Biomass Co-pyrolysis Research and its Technological Progress

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Abstract

Biomass pyrolysis technology is an effective way for us to cleanly utilize biomass energy. With the development of the current social productive forces, the world's demand for energy is getting higher and higher, and the development of physical energy is an effective way to effectively solve the current energy shortage problem. Biomass is the only renewable carbon source. Pyrolysis can produce bio oil, combustible gas, biochar and other chemical raw materials, which has both economic and environmental benefits; Co-pyrolysis technology is an important means to obtain high-quality pyrolysis oil, combustible gas, and coke, which can simplify pollution control and reduce pollutant emissions. Starting from the pyrolysis mechanism and pyrolysis process of biomass, this paper analyzes the influence of heating rate, pyrolysis temperature, pyrolysis atmosphere, and other conditions on biomass pyrolysis, thus providing a theoretical basis for the development of biomass pyrolysis technology.

Keywords

Biomass; Co-pyrolysis; Pyrolysis Mechanism; Influencing Factors; Prospect.

1. Introduction

As an environmentally friendly renewable energy, biomass energy has become one of the hot spots in the field of renewable energy research at home and abroad. In many areas, biomass energy has replaced fossil fuels, and its effective conversion rate and clean utilization rate have drawn growing attention and favor from people all over the world. As a clean and renewable energy, biomass energy is the fourth-largest source of energy after coal, oil and natural gas, accounting for 14% of the global primary energy. In China, just a little amount of biomass energy is being used, and energy consumption mainly depends on fossil energy. Thus, it is crucial for using biomass energy effectively. The development trend of biomass energy, is put forward in order to address environmental pollution and achieve the efficient and clean utilization of resources.

2. Analysis of Factors Affecting Biomass Pyrolysis

Biomass pyrolysis refers to the generation of pyrolysis gas, bio-oil and bio-char from biomass through cracking and polycondensation, so as to realize its resource utilization and clean utilization. It is a process in which biomass is heated without the presence of oxygen to produce biochar, pyrolysis gas, and bio-oil. It primarily consists of three steps, including initial evaporation of water, primary decomposition, secondary reaction oil cracking and repolymerization. High oxygen concentration, low calorific value, and high corrosiveness are the main characteristics of the pyrolysis oil derived from biomass pyrolysis alone. There are three main products that can be pyrolyzed in biomass pyrolysis, which are cellulose, hemicellulose and lignin. Hemicellulose decomposes first, followed by cellulose, and lignin decomposes in a higher temperature range due to its own stability. In order to increase the production and quality of the pyrolysis products, biomass co-pyrolysis involves using two or more different types of materials as raw materials. As there are many intermediate reaction routes in the cleavage process, several complex reactions take place throughout it, but the main reactions are pyrolysis and polycondensation. The yield and composition of biomass pyrolysis products are affected by factors such as heating rate, pyrolysis temperature, and pyrolysis atmosphere. For the study of biomass pyrolysis, it is important to understand how various factors affect this process.

2.1. Heating Rate

The distribution of the pyrolysis products is significantly influenced by whether the volatiles go through secondary reactions. It is easier to obtain biochar from the pyrolysis of biomass when the heating rate is slow. However, when the heating rate is rapid, the residence time of biomass in each temperature section becomes shorter, and the probability of secondary reaction of volatile matter at high temperatures decreases. It is beneficial to improve the yield of gas and liquid products [1]. Chen D Y[2] discovered that the yield of biochar was negatively correlated with the heating rate, and the gas yield was positively correlated with the heating rate. The heating rate also affects the composition of pyrolysis products. The amount of aromatic components in bio-oil and the amount of CO and hydrocarbon gases in the pyrolysis gas will both rise with a greater heating rate.

2.2. Pyrolysis Temperature

Distinct pyrolysis temperatures result in different pyrolysis products, and raising the pyrolysis temperature might increase secondary reactions involving volatiles as well as the cleavage of C-C and H-H bonds. Ma Zhongqing[3] noticed in his studies on the pyrolysis of Masson pine that with the increase of pyrolysis temperature, the volume fraction of CO_2 dropped significantly, and the volume fraction of hydrocarbon gas steadily reduced. The increase of the pyrolysis temperature accelerates the heat transfer during the pyrolysis process, and the breakdown of biomass into smaller molecules will be accelerated by oxygen-containing functional groups like hydroxyl and carboxyl groups in the macromolecular structure. However, the yield of bio-oil is also affected by the pyrolysis temperature. The yield of bio-oil increases with an increase in the pyrolysis temperature, but a high enough pyrolysis temperature will result in a decrease of the yield of bio-oil, according to Ma Z Q[4]'s study of the pyrolysis of palm shell at various temperatures.

2.3. Pyrolysis Atmosphere

Biomass pyrolysis[5] is typically conducted under an inert atmosphere, and choosing an appropriate pyrolysis atmosphere can modify the distribution of pyrolysis products and assist in obtaining high-quality pyrolysis products. The production of volatile matter and the yield of bio-oil can both be increased by adding CO_2 to the atmosphere. Since it can improve the CO content in the pyrolysis gas, increase the specific surface area of biochar, and encourage the fracture of aromatic structures. When there is oxygen in the pyrolysis atmosphere, it will promote the cleavage of functional groups in the biomass and the precipitation of volatile matter due to reduce the yield of CH_4 and the precipitation temperature of CO and CO_2 , and generate more H_2 and bio-oil, but excessive oxygen content will promote the reforming of bio-oil and the cracking of phenolic compounds.

3. Biomass Pyrolysis Process and Mechanism

Research from both domestic and foreign universities has discovered that the biomass pyrolysis reaction primarily consists of the reactions of dehydration, decarbonylation, decarboxylation, and reverse aldol condensation. It also includes the reaction in which cellulose, hemicellulose, and lignin are cracked. The polycondensation reaction of the residue produces coke. Biomass pyrolysis technology can be divided into catalytic pyrolysis and hybrid pyrolysis. Catalytic pyrolysis is the technique of altering the composition of biomass pyrolysis gas while using catalysts to produce high yield and high-quality bio-oil. Biomass catalytic pyrolysis mainly includes two conversion methods. The first involves adding catalysts to the biomass pyrolysis process for direct catalytic pyrolysis, while the second is to convert biomass into bio-oil through rapid pyrolysis, followed by catalytic upgrading.

Biomass is mainly composed of cellulose, hemicellulose and lignin, and its pyrolysis process can be divided into four stages[6]. Hemicellulose is composed of a variety of carbohydrates. The side chain and main chain glycosidic bonds are initially partly disrupted during pyrolysis, and subsequently the main chain glycosidic bonds are totally destroyed. In this process, dehydration, elimination, and ring opening mainly occur reaction. Cellulose is a macromolecular polysaccharide. Each cellulose chain consists of a reducing end, a non-reducing end and several internal units. The pyrolysis process mainly occurs depolymerization, dehydration, ring opening and cyclization. With the occurrence of the dehydration reaction, the hydroxyl group gradually drops, the C=O bond and the C=C bond gradually increase. The cellulose is further decomposed into furans, anhydrosaccharides, and light oxides. Lignin is a complex three-dimensional amorphous polymer in which β -O-4 bonds and α -O-4 bonds dominate. The basic reactions for the decomposition of the β -O-4 bond include the MaccoII elimination reaction, the retro-alkene reaction, and the homolysis of the C-O bond, while the decomposition of α -O-4 bond mainly occurs C-O homolysis and C-C homolysis. It is challenging to investigate the mechanism of biomass pyrolysis, since the pyrolysis mechanism of various types of biomass is quite different. Generally, the overall pyrolysis law of biomass is summarized by studying the pyrolysis mechanism of different biomass components, such as cellulose, hemicellulose, and glucose. Studies have shown that biomass degradation also follows the free radical reaction mechanism. For mechanism research, it is a common method to use model compounds that are similar to the original structures of biomass components.

4. Conclusion and Outlook

With the current shortage of energy, biomass energy as a clean renewable energy has gradually attracted people's attention. Through processes including dehydration, depolymerization, ring opening, and polycondensation, biomass is converted into three-phase products that are gas, liquid, and solid during the pyrolysis process. The pyrolysis products are greatly affected by the heating rate, temperature, pyrolysis atmosphere and other factors. The effect of biomass pyrolysis is obviously improved by introducing catalyst in the process of biomass pyrolysis. The production of fuels and chemicals from biomass resources has received extensive attention due to the renewable nature of biomass, zero net CO_2 emissions, and compatibility with the environment. Therefore, biomass pyrolysis technology has distinct benefits in the field of biomass energy and can create bio-oil, a liquid product with the ability to replace petroleum fuel and chemical application prospects. In order to obtain high-quality co-pyrolysis products, it is necessary to determine the optimal mixing mass ratio of biomass and co-pyrolysis organic matter and the mechanism of co-pyrolysis synergistic effect, in order to realize the control of target product selectivity, stability and economy in the process of biomass thermochemical conversion, and realize the industrialization and automation of biomass thermochemical conversion and utilization. Biomass co-pyrolysis technology is an important chemical

conversion technology to convert biomass into energy, and its product has potential as an alternative energy source. It is a major area of research for both domestic and international scholars, and its future is quite bright. At present, biomass co-pyrolysis technology mainly has the following hotspots:

(1) The synergistic effect mechanism of co-pyrolysis of different types of biomass and organic matter, such as soap-stock and oil shale, was studied to determine the best mass ratio of biomass and organic matter for co-pyrolysis.

(2) Effects of different pretreatment methods, such as baking pretreatment and microwave pretreatment, or catalysts on CO pyrolysis reaction mechanisms and pyrolysis products; selecting appropriate pretreatment methods and catalysts, and optimizing the design of catalyst acidity, particle size, pore size distribution, and surface area, etc.

(3) The CO pyrolysis reaction mechanism of biomass and organic matter in different pyrolysis reactors, the influence of pyrolysis reactor on CO pyrolysis products was discussed, and the production of stable products was promoted by optimizing reactor size and process conditions.

(4) Upgrading of co-pyrolysis products were according to their different application purposes.

References

- [1] Lv Bo, Ma Mingming, Su Xiaoping, Ma Gui, Lin Shaoxuan, Li Jieyuan. Research progress of biomass co-pyrolysis[J].Chemical Science and Technology,2021,29(06):54-58.DOI:10.16664/j. cnki.issn 1008-0511.2021.06.005.
- [2] Chen D Y, Zhou J B, Zhang. Q S. Effects of heating rate on slow pyrolysis behavior, kinetic parameters and products properties of moso bamboo[J]. Bioresource Technology, 2014, 169 : 313-319.
- [3] Ma Zhongqing, Zhang Qisheng. Effects of temperature on the yield and properties of masson pine pyrolysis products [J]. Journal of Zhejiang A&F University, 2016, 33(01): 109-115.
- [4] Ma Z Q,Chen D Y,Gu J et al.Determination of pyrolysis characteristics and kinetics of palm kernel shell using TGA–FTIR and model-free integral methods[J]. Energy Conversion and Management, 2015, 89 : 251-259.
- [5] Liu Zhuang, Tian Yishui, Ma Dachao, Hu Erfeng, Shao Si, Li Moshan, Dai Chongyang. Typical influencing factors and technological research progress of biomass pyrolysis [J]. Renewable Energy, 2021, 39(10): 1279-1286 .DOI: 10.13941/j.cnki.21-1469/tk.2021.10.001.
- [6] Chen Lei, Chen Hanping, Lu Qiang, Song Yang, Ding Xuejie, Wang Xianhua, Yang Haiping. Lignin structure and pyrolysis properties [J]. Chinese Journal of Chemical Engineering, 2014, 65 (09): 3626-3633.
- [7] Wang S R Ru B Lin H Z et al. Degradation mechanism of monosaccharides and xylan under pyrolytic conditions with theoretic modeling on the energy profiles[J]. Bioresource Technology, 2013, 143 : 378-383.
- [8] Lu Q,Hu B,Zhang Z X et al. Mechanism of cellulose fast pyrolysis: The role of characteristic chain ends and dehydrated units[J]. Combustion and Flame, 2018, 198: 267-277.
- [9] Dai G X, Zhu Y N, Yang J Z et al. Mechanism study on the pyrolysis of the typical ether linkages in biomass[J]. Fuel, 2019, 249 : 146-153.
- [10] Somerville M, Deev A. The effect of heating rate, particle size and gas flow on the yield of charcoal during the pyrolysis of radiata pine wood[J]. Renewable Energy, 2020, 151(prepublish): 419-425.
- [11] Efika C E,Onwudili J A,Williams. Influence of heating rates on the products of high-temperature pyrolysis of waste wood pellets and biomass model compounds[J]. Waste Management, 2018, 76: 497-506.
- [12] Wang S R, Ru B, Lin H Z, et al. Degradation mechanism of monosaccharides and xylan under pyrolytic conditions with theoretic modeling on the energy profiles [J]. Bioresource Technology, 2013, 143: 378-383.

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- [13] Dai Chongyang, Tian Yishui, Hu Erfeng, Li Moshan, Ma Dachao, Shao Si. Research on co-pyrolysis characteristics of biomass and low-rank coal and its technological progress [J]. Journal of Solar Energy, 2021, 42(12): 326-333. DOI: 10.19912/j.0254-0096.tynxb.2021-0287.
- [14] Lin Bowen. Co-pyrolysis behavior and synergistic effect of biomass and coal [D]. Zhejiang University, 2021. DOI: 10.27461/d.cnki.gzjdx.2021.000465.
- [15] Xu Qing, Peng Liming, Ling Changming, Peng Weichao, Yang Wei. Research progress of co-pyrolysis technology of biomass and four different organics [J]. Journal of Guangzhou Institute of Navigation, 2019,27(02):73-78+69.
- [16] Jyoti Prasad Chakraborty and Satyansh Singh. Biomass Pyrolysis: Current Status and Future Prospects.
- [17] AGRICULTURAL POLICIES AND BIOMASS FUELS S.Flaim and D.Hertzmark Solar Energy Research Institute (SERI), Golden, Colorado 80401.
- [18] Li Yang, Li Kai, Zhang Zhenxi, Feng Shiyu, Hu Bin, Lu Qiang. Research progress on catalytic pyrolysis of biomass with alkaline earth metal oxide-based catalysts [J]. Biomass Chemical Engineering, 2021,55(06):39 -48.