Research on Pollutant Emission Characteristics of Typical Biomass-fired Boilers

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Abstract. The combustion of biomass fuel boilers not only produces inorganic pollutants such as carbon oxides, nitrogen oxides, sulfur compounds, but also organic pollutants such as VOCs and PAHs, which directly affect the global biogeochemical cycle and atmospheric changes. Compared with foreign countries, there is relatively less research and related standards on the emission of organic pollutants from biomass fuel boilers in China. Therefore, it is necessary to study the emission characteristics of organic pollutants from biomass boilers, which can provide reference for the establishment of organic pollutant emission standards for biomass fuel boilers in China.The emission characteristics of volatile organic compounds(VOCs) and polycyclic aromatic hydrocarbons(PAHs) organic pollutants in the flue gas of three typical biomass-fired boilers in Chongqing were studied, and the emission concentrations of particulate matter, sulfur dioxides(SO2), and nitrogen oxides(NOX) were measured.The results show that the sulfur dioxide emissions from the three types of biomass-fired boilersrs are lower than the local standards in Chongqing, while nitrogen oxides and particulate matter have a phenomenon of exceeding the emission limits of the local standards in Chongqing. The main components of VOCs emitted from biomass powder and biomass particle combustion are OVOCs and aromatic hydrocarbons, while the main components of VOCs emitted from wood biomass combustion are alkynes. The gas-solid distribution pattern of PAHs during the combustion of three types of biomass is basically consistent. Low ring PAHs are mainly enriched in the gas phase, while medium and high ring PAHs are mainly enriched in particulate matter.

1. Introduction

Biomass is considered an environmentally friendly fuel due to its advantages of zero CO2 emissions, low SO2 and NOx emissions, and low ash content.According to incomplete statistics, 13% of China's energy supply comes from biomass[1].The 13th Five Year Plan for the Development of Biomass Energy has raised the target of biomass commercial energy production capacity from 100Mt standard coal in 2020 to 200Mt standard coal by 2025. The annual production of biomass dry matter in China reaches 6 billion tons, equivalent to approximately 500 million tons of standard coal, which is 2.5 times the total annual energy consumption in the country[2].The "biomass economy" supported by the biomass industry is considered by the international academic community to be the next economic form of the upcoming "successor" petrochemicals and "hydrocarbon economy"[3].Biomass fuel boilers are a product that emerged in the era of biomass economy. Currently, the number of biomass fuel boilers in China has increased from 10000 in 2013 to 54000 in 2022.

The pollution gases and particulate matter emitted from biomass combustion are one of the main sources of atmospheric chemical composition in the troposphere, which directly affects the global biogeochemical cycle [4].It is estimated that the inorganic pollutants emitted from biomass combustion contribute significantly to the formation of Asian brown clouds [5].At the same time, biomass combustion can also produce or emit a large amount of toxic organic pollutants, which are important direct sources of some VOCs and carcinogenic PAHs in the atmosphere and affect global atmospheric changes [6].Therefore, whether from the perspective of global or regional environmental dynamics and evolution, or from the perspective of regional air quality processes and human health protection, research on biomass combustion pollution emissions and environmental impacts is crucial.

The types of biomass include agricultural biomass, forestry biomass, aquatic biomass, microorganisms, and livestock manure. The formed biomass fuels used in boilers mainly include agricultural biomass and forestry biomass, such as straw, rice husks, oil plants, trees, herbaceous plants, sawdust, fruit shells, and fruit pits.Due to the current lack of quality standards for biomass

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briquettes, specialized combustion equipment, pollution control technologies, and flue gas emissions from biomass fuel boilers in China, there have been uneven fuel quality and poor flue gas management in various regions, which has exposed serious pollution and regulatory difficulties in the emission of pollutants from biomass fuel boilers.Relevant environmental monitoring shows that some biomass fuel boilers not only have excessive concentrations of particulate matter and NOx, but also emit organic pollutants such as VOCs and PAHs [7], which goes against the government's original intention to develop biomass energy.Therefore, there is an urgent need to conduct research on the emission of pollutants from biomass boilers, in order to provide a reference basis for establishing domestic organic matter emission standards for biomass fuel boilers.

The research on the emission characteristics of pollutants from biomass fuel boilers is still in its early stages, and related research mainly focuses on simulation detection of biomass field incineration and civilian combustion. As for biofuel boilers, they emit relatively more pollutants such as SO2, NOx, and particulate matter [8-10], while there is very little research on the detection and characteristic analysis of VOCs emissions. Moreover, the research results differ significantly from the actual combustion conditions in industrial boilers, making it difficult to reflect the actual emission characteristics of pollutants from biomass fuel boilers in China [11-13].Lin Yujun et al. studied the pollution characteristics of PAHs in the particulate and gas phases of exhaust ducts of different types of industrial biomass fuel boilers, providing a basis for identifying pollution sources, assessing health risks, and formulating relevant environmental policies [14].Zhao Jinping et al. tested the dioxin emissions from typical biomass combustion boilers in the south, and the results showed that the concentration of dioxins emitted from small biomass combustion boilers was higher than that from large biomass combustion boilers [15].At present, there is relatively little research on the multi-component emissions and organic pollution control of biomass fuel boilers with different types of biomass fuels.

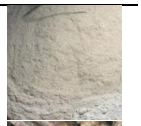
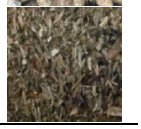
Based on this, this paper detects the emissions of particulate matter, flue gas components, VOCs, and PAHs pollutants in the flue gas of three types of biomass fuel boilers, and studies the distribution characteristics of organic pollutants emitted from flue gas of different types of biomass fuel boilers.

2. Materials and Methods

2.1. Experimental subjects

The tonnage and fuel type of biomass fuel boilers have an impact on their emission characteristics. In order to comprehensively understand the pollutant emission characteristics of biomass fuel boilers, this study selected three different types of biomass fuel boilers for pollutant emission testing.

Table 1. Basic information of biomass fuel boilers

Number	Tonnage	Fuel	Operation date	Fuel consumption	Pollution control	Fuel image
1	10t	Biomass powder	2018	2t•h-1	Water film dust removal	
2	2t	Biomass particles	2017	0.5t•h-1	Water film dust removal	
3	1t	Woody biomass	2017	0.3t•h-1	Water film dust removal	

The three typical fuels selected in this paper are biomass powder, biomass particles, and woody biomass. Biomass powder and biomass particles are processed formed biomass, while woody biomass is primary biomass.There are nearly 200 industrial biomass fuel boilers in Chongqing, all of which are below 10 tons. The main fuel for biomass is formed biomass particles, followed by biomass powder and woody biomass.For the smoke pollutants emitted from the combustion of biomass fuel boilers, generally small biomass fuel boilers have not been effectively treated, while larger biomass fuel boilers have installed simple dust removal facilities such as water film dust removal and mechanical dust removal. At present, there are no treatment facilities for tail organic pollutants.Therefore, this paper selects biomass fuel boilers of different tonnage and fuels in Chongqing as the research objects, as shown in Table 1.

2.2. Analysis methods

2.2.1 Analysis methods for biomass fuels

The collection and preparation of biomass fuel shall be carried out in accordance with GB/T 28730-2012, and the industrial analysis and elemental analysis of biomass fuel shall be carried out in accordance with GB/T 10180-2017.

2.2.2 Analysis methods of gaseous pollutants

The sampling port is located behind the flue gas treatment facility and in front of the chimney discharge port. This paper uses an electrochemical flue gas analyzer to measure the concentrations of conventional components such as O2, CO, NO, NO2, and SO2 in the flue gas on site, and the CO2 concentration is calculated. Using an automatic smoke and dust analyzer to test the concentration of particulate matter in flue gas on site.

2.2.3 Analysis methods of VOCs

The sampling port is located behind the flue gas treatment facility and in front of the chimney discharge port. The layout of VOCs sampling points complies with the requirements of GB/T16157-1996. VOCs in flue gas and fly ash were measured according to HJ 734-2014 and HJ 605-2011, respectively.

2.2.4 Analysis methods of PAHs

The sampling port is located behind the flue gas treatment facility and in front of the chimney discharge port. The layout of PAHs sampling points complies with the requirements of GB/T16157-1996. VOCs in flue gas and fly ash were measured according to HJ 646-2013 and HJ 834-2017, respectively.

2.2.5 Experimental instruments

Smoke analyzer (Testo 350), Automatic smoke and dust comprehensive tester (ZR-3260), Gas chromatography-mass spectrometry (GCMS-QP2020), Gas chromatograph (ISQ 7000), Electronic balance (JY5002), Element analyzer(elementar vario MACRO).

Table 2. Industrial analysis and elemental analysis of biomass fuels

Fuel type	Industrial analysis(wt.%)				Elemental analysis(wt.%)				
	Mar	Ad	Vd	FCddiff	Cdaf	Hdaf	Ndaf	St,d	Odafdiff
Biomass powder	10.23	1.34	52.06	36.37	45.06	3.064	2.86	0.202	48.814
Biomass particles	9.28	1.4	50.89	38.43	45.55	2.886	2.22	0.173	49.171
Woody biomass	11.64	1.68	56.47	30.21	44.24	4.326	3.428	0.194	47.812
Anthracite	7.26	19.97	25.97	46.8	68.75	1.641	0.91	2.608	26.091

Diff:calculated difference

3. Results and Discussion

3.1. Analysis of biomass fuel composition and combustion characteristics

3.1.1. Composition Analysis of Biomass Fuel

The three typical fuel types selected in this paper are biomass powder, biomass particles, and woody biomass. The elemental analysis and industrial analysis of three types of biomass fuels are shown in Table 2.

The elemental analysis results show that compared with anthracite, the content of C and S elements in biomass fuel is generally lower, but the content of N and O elements is higher. Due to the combustion temperature of biomass fuel boilers ranging from 800℃ to 1000℃, the NOx generated during combustion is mainly fuel type NOx.Therefore, when the N content is high, the NOx concentration emitted from combustion is also higher, which is consistent with the results of on-site testing.The industrial analysis results show that compared with anthracite, biomass fuel has higher volatile matter (Vd), while ash (Ad) and fixed carbon (FCd) content are lower. When biomass combustion is not sufficient, volatile organic compounds are easily generated with high volatile content, which is consistent with the results of on-site testing in this article.

3.1.2. Analysis of biomass combustion characteristics

The combustion of biomass fuel includes three stages: preheating and drying, volatile analysis combustion, and fixed carbon combustion.In biomass fuel boilers with good combustion conditions, the fuel is fully burned and produces fewer carbon black particles and organic particles. The main components of particulate matter in flue gas are alkali metals such as K2SO4 and KCl, which generate fly ash particles through homogeneous/heterogeneous condensation.Compared with coal-fired boilers, the concentration of particulate matter in the flue gas of biomass fuel boilers is lower, but the content of PM2.5 is higher than that of coal-fired boilers. The particulate matter in biomass fuel flue gas is mainly generated by non combustible substances such as alkali metals and has a particle size below 1μm.

In the combustion process of biomass fuel, the main sources of SO2 are the oxidation of organic sulfur in the fuel and the decomposition of inorganic sulfur.Due to the furnace temperature of biomass pellet fuel combustion being below 1300℃, thermal NOx is not generated during the biomass fuel combustion process, mainly fuel type NOx. In summary, it can be seen that the content of SO2 and NOx generated during biomass fuel combustion is positively correlated with the S and N elements in the fuel. Compared with coal, biomass formed fuel has a lower content of SO2 produced by combustion due to its lower S element content.

Biomass fuel flue gas is a mixed gas with a complex environment of high temperature and humidity. The content of SO2 and NOx in the flue gas is low, while the content of particulate matter and VOCs is relatively high.

3.2. Emission characteristics of gaseous pollutants from biomass fuel boilers

Taking the No.1 biomass fuel boiler as an example, the instantaneous emission concentrations of CO2, CO, SO2, NO, NO2, and NOx fluctuate within a certain range. The experimental results are shown in Figure 1.The results show that the concentration of NO2 has always been low, and the proportion of NO in NOx is relatively large. The trend of NO and NOX changes is basically consistent. CO2 and CO come from the combustion of carbon containing substances in the fuel. When the fuel is fully burned, more CO2 is generated and less CO. SO2 comes from the combustion of sulfur-containing substances in the fuel. The experimental results show that the concentration trends of SO2 and CO2 are relatively consistent, which also indicates that these two pollutants directly originate from combustion. It can be inferred that the complete combustion of fuel can be determined based on the concentration changes of SO2 and CO2.

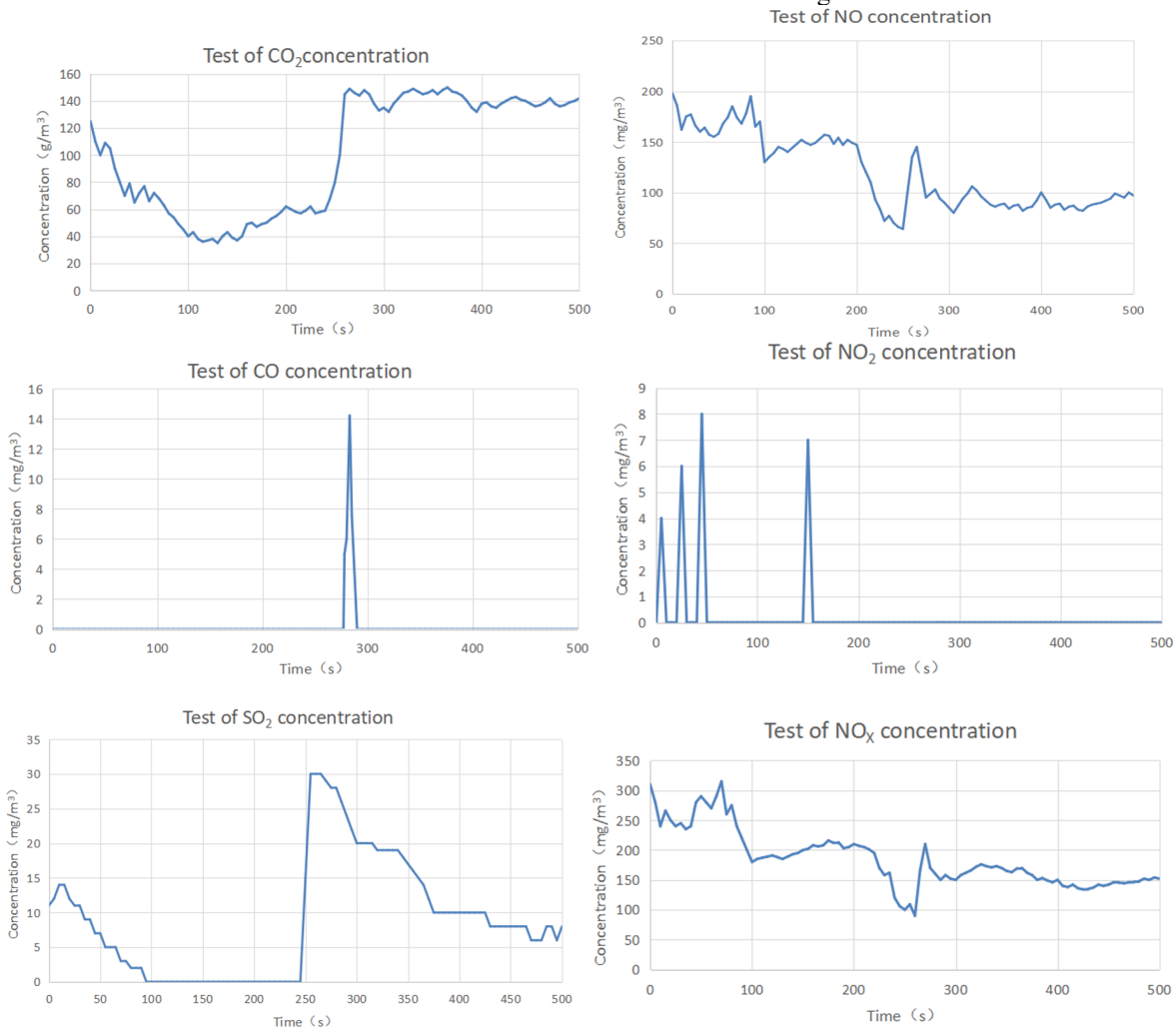


Figure 1. Instantaneous emission characteristics of gaseous pollutants from biomass fuel boiler No.1

The emission of gaseous pollutants from biomass fuel boilers is influenced by the combustion state. At around 250 seconds, the concentrations of CO2, CO, SO2, NO, and NOx all suddenly increased, which may be due to a sudden change in the combustion state inside the biomass fuel boiler. When biomass fuel boilers transition from normal combustion state to flameout state, the incomplete combustion of fuel leads to a significant increase in CO concentration, while the emission concentrations of NO and NOx decrease.

Table 3. Pollutant emission concentration from biomass fuel boilers

Fuel	CO(mg/m3)	NO(mg/m3)	NO2(mg/m3)	SO2(mg/m3)	NOX(mg/m3)	Particulate matter(mg/m3)
Biomass powder	0.3	113.2	7.6	0.2	170.2	73.4
Biomass particles	899.6	36.2	0.3	1.2	58.6	68.8
Woody biomass	405.4	46.5	0.2	0	69.7	102.5

The emission concentration of pollutants during normal combustion of biomass fuel boilers is shown in Table 3. Overall, the fuel type has a significant impact on the emission concentration of pollutants. Due to the low sulfur content of biomass fuel, the emission concentrations of SO2 from the three boilers are relatively low.

3.3. Emission characteristics of VOCs from biomass fuel boilers

The volatile organic compounds generated during biomass combustion cannot be completely burned, while the excess volatile organic compounds are discharged into the atmosphere with the smoke.The formation of VOCs is greatly influenced by biomass raw materials and combustion conditions, and their main components include alkanes, olefins, halogenated hydrocarbons, benzene series, esters, ketones, and other categories.The total VOCs composition characteristics of three types of biomass fuel boilers are shown in Figure 2.When the fuel is biomass powder, the main component of VOCs emissions is OVOCs, accounting for about 35% of the total mass of VOCs, while aromatic hydrocarbons account for about 32% of the total mass of VOCs.When the fuel is biomass particles, the main component of VOCs is aromatic hydrocarbons, accounting for about 41% of the total mass of VOCs, while alkanes account for about 27% of the total mass of VOCs.When the fuel is woody biomass, the main component of VOCs is alkynes, accounting for about 73% of the total mass.The experimental results show that there is a significant difference in the types of VOCs emissions from the three types of biomass fuel boilers. Compared with formed biomass fuel, wood biomass fuel has the characteristics of loose structure and easy rapid volatilization, which is basically consistent with the conclusion that the volatile content of non formed fuel is higher than that of formed biomass fuel.

The main components of total VOCs in three types of biomass fuel boilers are shown in Figure 3.When using biomass powder as fuel, toluene, acetaldehyde+dimethylbenzaldehyde, acetone, and formaldehyde account for 27%, 13%, 9%, and 6% of the total mass of VOCs, respectively.When using biomass particles as fuel, toluene, m/p-xylene, hexanal+dimethylbenzaldehyde, and acetylene account for 21%, 10%, 8%, and 4% of the total mass of VOCs, respectively.When using wood biomass as fuel, acetylene, benzene, and ethylene account for 73%, 3%, and 1% of the total mass of VOCs, respectively. The main reason for the high proportion of acetylene reaching over 70% is the insufficient combustion of woody biomass.

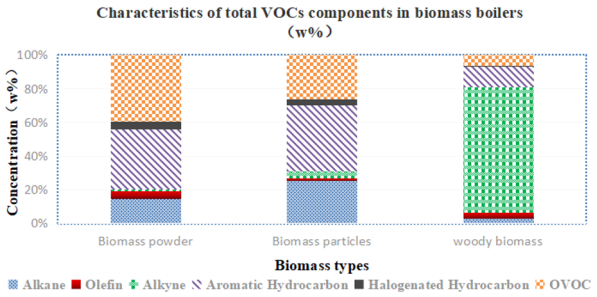


Figure 2. Characteristics of total VOCs components in biomass boilers

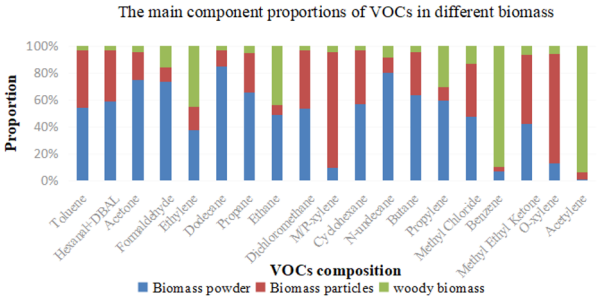


Figure 3. The main component proportions of VOCs in different biomass

The OVOCs generated during combustion in biomass fuel boilers mainly come from the decomposition of ester compounds. Due to the direct correlation between the generation of OVOCs and fuel type and boiler type, the proportion of OVOCs in the three types of biomass fuel boilers varies. The experimental results show that among the three types of biomass fuel boiler flue gas, the components with the highest proportion of carbonyl compounds include cyclohexanone, formaldehyde, acetaldehyde, and acetaldehyde.Compared with woody biomass, higher concentrations of toluene were detected in the boiler flue gas of biomass particles and biomass powder, which may be due to the doping of auxiliary materials in the processing of formed biomass fuel.

3.4. Characteristics of polycyclic aromatic hydrocarbon components in biomass fuel boilers

Determine 16 polycyclic aromatic hydrocarbons in three types of biomass fuel boilers according to national standard methods. The distribution of polycyclic aromatic hydrocarbon emission factors in the smoke gas phase (GP) and smoke solid phase (SP) is shown in Figure 4.The experimental results indicate that compared to biological powders and biomass particles, the content of PAHs in the smoke of woody biomass fuel is higher. There may be two reasons for this result: it may be due to the small particle size and large specific surface area of woody biomass, which leads to greater adsorption during full combustion. Another reason may be the addition of unknown substances in biomass, which may be due to the high content of PAHs.

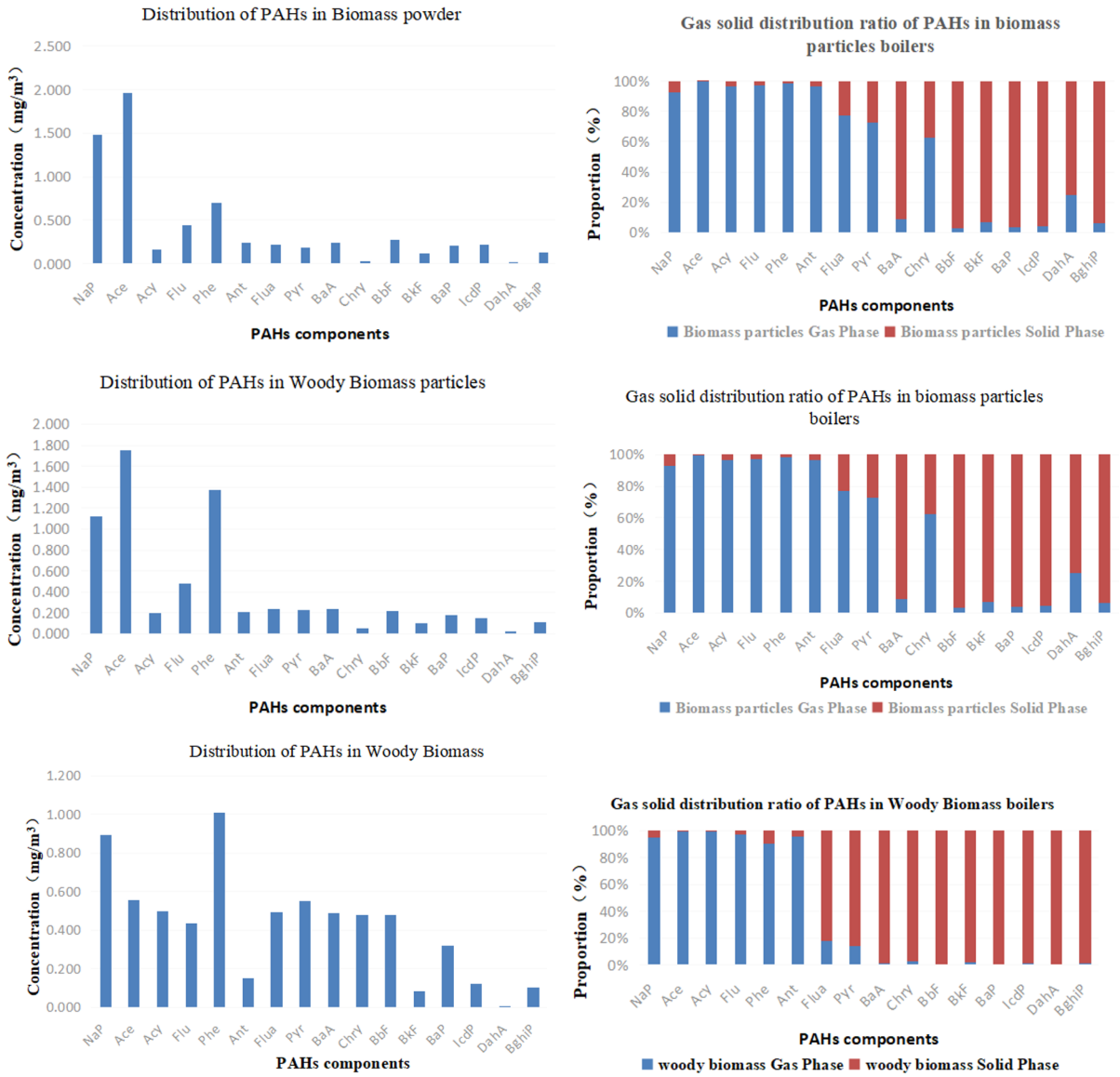


Figure 4. Gas solid distribution ratio of PAHs emitted from combustion of three types of biomass fuel boilers

4. Conclusion

Based on the results and discussions presented above, the conclusions are obtained as below:

By testing the composition of three types of biomass fuels, it can be seen that compared with anthracite, the C and S element content, ash content, and fixed carbon content of biomass fuels are generally lower, but the N, O, and volatile content are higher, which is consistent with the experimental results in this article.

This article tests the instantaneous emissions of CO, NO, SO2, and NOx from biomass fuel boilers. The test results indicate that fuel type has a significant impact on the emission concentration of pollutants. Due to the low content of S element in biomass, the emission concentrations of SO2 from the three types of biomass fuel boilers are also very low. The emission of fuel type NOx is related to the degree of combustion of the fuel itself. Comparative experiments have found that the combustion of biomass powder is more complete, and the concentration of nitrogen oxide emissions is the highest.

This paper tested the VOCs composition characteristics of three different types of biomass fuel boilers. The main components emitted from biomass powder and biomass particles are OVOCs and aromatic hydrocarbons, which originate from the decomposition of ester compounds. The components with higher concentrations of OVOCs emissions include toluene, cyclohexanone, and acetone. The main component emitted from the combustion of woody biomass fuel is alkyne, which mainly comes from incomplete combustion of the fuel.

This paper has obtained the gas-solid distribution diagrams of PAHs for three different types of biomass fuel boilers. The experimental results show that the content of three biomass fuels in flue gas is between 4.75-7.38mg/m3, and the content of three biomass fuels in solid smoke is between 1.19-6.42mg/m3. The gas-solid distribution pattern of PAHs in the three types of biomass combustion sources is basically consistent. Low ring PAHs have strong volatility and are mainly enriched in the gas phase, while medium and high ring PAHs are mainly enriched in the solid particles of smoke and dust. However, the content

of PAHs in the smoke and dust of woody biomass fuel is higher than that in biomass powder and particles.

Acknowledgments.

This work was was supported by Science and Technology Project (Grant No. CQSJKJ2023027). This study was supported by Chongqing Administration for Market Regulation (Grant No. CQSJKJ 2020018, CQSJKJ2021035, CQSJKJ2022009), Science and Technology Project (Grant No. 2023MK105) of State Administration for Market Regulation, and Research Institution Performance Incentive Guidance Special Project (Grant No. CSTB2023JXJL-YFX0025) of Chongqing Science and Technology Bureau. These entities provided the research funding and platform for the work.

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