and can also shorten the reaction time. The reactor has advantages such as high energy utilization efficiency and fast reaction speed, but requires modification of the microwave reactor, and the safety of microwave radiation on equipment and personnel is also a concern.

3.3.4. Rotating bed reactor. This reactor mainly uses the action of the rotating bed to mix coal and supercritical water, and through the centrifugal force of the rotating bed, separates the produced gas. The reactor has the advantages of high reaction efficiency and fast reaction speed, but the rotating bed requires high equipment stability, and the equipment cost is high.

In summary, the above several supercritical water gasification reactors for coal to produce hydrogen have their own advantages and disadvantages, and the selection and design need to be based on actual situations and needs.

3.4. Heating methods

The main function of the heating method is to provide the necessary heat for the reaction, raising the reaction temperature to the required range and promoting the transformation of reactants into hydrogen. Each heating method has its own advantages and disadvantages, so selecting the appropriate method is crucial for improving energy utilization efficiency and reducing production costs. Common heating methods include electric heating, microwave heating, fuel combustion heating, and heat exchange heating, each with its own benefits and drawbacks.

3.4.1. Electric heating. Electric heating is a traditional heating method that can convert electrical energy into thermal energy through resistive wires, electric heating rods, etc., to heat supercritical water and coal. Electric heating has the advantages of fast heating speed and high heating efficiency, but the equipment cost is relatively high.

3.4.2. Microwave heating. Microwave heating is a very effective heating method that can transfer energy to supercritical water and coal through microwave radiation, thereby promoting gasification reactions. Microwave heating has the advantages of fast heating speed, high energy utilization efficiency, and short reaction time, but it requires modification of the microwave reactor, and the safety of microwave radiation for equipment and personnel is also a concern [11].

3.4.3. Fuel combustion. Heating Fuel combustion heating is a common heating method that can heat supercritical water and coal through the heat generated by fuel combustion. Fuel combustion heating has the advantages of high heating efficiency and low equipment cost, but the exhaust gas emissions and fuel supply need to be considered.

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3.4.4. Heat exchange heating. Heat exchange heating is a method of heating using the principle of heat conduction. It can heat coal by conducting high-temperature and high-pressure supercritical water to the coal through a heat exchanger. Heat exchange heating has the advantages of high energy utilization efficiency and uniform heating, but the efficiency of heat conduction and the pressure resistance of equipment also need to be considered.

For coal supercritical water gasification hydrogen production, the choice of heating method needs to consider multiple factors, including reaction speed, energy utilization efficiency, equipment cost, etc. Depending on the specific situation, a suitable heating method can be selected to achieve the development and application of efficient and sustainable coal supercritical water gasification hydrogen production technology.

4. Discussion

Supercritical water gasification of coal for hydrogen production is a complex reaction process that requires consideration of multiple factors [12]. It can be concluded that the solid carbonaceous portion of the raw coal is the main source of hydrogen gas, while the non-carbonaceous portion will affect the composition and quality of the reaction products. Therefore, using low ash, low sulfur, and low nitrogen coal as raw materials can reduce the impurity content in the products, improve their quality and purity. Catalysts can promote reaction rate and selectivity, thus enhancing product quality and purity. For coal supercritical water gasification, some metal catalysts such as nickel, iron, and cobalt are widely used. Among them, nickel catalysts have high catalytic activity and stability, effectively promoting gasification and reduction reactions, and increasing hydrogen yield and selectivity.

The selection of the reactor needs to consider factors such as reaction conditions such as temperature, pressure, and flow rate, as well as ensuring the sealing and stability of the reactor. In terms of heating methods, the use of a high-pressure high-temperature reactor is necessary, while considering mass and heat transfer issues within the reactor to improve reaction efficiency and product quality. Traditional heating methods include electric and flame heating, but these methods have energy loss and safety hazards. In contrast, microwave heating is an efficient, fast, and controllable heating method that can improve reaction efficiency and product purity.

5. Conclusion

With the continuous increase in energy demand and the increasingly prominent problem of environmental pollution, hydrogen has attracted more and more attention as a clean and efficient energy source. Coal supercritical water gasification hydrogen production technology is a high-efficiency and low-cost hydrogen production technology. This article reviews four aspects of coal supercritical water gasification hydrogen production technology: raw material selection, catalyst, reactor, and heating method, and concludes that the best technical route is the combination of coal with low ash, sulfur, and nitrogen content, nickel catalyst, high-pressure and high-temperature reactor, and microwave heating method. This combination can improve reaction efficiency and product purity, achieving clean conversion and efficient utilization of coal.

Supercritical water gasification hydrogen production technology now has wide market applications in the industrial field. The harmful gas content in the exhaust gas produced is low in terms of carbon dioxide and sulfur dioxide, effectively reducing air pollution and greenhouse gas emissions. Moreover, using coal for hydrogen production fully utilizes China's resources in the coal concentration areas such as northern Shaanxi, Shanxi, and Inner Mongolia, and produces new energy that meets the environmental protection requirements of the new era. In the future, this technology will be further studied for optimization and upgrading to increase hydrogen production and quality. At the same time, the application of this technology in different fields will be further explored to expand its market prospects and economic benefits.

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