Analysis Of Pyrolysis Products of Cotton Straw Based on Reaction Kinetics and Random Forests

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Abstract. In this study, focusing on the sustainable use of biomass energy, the catalytic mechanism of desulfurized ash on pyrolysis products was investigated using cotton straw as an example. The effects of different pyrolysis combinations were compared by correlation analysis, and the key role of desulfurized ash in promoting the pyrolysis of cotton straw was found. The gas ratios produced at different mixing ratios as well as the pyrolysis products and gas yields of CE and LG were further analyzed. A catalytic reaction mechanism model was developed, and the reaction kinetics were analyzed in depth. Finally, the yield of pyrolysis products was predicted by a random forest classification model, which provides theoretical support for the efficient utilization of biomass energy. These research results are expected to promote the development of renewable energy field.

Keywords: Pearson correlation analysis; catalytic reaction mechanism modeling; random forests.

1. Introduction

Biomass energy has attracted much attention as an environmentally friendly and renewable energy resource, and its effective utilization is crucial for reducing environmental pollution and promoting sustainable energy development [1]. The efficient utilization of waste resources such as cotton straw has become one of the hotspots of current research [2]. In this context, in this study, oligocellulosic sugars (CE) and lignin (LG) were selected as model compounds to represent the biomass and chemical structure characteristics of cotton straw, and the catalytic mechanism of desulfurized ash in the pyrolysis process of cotton straw was investigated. The effect of desulfurized ash on the pyrolysis products was investigated by comparing the effects of different pyrolysis combinations, which provided important theoretical support for a deeper understanding of the biomass conversion process.

In this study, the effects of desulfurization ash/biomass ratios on product yields were firstly compared under different pyrolysis combinations, and the correlation coefficients were explored by Pearson correlation analysis. In addition, the effect of desulfurized ash on pyrolysis gas yield was explored by plotting the bar graph of gas ratio and analyzing the difference in gas yield of desulfurized ash under different pyrolysis reactions. Finally, the catalytic reaction mechanism models of desulfurization ash for CE and LG were established, and the quantitative prediction of pyrolysis products was carried out by using the random forest classification model, which provides important research support for the efficient utilization and sustainable development of biomass energy.

2. Correlation Analysis

The experimental data, which are the mass fractions of four products obtained from the thermal decomposition products of DA/CS, DFA/CE, and DFA/LG. Including tar, water, char, syngas. We can see that the yields of these four products will vary with the composition and ratio of the compounds.

The data discusses the yield of gaseous components obtained from mixtures of different raw materials during pyrolysis. Different mixing ratios were used in the experiment to observe the pyrolysis process of DFA with different raw materials such as CS, CE, and LG. Through these data, it is possible to compare the production of gaseous components under different mixture combinations and understand the impact of different raw material compositions on pyrolysis reactions. In each experiment, the yields of gaseous components such as H2, CO, CO2, CH4, C2H6, C3H8, C3H6, C2H4, and C4H10 were given. Furthermore, the differences in gas yields among different pyrolysis combinations can be compared.

Pearson correlation analysis variables were used to configure the variables individually [3], as shown in Table 1.

Table 1. Variable configuration

X	DFA/CE, Syngas yield
Y	DFA/CS, Char yield
Z	DFA/CS, Water yield
W	DFA/CS, Tar yield

First, we test whether there is a statistically significant relationship ($P<0.05$) between independent and dependent variables. Then we analyze the positive and negative directions of the correlation coefficient and the degree of correlation. Finally, we summarize the analysis results. The correlation coefficient table corresponding to each variable is shown in Table 2.

Table 2. Correlation coefficients

	DFA/CS	Syngas yield	Char yield	Water yield	Tar yield
DFA/CS	1(0.000***)	0.513(0.158)	0.845(0.004***)	0.985(0.000***)	-0.929(0.000***)
Syngas yield	0.513(0.158)	1(0.000***)			
Char yield	0.845(0.004***)		1(0.000***)		
Water yield	0.985(0.000***)			1(0.000***)	
Tar yield	-0.929(0.000***)				1(0.000***)

The correlation coefficients displayed in the thermal diagram are in Fig. 1.

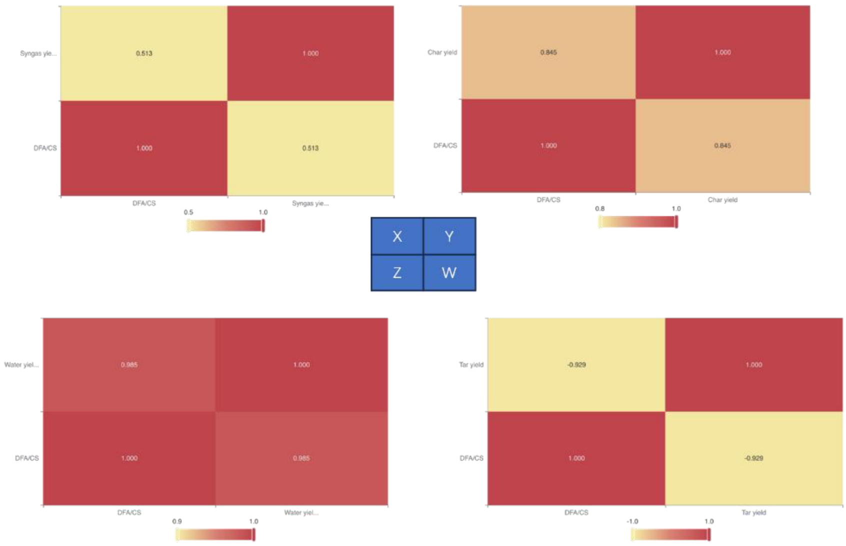


Fig. 1 Heatmap

Based on Table 2 and Fig. 1, we can obtain the following analysis results:

Correlation between variables: After testing four different variables (DFA/CS, Syngas yield, Char yield, Water yield, Tar yield), it was found that there is a correlation between DFA/CS and other variables:

(1) There is a moderate positive correlation with Syngas yield (correlation coefficient of 0.513, but P value is not significant).

(2) There is a strong positive correlation with Char yield (correlation coefficient of 0.845, significant P-value).

(3) There is a strong positive correlation between water yield and water yield (correlation coefficient is 0.985, P-value is significant).

(4) There is a strong negative correlation with Tar yield (correlation coefficient is -0.929, P value is significant).

The strength and direction of correlation coefficients: The numbers in the correlation coefficient table can help us understand the degree of correlation between variables. Generally speaking, the larger the absolute value of the correlation coefficient, the stronger the relationship between variables. At the same time, its positive and negative signs also reflect the direction of correlation between variables, that is, whether the two variables are positively correlated (changing in the same direction), negatively correlated (changing in the opposite direction), or uncorrelated. Specifically:

(1) There is a moderate positive correlation between Syngas yield and DFA/CS.

(2) There is a strong positive correlation between Char yield, Water yield, and DFA/CS.

(3) There is a strong negative correlation between Tar yield and DFA/CS.

3. Variance Analysis

The column mixing diagram for each pyrolysis combination is shown in Fig. 2.

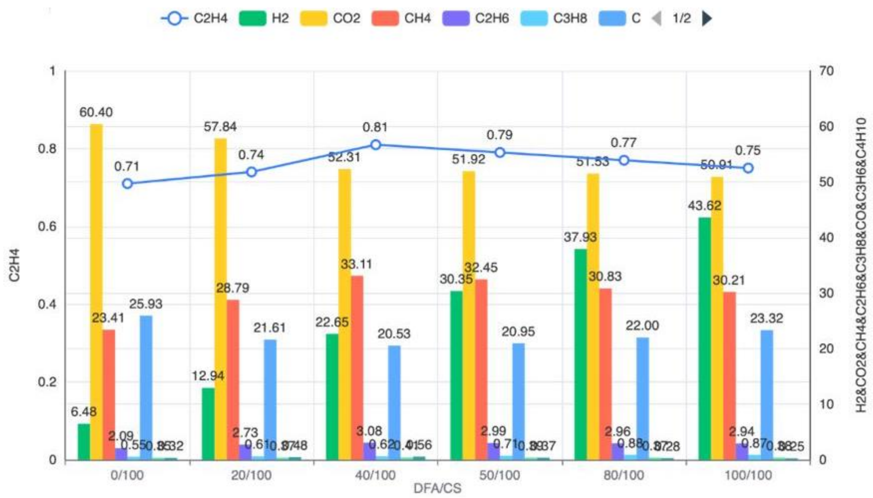
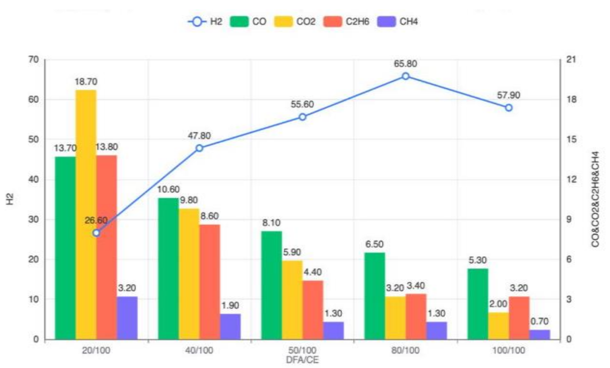


Fig. 2 Yield of gaseous components from DFA/CS pyrolysis

Fig. 2 shows that as the mixing ratio of desulfurization ash and cotton stalks increases, the amount of gas generated during the pyrolysis process also increases. The main pyrolysis gas components include CO2, CH4, H2, and CO, and small amounts of C3H8, C3H6, C2H4, and C4H10 were also detected. The experimental results show that in the presence of desulfurization ash, it plays a significant catalytic role in the generation of the main components of pyrolysis gas. With the increase of the desulfurization ash/cotton stalk mixing ratio, the generation of CO2 and CO is inhibited, and their production gradually decreases. For example, when the mixing ratio of desulfurization ash/cotton stalk is 100/100, the yields of CO2 and CO are 50.01% and 23.32% of the yields of cotton stalk pyrolysis alone, respectively; When the mixing ratio is 50/100, the yields of CO2 and CO are 14.04% and 19.21%, respectively, of the yields of cotton stalk pyrolysis alone. On the contrary, desulfurization ash significantly promotes the generation of H2 during the pyrolysis process of cotton stems. For example, when the mixing ratio of desulfurization ash/cotton rod is 50/100 and 100/100 respectively, the yield of H2 is 4.68 times and

times that of cotton rod pyrolysis alone. As the mixing ratio of desulfurization ash/cotton rod increases, the yields of CH4 and C2H6 first increase and then decrease. The maximum yields of both occur at a mixing ratio of 40/100, which is 33.11 mL/g and 3.08 mL/g, respectively.

In summary, Fig. 2 shows that desulfurization ash has a significant catalytic effect on the pyrolysis of cotton stems. It not only promotes the thermochemical decomposition of cotton stalks, increases the yield of pyrolysis gas, but also significantly changes the yield of each component in the pyrolysis gas. Specifically, desulfurization ash inhibits the generation of CO2 and CO, while increasing the production of H2. Within a certain range, desulfurization ash also has a significant promoting effect on the generation of hydrocarbons such as CH4 and C2H6.



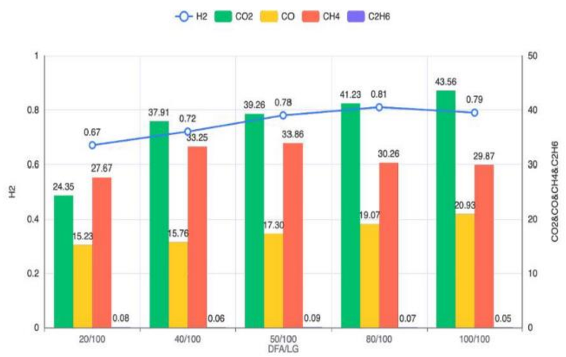


Fig. 3 Yield of gaseous components from DFA/CE pyrolysis **Fig. 4** Yield of gaseous components from DFA/LG pyrolysis

According to Fig. 3 and Fig. 4, the effect of desulfurization ash on the gas yield of cotton stalk pyrolysis varies under different mixing ratios. With the increase of desulfurization ash content, there is a significant change in the yield of different components.

(1) H2 yield: Under the mixed ratio of desulfurization ash/CE and desulfurization ash/cotton rod, the H2 yield in the pyrolysis gas is greater than that of desulfurization ash/LG. This indicates that under these conditions, desulfurization ash promotes the chemical reaction of hydrogen free radicals generated by CE pyrolysis to generate H2.

(2) CO and CO2 yields: During the pyrolysis process of cotton stalks, CE and LG are important sources of CO and CO2 in the pyrolysis gas. As the content of desulfurization ash increases, desulfurization ash inhibits the reaction of CE decomposition to generate CO and CO2, resulting in a decrease in the yield of CO and CO2 in the desulfurization ash/CE pyrolysis gas. On the contrary, desulfurization ash promotes the chemical reaction of LG pyrolysis to generate CO and CO2, which increases the yield of CO and CO2 in desulfurization ash/LG pyrolysis gas.

(3) CH4 yield: The CH4 in the pyrolysis gas of desulfurization ash/cotton stem mainly comes from the fracture of the methoxy side chain rich in LG in the cotton stem. The thermal decomposition of CE can only produce a small amount of CH4, and desulfurization ash has a significant inhibitory effect on this process.

(4) C2H6 yield: Under low-temperature pyrolysis conditions, the aromatic ring structure of LG is difficult to be destroyed, so the thermal decomposition of LG is difficult to generate C2H6. In contrast, C2H6 in the pyrolysis gas of cotton stems mainly comes from the decomposition of CE. However, with the increase of the desulfurization ash/CE mixture ratio, the yield of C2H6 generated by CE pyrolysis significantly decreases. This is because the promotion effect of desulfurization ash on CE pyrolysis inhibits the process of CE structural unit ring opening and hetero cracking to produce C2H6 free radicals.

The pyrolysis process of lignin is shown in the following Fig. 5.

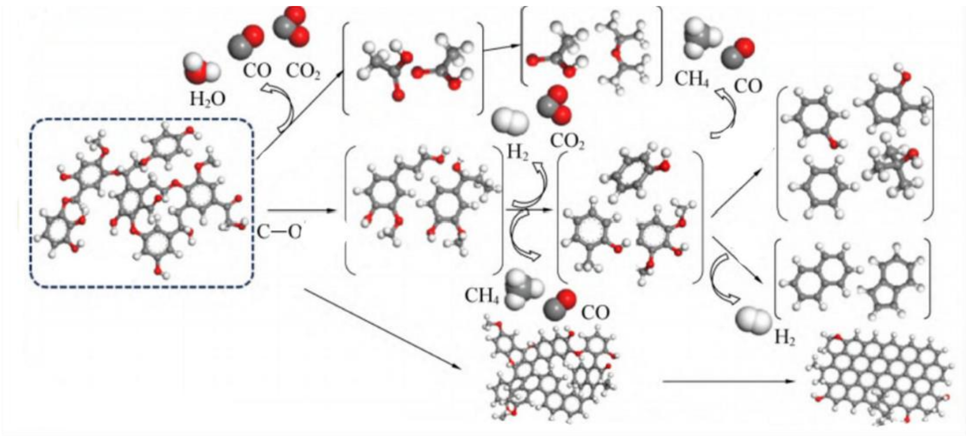
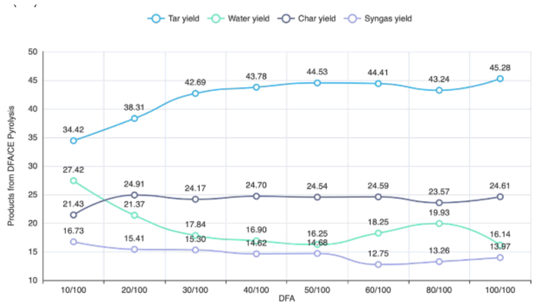


Fig. 5 Mechanism of lignin pyrolysis

In summary, the impact of different mixing ratios on the gas yield generated by the reaction depends on the relative content of cellulose (CE) and lignin (LG) in the cotton stem, as well as the catalytic and inhibitory effects of desulfurization ash in the reaction.

4. Analysis of Pyrolysis Products and Pyrolysis Gas Yields

Firstly, we draw the yield bar charts of each product for CE and LG as shown in Fig. 6 and Fig. 7.



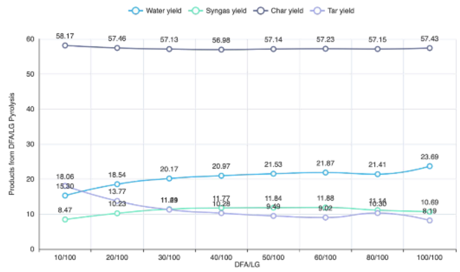


Fig. 6 Column chart of DFA/CE reaction product yield **Fig. 7** Column chart of DFA/LG reaction product yield

Compared with Fig. 6 and Fig. 7, Char yield and Syngas yield were similar in the same proportion of the mixture in both combinations, with no significant difference. However, there was a significant difference between Water yield and Char yield. Under the same proportion of mixture, Water yield reacted significantly higher in DFA/CE than in DFA/LG, while Char yield reacted significantly higher in DFA/LG than in DFA/CE. In summary, it can be seen that in the DFA/CE reaction, desulfurization ash significantly promotes the generation of pyrolysis water during the pyrolysis process, while in the DFA/LG reaction, desulfurization ash significantly promotes the generation of pyrolysis oil during the pyrolysis process. Therefore, in the DFA/CE reaction, desulfurization ash significantly promotes the thermal decomposition of cotton stems and the generation of pyrolysis water and pyrolysis oil. Within a certain ratio range, desulfurization ash increases the yield of pyrolysis gas.

The yield bar charts of two different gases in the reaction are as follows:

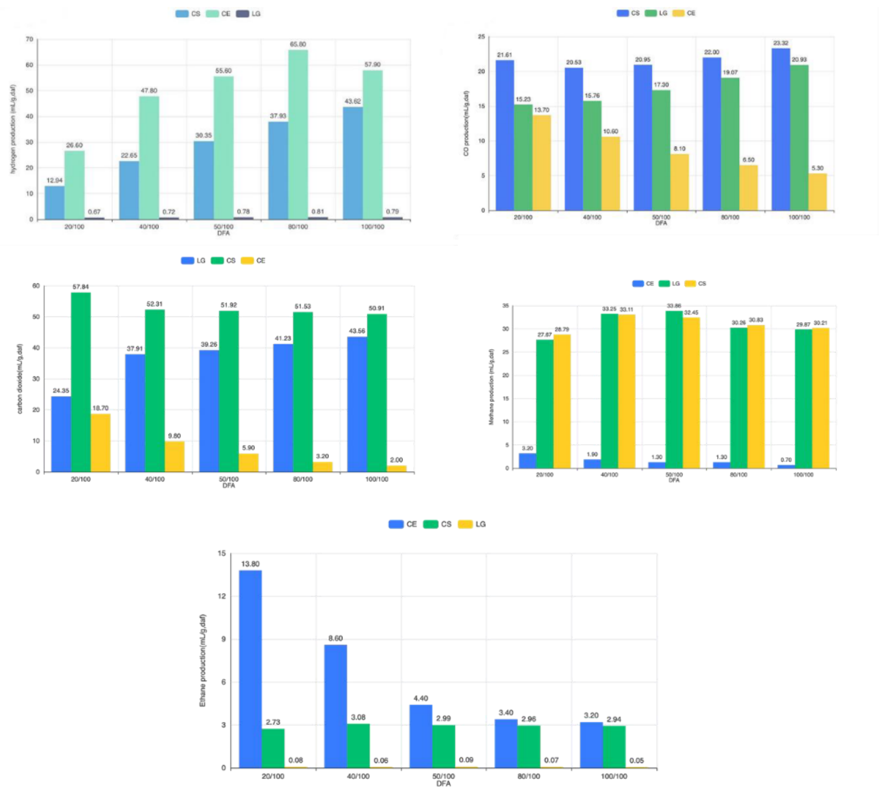


Fig. 8 Yield distribution of different gases in two reactions

According to Fig. 8, it can be seen that the function of desulfurization ash is to enhance or suppress the generation of pyrolysis products of CE and LG. Under the mixed ratio of desulfurization ash/CE, as the content of desulfurization ash increases, the yields of CO, CO2, and C2H6 gradually decrease. This indicates that the promoting effect of desulfurization ash on the pyrolysis of CE results in the production of more and smaller molecular weight free radicals, thereby inhibiting the process of CE structural unit ring opening and hydrocracking to produce CO, CO2, and C2H6.

Under the mixed ratio of desulfurization ash to LPG, with the increase of desulfurization ash content, the yields of CO, CO2, and C2H6 gradually increase, indicating that desulfurization ash promotes the chemical reaction of LG pyrolysis to generate CO, CO2, and C2H6. Under the mixed ratio of desulfurization ash to cotton stalks, the effect of desulfurization ash on the pyrolysis gas yield of cotton stalks is complex, but overall, desulfurization ash has an inhibitory effect on the CH4 yield and a slight promoting effect on the yields of H2, CO, CO2, and C2H6.

Therefore, the effect of different desulfurization ashes on the gas yield generated by the reaction under the same mixing ratio depends on the different model compounds and their relative content in the mixture, as well as the relative strength of the catalytic and inhibitory effects of desulfurization ashes on the pyrolysis of different model compounds.

5. Catalytic Reaction Mechanism Model

The reaction process is divided into two stages:

The first stage: free water precipitates, H bond breaks to generate water, CE polymerization degree decreases, active cellulose is produced, and lignin generates gases such as CO, CO2, CH4.

The second stage: active cellulose undergoes further reaction, generating a large amount of light gas, solid C, and tar. Lignin undergoes secondary decomposition to produce free radicals, which further dehydrate. The recombination and re condensation of volatile products promote carbon deposition, ultimately generating a mixture of water, C, tar, CO, CO2, and CH4 gases.

The reason for the decrease in bio-oil as the catalyst increases:

The effect of catalysts on a single cracking reaction: the active components disrupt the cyclic structure and promote the formation of small molecules.

The effect of catalysts on secondary cracking reaction: The catalyst reacts with the bio-oil from primary cracking, promoting the cracking of aromatic compounds into small molecules and gaseous products.

We adopt the Coats Redfern model [4]. Firstly, both CE and LG generate water, assuming that the generation rate is related to the concentration of reactants, i.e. $v = k * c$; Assuming that the remaining reaction products of CE are mainly tar, solid carbon, and pyrolysis gas, with a ratio of 1:1:2, and the remaining products of LG are the same, with a ratio of 1:2:1; The addition of a catalyst causes the tar to decompose into a pyrolysis gas. Therefore, the proportion of H element in the product increases. From the analysis of the previous three questions, it can be seen that the catalytic effect of the catalyst on LG is stronger than that of CE. The specific model formula is as follows:

$$\frac{da}{dt} = \mathrm{A}e^{-}\left(\frac{E}{RT}\right)(1-a)^n \tag{1}$$

In this equation: $\frac{da}{dt}$ is the reaction rate, which represents the rate of change of reaction degree (conversion rate) a overtime. A is the pre index, which is related to the properties of the reactant and reaction conditions. E is the activation energy, representing the energy required for the reaction. R is the ideal gas constant. T is the temperature (Kelvin). $F\ (a)$ is a function of conversion rate used to consider the impact of reaction mechanism on kinetics. Where $F\ (a) = (1-a)^n$. The main advantage of this model is that it can be used to analyze the pyrolysis process of solid materials and derive parameters such as activation energy and pre index of the reaction [5]. However, it should be noted that the Coats Redfern model is an empirical model that typically assumes that the reaction mechanism is not previously known.

6. Yield Forecasting Model

First, we configure variables, X: {Water yield, Char yield, Syngas yield, Tar yield}, Y: {DFA/CS}. Then, based on the algorithm of the random forest classification model, we obtained the importance ratio of each feature [6], the confusion matrix displayed in the thermal map, and obtained the corresponding model evaluation, as shown in Fig. 9.

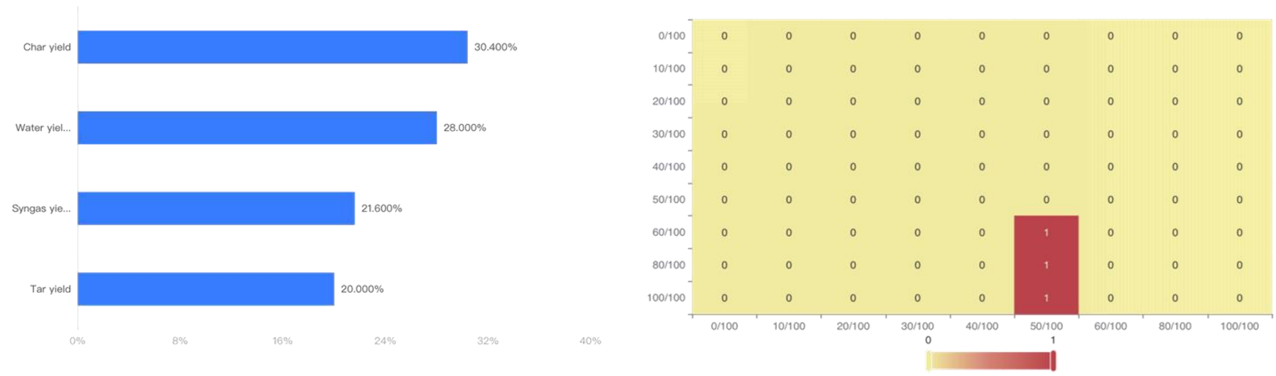


Fig. 9 Bar chart and thermal chart

Finally, we obtained the prediction results based on the algorithm, as shown in Table 3.

Table 3. Prediction results

Prediction result Y	DFA/CS	Result 0/100	Result 10/100	Result 20/100	Result 30/100	Result 40/100	Result 50/100	Water yield	Char yield	Syngas yield	Tar yield
50/100	60/100	0.01	0	0.13	0.29	0.14	0.43	30.07	29.47	27.62	12.84
50/100	80/100	0.01	0.03	0.13	0.29	0.13	0.41	30.68	29.64	27.11	12.57
50/100	100/100	0.01	0.03	0.13	0.29	0.13	0.41	31.02	29.87	26.98	12.13

Explanation: The above table shows the preview results and only displays some data. Please click the download button to export all data. The above table shows the classification results of the random forest model on the test data, with the classification result values being the classification group with the highest prediction probability.

7. Summary

In this study, we deeply investigated the catalytic mechanism of desulfurized ash in the pyrolysis of cotton straw. Through a comparative analysis of different pyrolysis combinations, we found that desulfurized ash as a catalyst had a significant effect on the yields of char, water, tar, and syngas, thus promoting the efficient utilization of cotton straw. Meanwhile, we predicted the yields of pyrolysis products and modeled the catalytic reaction mechanism of desulfurized ash for CE and LG, which provided important theoretical support for biomass conversion. The application of the random forest classification model further strengthened the ability to accurately predict the amount of pyrolysis products. These research results provide an important reference for the sustainable utilization of biomass energy and the development of environmentally friendly energy and provide useful insights for future research and application in the field of green energy.

References

[1] Biomass energy has attracted much attention as an environmentally friendly and renewable energy resource, and its effective utilization is crucial for reducing environmental pollution and promoting sustainable energy development.

[2] Wei J, Liang G, Alex J, et al. Research progress of energy utilization of agricultural waste in China: Bibliometric analysis by citespace[J]. Sustainability, 2020, 12(3): 812.

[3] Bishara A J, Hittner J B. Testing the significance of a correlation with nonnormal data: comparison of Pearson, Spearman, transformation, and resampling approaches[J]. Psychological methods, 2012, 17(3): 399.

[4] Mian I, Li X, Jian Y, et al. Kinetic study of biomass pellet pyrolysis by using distributed activation energy model and Coats Redfern methods and their comparison[J]. Bioresource technology, 2019, 294: 122099.

[5] Çepelioğullar Ö, Haykırı-Açma H, Yaman S. Kinetic modelling of RDF pyrolysis: Model-fitting and model-free approaches[J]. Waste management, 2016, 48: 275-284.

[6] Zhao Y, Zhu W, Wei P, et al. Classification of Zambian grasslands using random forest feature importance selection during the optimal phenological period[J]. Ecological Indicators, 2022, 135: 108529.