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Research on the Effects of Supercritical Water /CO_2 Mixed Environment on Biomass

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Abstract

The supercritical water/CO_2 mixed environment, through its unique physicochemical properties and synergistic effects, not only enables the decomposition of biomass but also the generation of energy gases and the capture of CO2, demonstrating a significant role in energy and high-value conversion. This paper studies the reactions of different biomass in a supercritical water /CO_2 mixed environment, systematically compares and analyzes the reaction results of various biomass, and ultimately concludes that CO_2 has the functions of improving thermal efficiency, hydrogen production and carbon sequestration in the supercritical water process.

Keywords

Supercritical Water; Carbon Dioxide; Biomass.

1. Introduction

With the acceleration of global industrialization, environmental issues have become increasingly prominent, and climate warming has become a common challenge faced by all mankind [1]. To address this crisis, in October 2018, the Intergovernmental Panel on Climate Change of the United Nations proposed the goal of "carbon neutrality" : to keep the global temperature rise within 1.5°C by the end of this century[2]. China's total energy consumption and carbon emissions rank among the top in the world. As a responsible major country, its low-carbon transformation is of vital importance to global climate governance. Therefore, China has put forward the "dual carbon" goals of striving to peak carbon dioxide emissions before 2030 and achieve carbon neutrality before 2060[3]. This commitment not only demonstrates the responsibility of a major country but also holds a milestone significance for the global response to climate change.

Supercritical water (SCW) refers to a unique fluid formed when the temperature and pressure are respectively above 374°C and 22 MPa. At this point, the density of water lies between that of liquid water and gaseous water, creating supercritical water[4]. Under supercritical conditions, water's properties are similar to those of a non-polar organic solvent. It can be miscible with organic substances and gases such as carbon dioxide, rapidly decomposing organic substances into small-molecule compounds within an extremely short period of time, ultimately forming gases such as CO_2, CO, H_2, CH_4, and low-carbon alkanes. Supercritical water technology utilizes the unique physical and chemical properties of supercritical water to effectively achieve the decomposition of biomass. The treatment of organic matter with supercritical water causes almost no secondary pollution after the treatment. Compared with other treatment technologies, it has the advantages of a wide treatment range, relatively simple process and good treatment effect, and thus has received extensive attention from scholars[5][6].

Under the current "dual carbon" background, the research direction of the SCWG process mainly focuses on exploring the influence laws of biomass gasification, while there is a lack of research on the application of CO_2 in the gasification of biomass by SCWG. If combustible energy gases can be generated on the one hand and CO_2 reduction and capture can be achieved on the other hand in the SCWG process, it will provide a new research idea for solving the current problems such as environmental deterioration and energy shortage.

2. Research on the Application of Biomass in a Supercritical Water /CO_2 Mixed Environment

Scholars at home and abroad have conducted extensive research on the interaction between supercritical water /CO_2 and biomass, covering a wide range of raw materials, and have made significant progress in reaction mechanisms and product regulation, such as:

Hu Yaping et al[7] used CO_2 with a purity of 99.999% as the reaction gas to conduct gasification research on urban sludge in subcritical water (360°C) and supercritical water (380-440°C) environments, successfully achieving the synergistic conversion of CO_2 and sludge to generate biofuels. Research has found that compared with N_2 atmosphere, CO_2 can significantly enhance the gasification efficiency of municipal sludge: as the reaction temperature rises, the gasification efficiency of sludge in CO_2 atmosphere increases sharply from 12.24% to 49.66%, and at 420°C, this efficiency is 9.35% higher than that in N_2 atmosphere. From the overall data perspective, the increase in sludge moisture content and reaction temperature can promote the growth of biogas production. In addition, CO_2 can react with water in the system to form carbonic acid, which not only increases the hydrogen concentration in the reaction system but also accelerates the hydrolysis of organic matter and the decarboxylation of organic acids by enhancing the acid catalytic effect, ultimately achieving an improvement in the quality of bio-oil.

In the study of CO_2-assisted co-pyrolysis of textile printing and dyeing sludge and super-accumulated bacteria biomass, SONG[8] et al analyzed the influence mechanism on the CO_2 reaction. The research results showed that CO_2 reduced the activation energy of the pyrolysis atmosphere. During the gasification process, it is not the case that the higher the CO_2 concentration, the higher the activation energy. The release of the C=O functional group is the maximum within the range of 0 to 400°Cin a CO_2 atmosphere. Copyrolysis assisted by CO_2 significantly alters the production pathway of biochar in a N_2 atmosphere. Compared with the strongest reaction temperature of 0 to 400°C under N_2 conditions, there is still a significant deviation at 400°C in N_2/CO_2 and CO_2 atmospheres. However, the strongest interaction occurs within the range of 500 to 1,000°C, indicating that co-pyrolysis in the presence of CO_2 has a significant impact on the reaction process in the gasification stage.

Yan M[9]et al conducted a study on the resource utilization of household kitchen waste (HKW). In the two-stage energy recovery process of hydrothermal carbonization (HTC) and supercritical water gasification (SCWG), it was found that HKW could be converted into potential solid fuel with an ignition temperature similar to that of lignite. Under HTC's 300°Cand a residence time of 75 minutes, energy-densified hydrogen-carbon (20.63MJ/kg) was obtained, at which point the highest fixed carbon and the lowest volatile substances were present.

Antonio[10] investigated the impact of CO_2 on the increase of syngas production during the supercritical water co-gasification of CO_2 and bagasse, and found that the increase in CO_2 concentration at the time of feed led to a decrease in H_2 production and an increase in CO production. Even at the lowest study concentration (15wt%), the addition of CO_2 led to a significant reduction in the molar ratio of H_2/CO, with an average reduction of 50% observed in all cases of temperature changes. However, no significant difference was observed in the total molar ratio of syngas produced at any concentration of CO_2.

Zhu[11] studied the Ni/Zro$_2$-catalyzed supercritical water hydrogen production from glycerol and found that 0.4Ni-0.6ZrO_2 (molar ratio) exhibited the highest activity in the forward WGSR, as its H_2 and CO_2 yields reached the highest. The H_2 yield was 155% higher than that without the catalyst, and the H_2 molar fraction was 32.6%. When no catalyst is used, it is only 14.4%, and the consumption ratio reaches the lowest. The 0.8Ni-0.2ZrO_2 (molar ratio) catalyst also demonstrated high activity in the forward catalytic conversion of water gas to CO. The Ni/ZrO_2 catalyst prepared by SCWS showed excellent performance stability and anti-coking ability for glycerol SCWG.

Zhao[12] et al quantitatively studied the relationship between biomass and biochar by selecting 12 common types of biomass (such as animal manure, waste wood, crops, and municipal waste) within the pyrolysis temperature range of 200°C to 650°C. The results indicated that the carbon content, carbon fixation, and carbon sequestration capacity of biochar were mainly controlled by the biomass raw materials.

Tian Chong[13] et al conducted supercritical water/CO conversion experiments under the conditions of simultaneously adding nickel-based catalysts and carbon sequeters (wollastonite). The results showed that when the initial pressure of CO was 6Mpa and the temperature was 400°C, the CO_2 mineralization efficiency reached the highest of 38.1%. When a catalyst is present, the efficiency of CO_2 mineralization increases because the reaction generates a higher concentration of H_2 and CO_2, which promotes the carbon fixation reaction between wollastonite and CO_2 and enhances the efficiency of CO_2 mineralization. Increasing the initial pressure of CO has a promoting effect on the carbon sequestration reaction, and the initial pressure of CO has a significant impact on the carbon sequestration efficiency.

Xie Zhengzhe[14] compared the carbon gasification efficiency of different catalysts for phenol gasification at 450°C for 10 minutes. The research found that after adding 10wt % of the Ni catalyst, the carbon gasification efficiency only increased to %. Adding 0.5Ru/CeO_2 and 1Ru/CeO_2 can increase the carbon gasification efficiency to 10% and 40% respectively, indicating that Ru has a significant impact on the carbon gasification efficiency. After adding 5Ni-1Ru/CeO_2, the carbon gasification efficiency increased to about 50%. The experimental results show that nickel has a good catalytic effect in supercritical water gasification. Bimetallic nanocatalysts have better catalytic effects than single-metallic nanocatalysts, which is due to the synergistic catalytic effect between nickel and ruthenium. Finally, the catalytic efficiencies of Co-Ni/AC, Ni-Co/AC and Mix/AC bimetallic nanocatalysts are not the same, which means that the effects of catalysts made by different methods are different. The Co-Ni/AC catalyst has the highest CH_4 production, reaching 30mmol/g, which is almost twice that of the Ni-Co/AC catalyst.

Yuan[15] et al prepared biochar from Isatidis Radix under pyrolysis temperatures ranging from 300°C to 700°C with a residence time of 10 minutes to 180 minutes. They found that increasing the pyrolysis temperature and extending the residence time could reduce the content of volatile substances, enhance carbon enrichment, and generate aromatic structures by lowering the H/C ratio. The biochar produced can exist more stably in the soil.

3. Conclusion

The supercritical water/CO_2 mixed environment, through its unique physicochemical properties and synergistic effects, not only enables the decomposition of biomass but also the generation of energy gases and the capture of CO_2, demonstrating a significant role in energy and high-value conversion. The influence mechanism of this article can be summarized as:

1) Enhance reaction efficiency. During the supercritical water gasification process of different biomass samples, the yields of H_2, CH_4 and CO increased significantly, proving that CO_2 has a significant impact on the degradation of biomass.

2) Hydrogen production. CO_2 can react with water in the system to form carbonic acid, increasing the hydrogen concentration in the reaction system and facilitating the generation of hydrogen.

3) Carbon sequestration. The addition of CO_2 can improve the gasification reaction of oily sludge and store CO_2 in the form of stable carbon in the solid-liquid phase products, thereby enhancing the stability of biomass.

Although many scholars have carried out corresponding research at present, it is still impossible to apply it on a large scale industrially due to problems such as the material of reaction equipment, and most of the reactants are biomass, industrial waste, etc. In the future, with the continuous advancement of technological innovation, the supercritical water /CO_2 mixed system will become the core technology for the efficient and green conversion of biomass. It will not only significantly enhance the conversion efficiency and reduce environmental impact, but also provide strong support for the "carbon neutrality" and "dual carbon" goals.

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