

Summary

The present study employs operations such as correlation analysis, differentiation analysis, and reaction kinetics modeling to accurately model and analyze the results and mechanisms of the catalytic pyrolysis of cotton stalks using desulfurized fly ash (DFA). The research is of significant importance in advancing the efficient utilization of cotton stalks in the renewable energy production domain.

For problem 1, a **systematic analysis** is conducted on the relationship between the proportion of DFA and the yields of pyrolysis products. Initial discussions involve **visualization methods**, such as chord diagrams, followed by an assessment of relationship strength using **Spearman correlation coefficients**. **Ridge regression model** is then applied to quantitatively analyze the relationship between product yields and DFA proportions. Subsequently, after the **differential analysis** of each product, the results showed that DFA significantly affected the yield of most products, so we believed that DFA could play a significant role in promoting the pyrolysis of cotton straw (CS), cellulose (CE) and lignin (LG).

For problem 2, utilizing data from Annex II, line graphs and stacked bar charts are employed for **data analysis** and **principle interpretation** of the impact of DFA blending ratios on the yields of pyrolysis gases for each group. Notably, DFA significantly enhances H₂ production in CE pyrolysis, with minimal impact on LG pyrolysis, indicating a close relationship with the chemical bond structures of CE and LG.

For problem 3, **preliminary experiments** include **normality tests** and **variance homogeneity tests** on experimental data. The **Welch's T-Test**, selected for compatibility with data features, is employed for **differential analysis**. Results reveal significant differences in the yields of CE and LG pyrolysis products, as well as the yields of various components of pyrolysis gases.

For problem 4, **domain knowledge** of biomass pyrolysis, especially in the context of wood fiber biomass, is introduced. Utilizing the **equal conversion rate kinetic method**, we build the pyrolysis reaction **kinetics model** with parameters. The curve-fit function in Python is then employed for parameter estimation, and **sensitivity analysis** is conducted to assess the stability and sensitivity of the model.

For problem 5, the **kinetic model** from the problem 4 is expanded to predict the yields of various products under any DFA blending ratios. Simultaneously, a **quadratic prediction model** is constructed for comparative experiments, revealing the superior accuracy of the kinetic prediction model with smaller errors.

Key word: Cotton stalk pyrolysis reaction, Ridge Regression model, Correlation analysis, Differentiation analysis, Reaction kinetics model

Content

Content	2
1. Introduction.....	4
1.1 Background.....	4
1.2 Problems Restatement	5
2. Assumption and Justification.....	5
3. Symbol Description.....	7
4. Problem Analysis.....	7
4.1 Question 1.....	7
4.2 Question 2.....	8
4.3 Question 3.....	8
4.4 Question 4.....	8
4.5 Question 5.....	9
5. Model establishment and solution of question 1	10
5.1 Analysis of relationship between the DFA mixing ratio and products yieds	10
5.1.1 <i>Visualization Analysis</i>	10
5.1.2 <i>Data preprocessing</i>	13
5.1.2.1 Outlier detection	13
5.1.2.2 Centralized Log-Ratio Transformation	13
5.1.3 <i>Correlation analysis</i>	13
5.1.4 <i>Ridge regression model construction</i>	14
5.2 Assessment of DFA's catalytic effect	15
6. Model establishment and solution of question 2	16
7. Model establishment and solution of question 3	19
7.1 Pre-experimental analysis.....	19
7.2 Differential Analysis.....	20
8. Model establishment and solution of question 4	21
8.1 Pre-experimental analysis.....	21
8.1.1 <i>Introduction to the chemical mechanism of pyrolysis</i>	21
8.1.2 <i>Predicted Catalysis Mechanism Analysis</i>	22
8.2 Reaction kinetic model.....	23
9. Model establishment and solution of question 5	24
10. Model evaluation and improvement	26
10.1 Model Advantages	26
10.2 Model Limitations	26
10.3 Model Improvement	27

11. Sensitivity Analysis	27
References	28
Appendix	29

1. Introduction

1.1 Background

The International Energy Agency (IEA) predicts a 70% increase in global energy demand and a 60% rise in greenhouse gas (GHG) emissions between 2011 and 2050^[1]. With the escalating challenges of GHG emissions and environmental pollution, biomass, such as agricultural waste, is garnering increased attention as a viable source of carbon-neutral energy, more so than ever before. Pyrolysis, among the various biomass conversion technologies, stands out as one of the most promising avenues for research. Agricultural waste, particularly cotton biomass waste, is a globally abundant and accessible resource, with an estimated annual yield of approximately 50 million tons, characterized by its rich components like cellulose and lignin, making it an ideal feedstock for thermochemical conversion processes.

Through the pyrolysis process, cotton stalk waste can be transformed into utilizable fuels such as syngas, pyrolysis water, char, and tar. However, the syngas and bio-oil obtained from this process often exhibit higher oxygen content and lower heating values, with suboptimal conversion rates. Hence, investigating the role and impact of catalysts, such as desulfurized ash, in the pyrolysis process is of paramount significance for enhancing yields and improving the quality of target products^[2].

This study delves into the catalytic effects and influences of catalysts during the pyrolysis of cotton stalks, shedding light on their role in promoting efficient utilization of cotton stalks in the realm of renewable energy production.

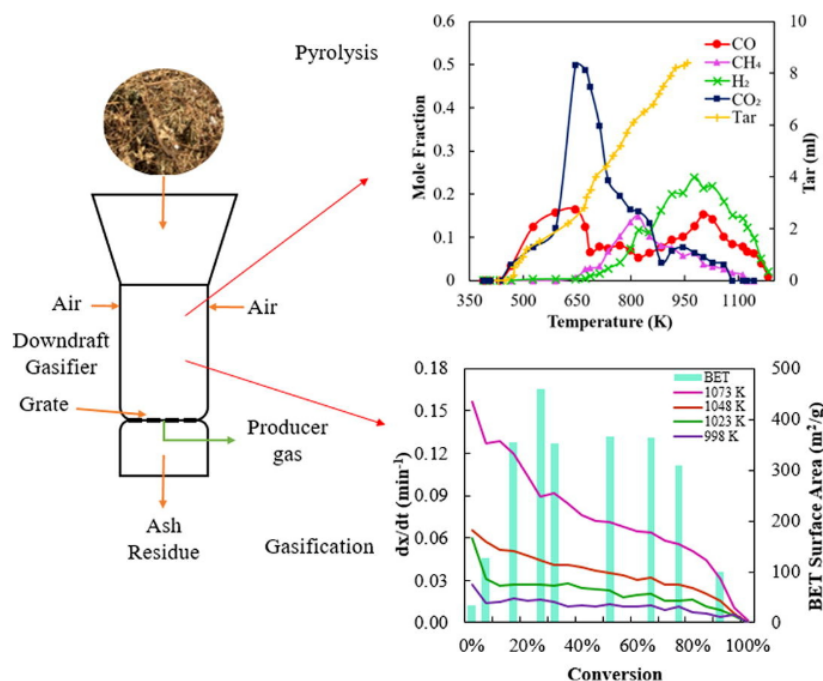


Figure 1 Pyrolysis Products of Cotton Straw

1.2 Problems Restatement

- 1 Regarding Annex I, which comprises three sets of experiments using cotton stalks (CS), cellulose (CE), and lignin (LG) as pyrolysis feedstocks, we investigate the relationship between the pyrolysis product yields (tar, water, char, and syngas) and the corresponding blending ratios of desulfurized ash. Furthermore, we explore whether desulfurized ash plays a significant catalytic role in this context.
- 2 For Annex II, involving three sets of experiments utilizing cotton stalks (CS), cellulose (CE), and lignin (LG) as pyrolysis feedstocks, we analyze the impact of desulfurized ash blending ratios on the pyrolysis gas production in the specified combinations. Relevant charts are presented to support our insights.
- 3 We examine whether significant differences exist in the pyrolysis product compositions of CE and LG, as well as in the pyrolysis gas yields, under the influence of desulfurized ash at identical proportions. We provide reasoned explanations for any observed disparities.
- 4 Investigating the catalytic reaction mechanisms of model compounds such as CE and LG with desulfurized ash, we aim to establish a reaction kinetics model for analysis.
- 5 Employing mathematical models or artificial intelligence learning methods, we aim to predict the pyrolysis product yields or quantities under conditions of limited data.

2. Assumption and Justification

To construct a more precise mathematical model, this paper makes the following reasonable assumptions or constraints based on practical considerations: To construct a more precise mathematical model, this paper makes the following reasonable assumptions or constraints based on practical considerations:

1. Constant Temperature Conditions

The pyrolysis reactions occur under constant temperature conditions, and the heating rates are uniform for each experimental group. Therefore, the temperature's influence on the pyrolysis product yields can be considered constant.

- The heating temperature and rate are crucial factors affecting pyrolysis reactions. However, since the primary focus of this experiment is the impact of the catalyst (desulfurized ash) on pyrolysis reactions, temperature is treated as an irrelevant variable. Additionally, as stated in the problem, all experiments are conducted at the same temperature, allowing us to consider the temperature's impact on pyrolysis product yields as constant.

2. Equilibrium State of Pyrolysis Products

The yields of each pyrolysis product in each experimental group are assumed to be at equilibrium and do not change with time.

- When studying the yields of chemical reaction products, a fundamental assumption is that the reaction has reached a steady state, and the quantity of products no longer varies with time. This assumption excludes the consideration of intermediate or transition states in the reaction.

3. Exclusion of External Factors

External factors that could potentially influence the pyrolysis process, such as reaction vessel characteristics and pressure, are not taken into account.

- This study focuses on the catalytic impact of desulfurized ash on pyrolysis reactions, considering other external factors as irrelevant variables. Ensuring the rationality and uniformity of irrelevant variables is a fundamental principle in chemical experiments.

4. Negligible Measurement Errors

Measurement errors in experimental data are negligible in the model.

- It is reasonable to assume that all experimental data provided in the problem are obtained through scientific and precise measurement methods, and measurement errors for the indicators in the experiment can be neglected.

5. Independence of Cellulose and Lignin Pyrolysis Reactions

Under the same desulfurized ash proportion, the pyrolysis reactions of cellulose (CE) and lignin (LG) are independent and can be studied separately.

- Cellulose and lignin possess distinct chemical structures and properties. While closely related in plant structures, literature review indicates that their pyrolysis processes do not significantly influence each other. By selecting these two components as model compounds, the study can finely control experimental conditions to investigate the targeted catalytic effects of desulfurized ash on different biomass components.

6. Linear Relationship of Catalyst Proportion and Activation Energy

Within a certain range, the proportion of the catalyst (desulfurized ash) is linearly related to the activation energy of the reaction.

- The catalytic principle of a catalyst in a chemical experiment is to lower the activation energy of the reaction. To facilitate the establishment of reaction kinetics models for cellulose and lignin pyrolysis, the relationship between the catalyst's quantity and its ability to reduce activation energy is simplified as a linear relationship within a certain range.

3. Symbol Description

Symbol definition	Symbol Description	Symbol definition	Symbol Description
β	Replace the Parameters	N	Sample Size
β_0	Constant Parameters	$F(x)$	Cumulative Distribution Function
β_j	Slope	α	Conversion Rate
X	Pyrolysis Product Yield	T	Temperature
b	Desulfurized Ash Mixing Ratio	$g(\alpha)$	Integration of the Mechanism Constant
v	Growth Rate	R	Molar Gas Constant
λ	Increase	c_i	Parameters of the Solution
A	Degree of Data Fitting	DFA	Desulfurized Fly Ash
CE	Cellulose	LG	Lignin

4. Problem Analysis

4.1 Question 1

The first question can be divided into two sub-questions: 1) analyze the relationship between the yields of pyrolysis products for cotton stalks, cellulose, and lignin and the blending ratio of desulfurized ash; 2) assess whether desulfurized ash significantly enhances the pyrolysis of cotton stalks, cellulose, and lignin.

For the first sub-question, given the available data, this study employs a progressively in-depth approach to analyze the relationships between multiple variables. Initially, through visualization and descriptive analysis, a preliminary understanding of the distribution and variations in the data

is obtained. Subsequently, by conducting Spearman correlation coefficient analysis between the yields of pyrolysis products and the desulfurized ash ratio for each combination, the existence and strength of correlations can be determined. Finally, to precisely analyze the specific relationships between the yields of each product and the desulfurized ash ratio, regression models need to be established, providing detailed insights into how the yields change with variations in the desulfurized ash ratio.

For the second sub-question, the assessment of the catalytic effect's significance can be addressed through differential analysis. Under uniform conditions with irrelevant variables controlled, if there is a noticeable change in product yields with an increase in the desulfurized ash ratio, it can be inferred that desulfurized ash has a significant catalytic effect. The significance of changes in product yields can be determined through differential analysis.

Overall, these analytical approaches aim to provide a comprehensive understanding of the relationships between pyrolysis product yields and desulfurized ash ratios, as well as to assess the significance of desulfurized ash as a catalyst in the pyrolysis process for different biomass components.

4.2 Question 2

Question two requires utilizing the provided data to visually represent the impact of desulfurized ash blending ratios on the yields of pyrolysis gases for each pyrolysis combination. As the desulfurized ash blending ratio constitutes a typical increasing sequential data series, this study opts for the use of line charts and stacked bar charts to illustrate and analyze the trends in the yields of various pyrolysis gases.

4.3 Question 3

Question three requires conducting differential analysis on the yields of pyrolysis products and the production of pyrolysis gases for cellulose (CE) and lignin (LG) under the catalytic effect of the same desulfurized ash proportion. Different forms of data may necessitate various methods for differential analysis in the field of data analytics. To choose the optimal differential analysis method, this study, prior to the differential analysis, performed pre-experimental operations such as normality testing and homogeneity of variance testing on the data. Based on the characteristics of the data, the most suitable differential analysis method was selected.

4.4 Question 4

Question four can be divided into two sub-questions: 1) analyze the desulfurized ash catalytic reaction mechanisms for model compounds such as cellulose (CE) and lignin (LG); 2) establish

corresponding reaction kinetics models.

For the first sub-question, this study employs a combined approach of theoretical analysis and data analysis. Initially, domain knowledge related to the pyrolysis of lignocellulosic biomass is introduced for a theoretical understanding of the pyrolysis reaction principles. Subsequently, through data arrangement and comparison, the specific impact mechanisms of desulfurized ash catalysis on various products are analyzed in detail.

Concerning the second sub-question, we utilize the kinetic method proposed by Kissinger, Akahira, and others^[3] to derive the specific form of the reaction kinetics equation. The Python curve-fit function is then employed to solve for the kinetic parameters, enabling the establishment of reaction kinetics models.

4.5 Question 5

Question five essentially involves a small-sample prediction problem, requiring the use of mathematical models or AI learning methods to predict the yields or quantities of pyrolysis products under limited data conditions. We have constructed both mathematical prediction models and machine learning prediction models. These models were employed to predict the yields or rates of pyrolysis products across the entire desulfurized ash ratio range of 0 to 100. Subsequently, an assessment of the predictive performance of the models was conducted.

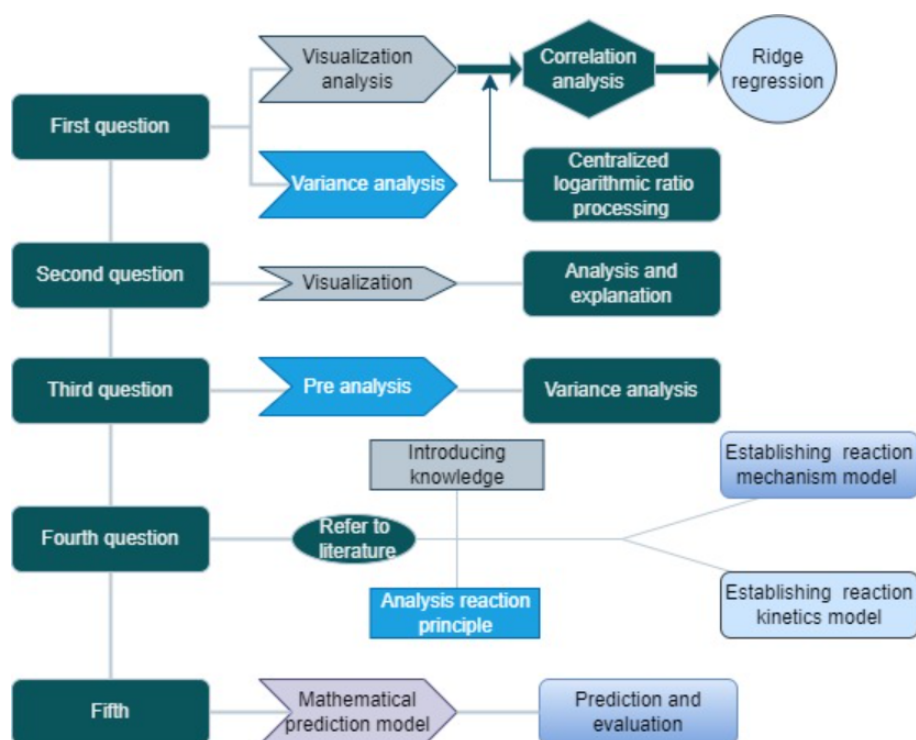


Figure 2 Problem Analysis Flowchart

5. Model establishment and solution of question 1

In the resolution process of Question One, this paper initially conducted visual displays and descriptive analysis of the relationship between the yields of pyrolysis products from cotton stalks, cellulose, and lignin, and the ratio of desulfurized ash mixture. Subsequently, we calculated the Spearman correlation coefficients between the desulfurized ash ratio and the yields of various pyrolysis products, assessing whether there was a correlation. Finally, a ridge regression model was established to fit the specific relationship between variables, enabling a precise quantitative analysis of the relationships between variables.

After clarifying the relationships between variables, this paper proceeded to analyze and determine whether desulfurized ash had a significant catalytic effect on the three pyrolysis reactions through differential analysis methods.

5.1 Analysis of relationship between the DFA mixing ratio and products yields

5.1.1 Visualization Analysis

To intuitively understand the relationship between the yields of various products and the ratio of desulfurized ash, this paper first visually presented the data in Annex I. As the desulfurized ash mixture ratio is a typical increasing sequence of data, nested pie charts and line graphs were initially employed for visual analysis to illustrate the changing trends in the yields of various products.

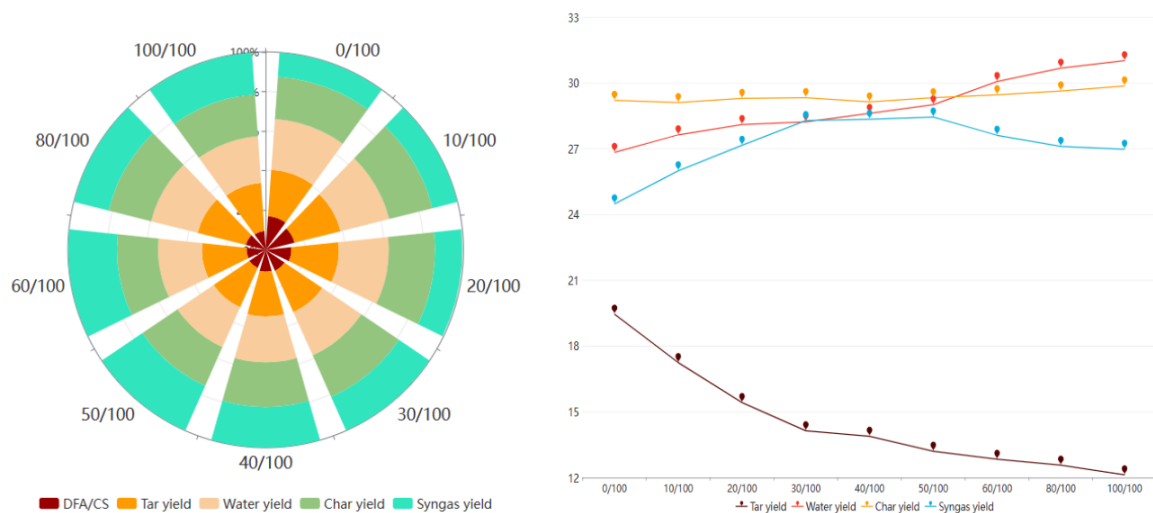


Figure 3 DFA/CS Pyrolysis Products Yield

Taking the pyrolysis reaction of cotton stalks (CS) as an example, with the increase in the DFA/CS mixture ratio (observed clockwise in the nested pie chart), the yield of Tar significantly

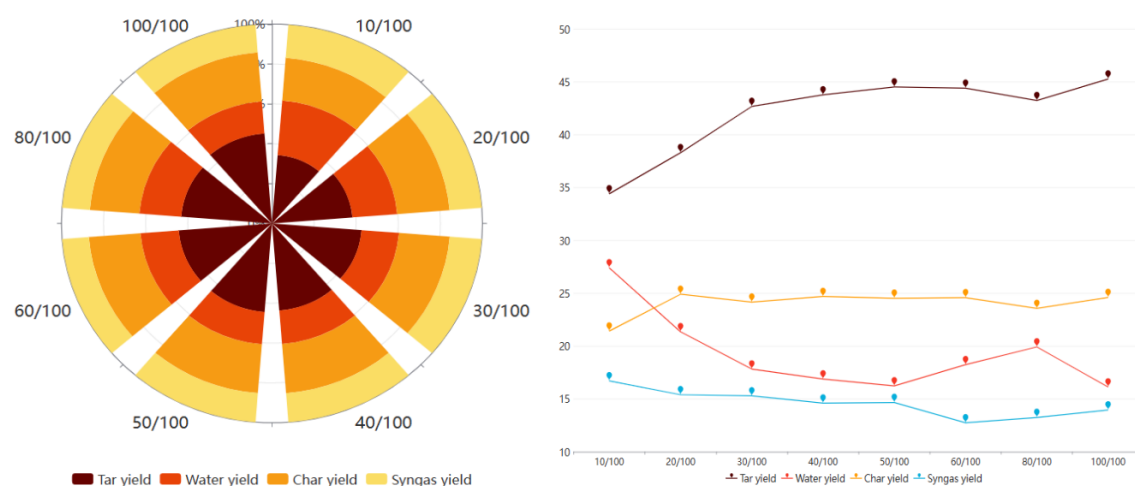


Figure 4 DFA/CE Pyrolysis Products Yield

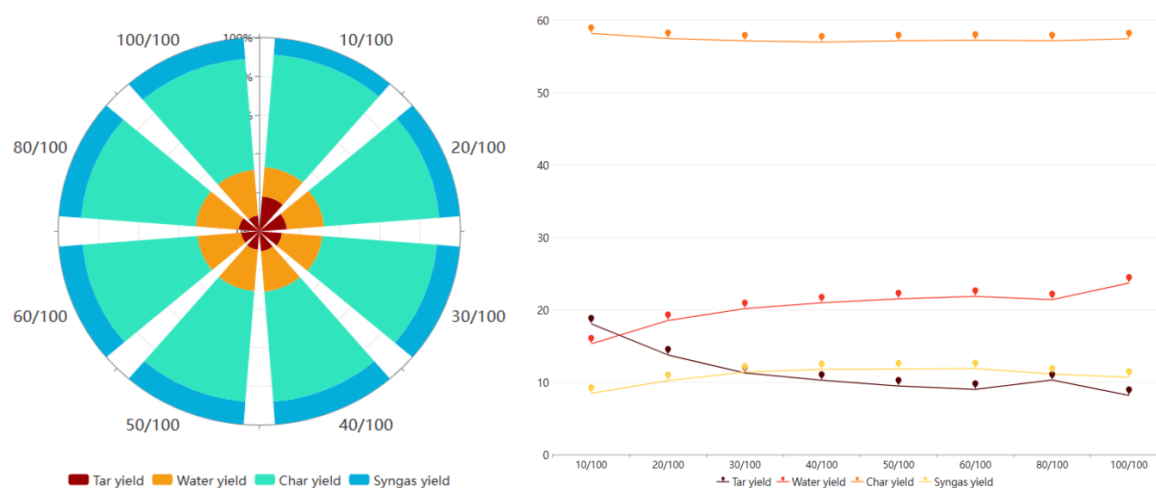


Figure 5 DFA/LG Pyrolysis Products Yield

decreases. When the DFA/CS mixture ratio is 100/100, the Tar yield in the pyrolysis of cotton stalks is 12.13%, only 62.33% of the Tar yield when cotton stalks are pyrolyzed alone. Desulfurized ash has a significant promoting effect on the generation of pyrolysis water. When the DFA/CS mixture ratio is greater than 50/100, the yield of pyrolysis water significantly increases. With the increase in the DFA/CS mixture ratio, the yield of pyrolysis oil shows a slow overall increase, and the yield of pyrolysis gas initially increases and then decreases, with its maximum yield occurring around a mixture ratio of 50/100, approximately 28.45%. This is an increase of 16.17% compared to the pyrolysis gas yield (24.49%) when cotton stalks are pyrolyzed alone. In summary, in the process of cotton stalk pyrolysis, desulfurized ash significantly promotes the thermal decomposition of cotton stalks, as well as the generation of pyrolysis water and pyrolysis oil. Within a certain ratio range, it also increases the yield of pyrolysis gas.

To further visually analyze the relationship between pyrolysis product yield and desulfurized ash ratio, we have created chord diagrams for the pyrolysis products in each pyrolysis combination with the desulfurized ash mixture ratio. Chord diagrams are primarily used to display relationships between multiple objects. The line connecting any two points on the circle is called a chord, and the chord represents the relationship between the two. In the analysis of complex data relationships, especially for bidirectional relationships and the analysis of data flow, chord diagrams have unique advantages.

Due to space limitations, we only present the diagram and analysis results for the pyrolysis of cellulose (CE) here; the others can be found in the appendix.

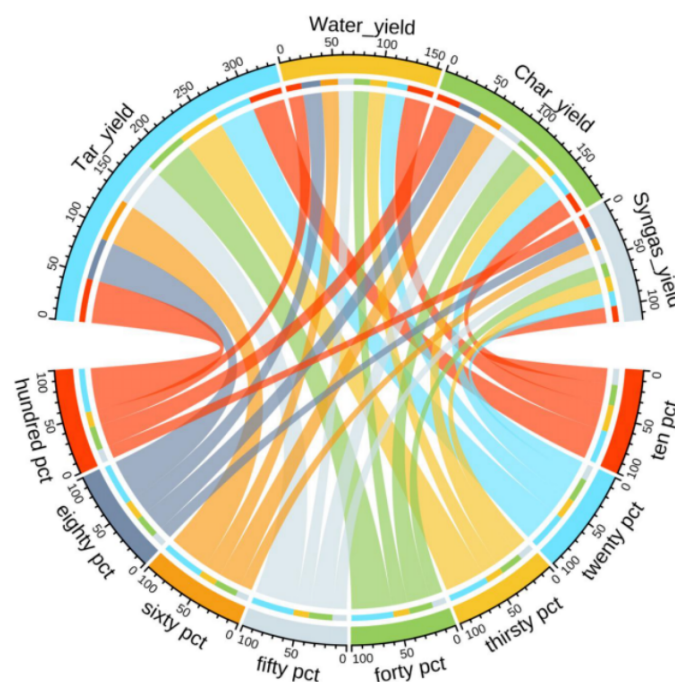


Figure 6 Graphs and analysis results of cellulose (CE) pyrolysis

Overall, regardless of the mixing ratio, Tar has the highest proportion, and Syngas has the smallest proportion among the pyrolysis products. Since the width of the colored bands represents the magnitude of substance production, from the diagram, it can be observed that the proportions of Tar and Char increase with the increase in the proportion of desulfurized ash input. The proportion of Water initially decreases and then increases with the increase in the proportion of desulfurized ash input, while the proportion of Syngas decreases with the increase in the proportion of desulfurized ash input, but the change is relatively small.

Through this chord diagram, we can make preliminary inferences about the relationship between desulfurized ash and various pyrolysis products in the combination where the model compound is CE: desulfurized ash has a significant promoting effect on the production of Tar

and Char, a slight inhibitory effect on the yield of Syngas, and its impact on Water is related to its own concentration, showing extreme values.

5.1.2 Data preprocessing

5.1.2.1 Outlier detection The paper first utilized SPSS software for outlier detection on all data, and the results indicated that all data fell within a reasonable range, with no outliers detected.

5.1.2.2 Centralized Log-Ratio Transformation The vector space in which the thermal decomposition products of each combination reside is a simplex space, which requires satisfying the constant-sum constraint that the sum of the proportions of each product is 100%. Therefore, traditional statistical analysis methods for ordinary data are not applicable to the proportion data of products. Through literature review, three reasons for the inapplicability are identified as follows:

- 1 The intuitive form of the data in simplex space is different from that in Euclidean space, making it challenging to interpret across spaces.
- 2 The covariance matrix of compositional data calculated on simplex space exhibits a distinct negative bias, contrasting sharply with the implications of Euclidean space.
- 3 Compositional data on simplex space lacks parameter distribution, making it difficult to model the variability pattern of the data.

Based on the aforementioned issues, this paper applies the central log-ratio transformation (clr) to the data in Annex I. The data after clr transformation can better reflect compositional characteristics, enhancing the interpretability of compositional data^[4]. The clr calculation formula is as follows:

$$\text{clr} = \left\{ \ln \frac{x_1}{g(x)}, \ln \frac{x_2}{g(x)}, \dots, \ln \frac{x_n}{g(x)} \right\} \quad \text{In that } g(x) = [x_1 \cdot x_2 \cdots x_n]^{\frac{1}{n}} \quad (1)$$

The data after central log-ratio transformation is provided in the supporting materials.

5.1.3 Correlation analysis

To assess the correlation between the desulfurization ash ratio and the yields of various pyrolysis products, it is essential to calculate the correlation coefficients between the desulfurization ash ratio and the yields of each pyrolysis product.

Additionally, considering the limited amount of experimental data in this study, conducting a correlation analysis between dependent and independent variables before constructing the model is necessary. If the correlation between the yields of pyrolysis products and the input ratio of

desulfurization ash is weak, it is advisable not to perform regression analysis for that specific product to avoid building inaccurate models with weak generalization capabilities.

Due to the small sample size and the absence of a clear normal distribution in the variable data, we opt to use the Spearman rank correlation coefficient for this correlation analysis. The objective is to determine whether there is a correlation between the yields of the four pyrolysis products and the desulfurization ash mixing ratio, as outlined in the following structure:

Substance	First parameter	Second parameter	Third parameter
Parameter_tar	6.07E+04	1.69E-01	-8.96E-01
Parameter_water	2.670937	0.136637	-0.81211
Parameter_char	1.49E+04	5.76E-01	-8.58E-03
Parameter_syngas	2.877523	0.064104	-1.37297

Figure 7 Correlation Analysis of CS

From the above results, it can be observed that in the CS pyrolysis combination, the absolute values of the correlation coefficients between tar, water, char, and the desulfurization ash ratio are all greater than 0.75, with minimal difference from 1. Hence, it can be considered as having a strong correlation. Specifically, tar has a negative correlation with the desulfurization ash ratio, while char and water have a positive correlation with the desulfurization ash ratio. On the other hand, the absolute value of the correlation coefficient for syngas is less than 0.2, indicating a very weak correlation with the desulfurization ash input ratio. Similar analyses can be applied to the CE and LG pyrolysis combinations.

5.1.4 Ridge regression model construction

Due to the small size of the provided data and the consideration that each model built has only a single independent variable, in order to avoid potential issues arising from the small data scale, it is necessary to eliminate the impact of the data itself as much as possible^[5]. Therefore, this study considers using ridge regression, introducing a penalty term to make the regression results more accurate and reliable. The mathematical model of ridge regression is expressed as follows:

$$\hat{\beta}^{\text{ridge}} = \arg \min_{\beta} \left\{ \sum_{i=1}^N (y_i - \beta_0 - \sum_{j=1}^p x_{ij} \beta_j)^2 + \lambda \sum_{j=1}^p \beta_j^2 \right\} \quad (2)$$

Here, β represents the estimated parameters of the linear model, including the constant term β_0 and the slope β_1 . The parameter λ is the penalty term used to address the singularity issues arising from the small size of the dataset.

Taking the CS pyrolysis reaction as an example, we perform ridge regression on the three products that meet the correlation coefficient conditions. The results are as follows:

$$\text{Tar: yield} = 0.094 - 0.345 * \text{proportion}$$

$$\text{Water:yield} = -0.045 + 0.146 * \text{proportion}$$

$$\text{Char:yield} = -0.009 + 0.027 * \text{proportion}$$

The ridge regression models for Water, Char, and Tar with respect to the proportion of desulfurized ash reveal the following insights: The slopes of the models for Water and Char are 0.146 and 0.027, respectively, indicating that desulfurized ash promotes the generation of Water and Char in the pyrolysis reaction. Moreover, the promoting effect of desulfurized ash on Water is significantly stronger. For Tar, the slope of the model is -0.345, suggesting a pronounced inhibitory effect of desulfurized ash on Tar production.

Due to space limitations, we have included the ridge regression results for CE and CS pyrolysis reactions in the appendix and will not present them here.

5.2 Assessment of DFA's catalytic effect

In this question, we cleverly transform the assessment of the catalytic effect of desulfurized ash into a differential analysis problem. If desulfurized ash significantly enhances the pyrolysis reaction of cellulose, based on the symmetry and singularity of the catalyst's catalytic effect on the reaction, different input ratios of the catalyst will inevitably result in significant changes in the yields of one or more pyrolysis products. Therefore, for a single product's samples, there must be significant differences between the data. If there is no difference between the data samples of all products' yields, it can be considered that desulfurized ash does not have a promoting effect on the reaction for that combination.

Hence, we employ the one-sample t-test method, setting the test value as a case within the range around the mean value. If the data of all cases for this sample exhibit significant differences from this test value, the result of this test indicates differences between the data, thus illustrating the significant promoting effect of desulfurized ash on the reaction.

Here, we take the combination with model compounds representing cotton stalks as an example. The one-sample t-test for the differences between the sample data of various pyrolysis reaction products under this combination is illustrated in the following figure:

Substance yield	Inspection value	Average	Standard deviation	t	P
Tar	19.46	14.547	2.431	-6.064	0.000***
Water	26.84	28.913	1.415	4.395	0.002***
Char	29.21	29.379	0.246	2.056	0.074*
S	26	27.161	1.279	2.724	0.026**

Figure 8 Differential One-sample T-Test

The results displayed in the above figure clearly indicate: the p-value for the Tar sample data is significantly less than 0.05, rejecting the null hypothesis (i.e., there is no difference between the sample data) to the greatest extent. Therefore, there is a significant and substantial difference

between the data for this substance sample, indicating a notable impact of desulfurized ash on the generation of Tar. Similarly, the p-values for the Water and Syngas samples are also less than 0.05, albeit slightly greater than the p-value for Tar. Hence, there is also a substantial difference between their data, suggesting that desulfurized ash has a considerable impact on the pyrolysis reaction under this combination. On the other hand, the p-value for Char is greater than 0.05, failing to reject the null hypothesis. Therefore, desulfurized ash almost does not affect the generation of Char. It can be concluded that desulfurized ash does not have a catalytic effect on the production of Char.

Due to space limitations, only the analysis for the CS pyrolysis combination is presented here. The detailed results of the differential analysis for the remaining two combinations (CE, LG) are available in the appendix.

The analysis results indicate that the addition of desulfurized ash significantly influences the yields of most products under various pyrolysis combinations. Thus, it is believed that desulfurized ash plays a significant promoting role in the pyrolysis of cotton stalks, cellulose, and lignin.

6. Model establishment and solution of question 2

To visually depict the impact of different ratios of the catalyst (DFA) on the yields of various pyrolysis gases, this paper first conducted a visualization of the relevant data. The desulfurized ash-to-model compound ratio was taken as the independent variable, while the yields of various pyrolysis gases in each pyrolysis combination were considered as dependent variables. Line charts and bar charts were created using the matplotlib library in Python for this purpose.

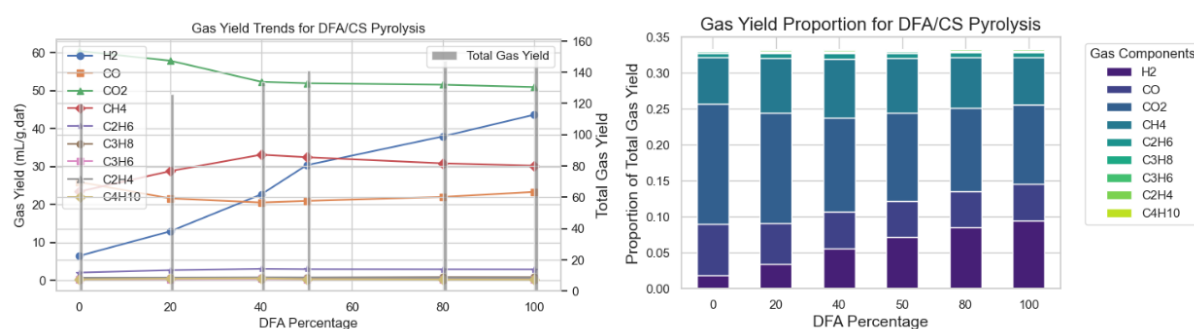


Figure 9 Gas Yield Trends for DFA/CS Pyrolysis

In the combination where CS serves as the pyrolysis feedstock, the total yield of pyrolysis gas significantly increases with the increase in the desulfurized ash blending ratio. Numerically analyzing, the gas yield grows from an initial 120.24 mL/g, daf to 153.25 mL/g, daf, representing an approximate 25% increase. This indicates that desulfurized ash can effectively promote the reaction of pyrolysis to produce synthesis gas. Analyzing the slope, the early-stage growth of

the total pyrolysis gas yield accelerates with the increase in the desulfurized ash blending ratio, while it slightly slows down in the later stage, possibly due to the saturation of catalytic binding sites.

Specifically, the production of H₂ gradually increases with the increase in the desulfurized ash blending ratio. Although the slope decreases with the increase in the blending ratio, it remains higher than other products, ultimately showing a remarkable increase of 600%. This suggests that desulfurized ash can significantly enhance the yield of H₂. The production of CO₂ gradually decreases with a noticeable change in trend, but the slope tends to zero when the blending ratio reaches 40%, indicating that the catalytic effect of desulfurized ash has reached its peak. The trends of CH₄ and CO production are characterized by an initial increase followed by a decrease and an initial decrease followed by an increase, respectively, with relatively small changes in magnitude.

Analyzing CO through variance analysis, the calculated variance of CO is 2.8 mL/g, indicating a relatively small variation in the sample data. Combined with a total variation rate of 10%, this suggests that the impact of desulfurized ash on CO is not significant. Gases such as C₂H₆, C₄H₁, C₄H₁₀, C₃H₈, C₂H₄ show almost no change in production. This indicates that, in the combination where CS serves as the pyrolysis feedstock, desulfurized ash, as a catalyst, can inhibit the generation of CO₂ while increasing the yield of H₂. Additionally, desulfurized ash exhibits different effects on the production rates of CH₄ and CO before and after the peak, indicating that the catalytic effect of the catalyst reaches its peak at a certain concentration, with an increasing effect before the peak and a decreasing effect after the peak.

The conclusions obtained from the above analysis can be verified by consulting the literature. Desulfurized ash, as an inorganic salt ion catalyst, has a strong catalytic effect on reactions that produce H₂O, promote H₂ production, and absorb CO₂, but does not have a significant catalytic effect on the secondary decomposition that produces the final mixed product.

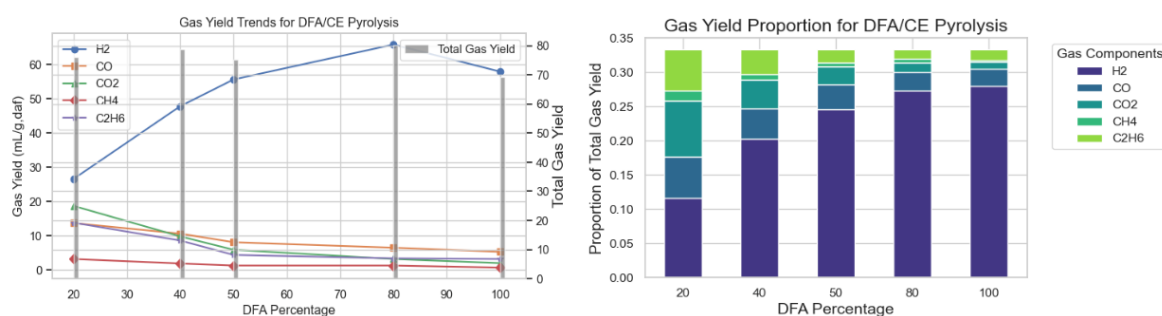


Figure 10 Gas Yield Trends for DFA/CE Pyrolysis

In the combination where CE serves as the model compound, the overall gas production fluctuates but is distributed around 65 mL/g. Numerically analyzing, the variance of the gas total is 12.4, and the standard deviation is less than 4, suggesting that the influence of the

desulfurized ash blending ratio on the total gas amount is not significant.

Specifically, the production of H₂ significantly increases with the increase in the desulfurized ash blending ratio, rising from 26 mL/g to 65.8 mL/g, with an increase of over 100%. However, during this period, the slope continuously decreases, and when the blending ratio reaches a certain value, further increasing the blending ratio leads to a decrease in H₂ production. This indicates that the catalytic effect of desulfurized ash on H₂ has a peak around a ratio of 80%. The closer to this peak, the slower the increase in the promoting effect, and after the peak, the promoting effect starts to decline. The production of gases such as CO, CO₂, CH₄, and C₂H₆ decreases with the increase in the desulfurized ash blending ratio, with a continuously decreasing slope. After reaching a certain value, an increase in the desulfurized ash blending ratio does not significantly affect gas production, and the decreasing slope approaches zero. This suggests that, in the combination where CE serves as the pyrolysis feedstock, desulfurized ash, as a catalyst, can inhibit the generation of CO, CO₂, CH₄, and C₂H₆ in pyrolysis reactions. The impact on H₂ shows different effects before and after a certain blending ratio, with the catalytic effect reaching a peak at a specific blending ratio, after which the catalytic effect decreases.

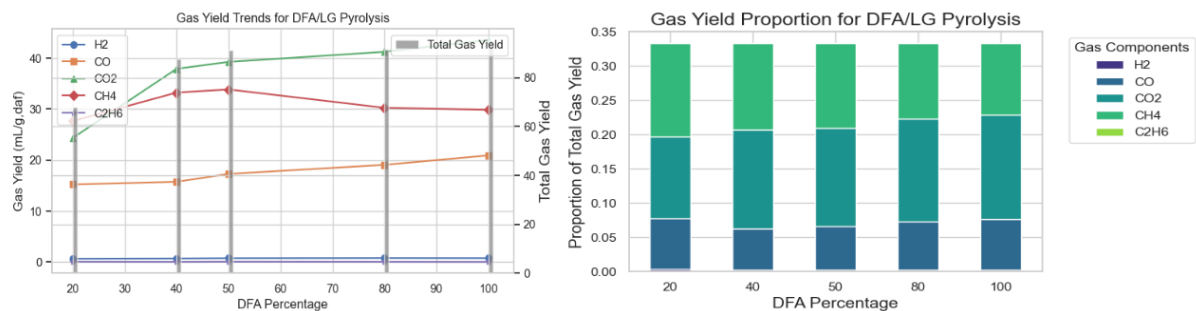


Figure 11 Gas Yield Trends for DFA/LG Pyrolysis

In the combination where LG serves as the model compound, the overall gas production increases with the increase in the blending ratio, with an increase from the initial value to the final value approaching 40%. However, from the perspective of the slope, it continuously decreases, indicating that desulfurized ash can significantly increase the total gas production in pyrolysis. Still, the degree of improvement has a limit, and the closer to the limit, the smaller the increment.

Specifically, the slopes of H₂ and C₂H₆ are almost zero, indicating almost constant yields. The yields of CO₂ and CO gradually increase, with CO₂ growing rapidly in the early stage with the increase in the desulfurized ash ratio, and the growth rate gradually decreasing later, possibly related to the saturation of catalytic sites. The yield of CH₄ first increases and then decreases, with a final increase of less than 10%, similar to the changes in the CS pyrolysis combination.

From the above discussion of the three sets of graphs, the catalytic effect of desulfurized ash as a catalyst in cellulose pyrolysis reactions generally follows the following pattern: it does not

have a significant impact on the yield of slightly complex organic compounds (such as C_2H_4), but it has a noticeable and single-effect on the yields of inorganic gases (such as H_2 , CO , CO_2 , etc.). This effect can be either consistently positive or consistently negative, depending on the composition of the model compound. This observation aligns with the chemical mechanisms indicated in the literature, laying the foundation for building the reaction kinetics model in the fourth question.

7. Model establishment and solution of question 3

For question three, under the condition of the same desulfurized ash ratio, this study conducted differential analysis on the yields of CE and LG pyrolysis products as well as the production of pyrolysis gases. Different forms and distributions of data call for various methods in data analysis, and choosing the most suitable analysis method is crucial in problem-solving. Therefore, this study first performed preliminary experiments such as normality tests and homogeneity of variance tests on the data. Based on the characteristics of the data, the optimal differential analysis approach was selected^[6].

7.1 Pre-experimental analysis

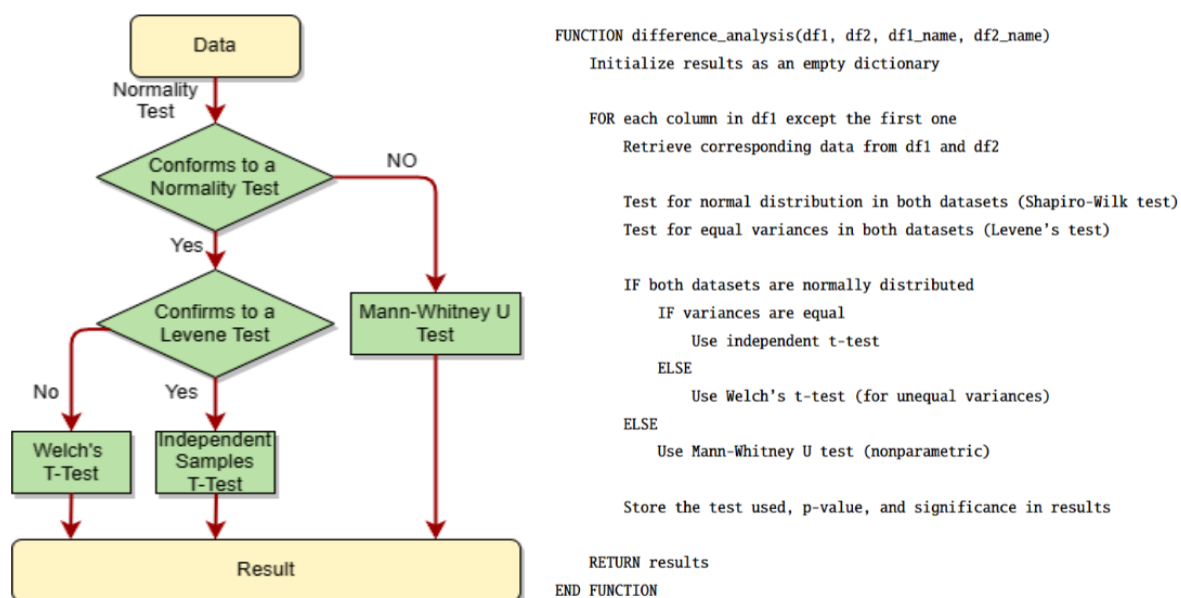


Figure 12 Pre-experiment analysis of processes and pseudocode

We first used the Shapiro-Wilk test to check whether the data on gas production from DFA/CE and DFA/LG pyrolysis followed a normal distribution. For data that did not meet the normal distribution assumption, we used the Mann-Whitney U Test for differential analysis. For data that met the normal distribution assumption, we further conducted the Levene test. The Levene test

is a statistical method used to examine whether the variances of two or more groups are equal, checking for homogeneity of variances, an important assumption in many statistical analyses, especially in methods comparing multiple groups, such as analysis of variance (ANOVA). The p-value is used to obtain the p-value of the Levene test. Comparing the p-value with the significance level (usually 0.05), the comparison result is assigned to equal-var. If equal-var is True, it indicates that the two datasets have homogeneity of variances. If it is False, it indicates that they do not have homogeneity of variances. For datasets with homogeneity of variances, Independent Samples T-Test is used for differential analysis, and for those without, Welch's T-Test is employed.

The formula for the normality test is as follows:

$$A^2 = -N - \frac{1}{N} \sum_{i=1}^N (2i - 1) [(\ln F(Y_i) + \ln(1 - F(Y_{N+1-i})))] \quad (3)$$

In that, the magnitude of the A value indicates the degree of fit between the data and the normal distribution curve. A smaller A value indicates a better fit. N is the sample size, and F(x) is the cumulative distribution function of the standard normal distribution.

The formula for the homogeneity of variance test is as follows:

$$MSA = \frac{\text{Sum of squares between groups}}{\text{degree of freedom}} = \frac{SSA}{k - 1} \quad (4)$$

SSA is the sum of squares of factor errors

$$MSE = \frac{\text{Sum of squares between groups}}{\text{degree of freedom}} = \frac{SSE}{n - k} \quad (5)$$

SSE is the sum of squares of random errors

$$F = \frac{MSA}{MSE} \sim F(k - 1, n - k) \quad (6)$$

F is the test statistic.

7.2 Differential Analysis

Due to space limitations, we only present the decomposed results for the gas products (data in Annex II) here. For the remaining structures, please refer to the appendix.

The results indicate that the gas products (H₂, CO, CO₂, CH₄, C₂H₆) generated from CS pyrolysis approximately follow a normal distribution. Using the T-test for differential analysis, it can be concluded that there are significant differences in the gas production between CE and LG pyrolysis under the same proportion of desulfurization ash catalysis.

Table 1 Results of the Variance Analysis

Products	Test Used	P-Value	SD	Products	Test Used	P-Value	SD
H ₂	T-Test	0.000071	TRUE	Tar	T-Test	2.56E-08	TRUE
CO	T-Test	0.001362	TRUE	Water	T-Test	0.049616	TRUE
CO ₂	T-Test	0.000188	TRUE	Char	T-Test	1.29E-14	TRUE
CH ₄	T-Test	9.62E-09	TRUE	Syngas	T-Test	0.000135	TRUE
C ₂ H ₆	T-Test	0.011604	TRUE				

¹ SD : Significant Difference

8. Model establishment and solution of question 4

8.1 Pre-experimental analysis

8.1.1 Introduction to the chemical mechanism of pyrolysis

Cellulose and lignin both belong to lignocellulosic biomass and share similar principles in their pyrolysis reactions. During the heating process of lignocellulosic biomass, the first step involves the breaking of polymer structure chemical bonds, leading to the release of volatile substances and rearrangement reactions within the residual matrix, known as primary reactions. After the formation of primary products, some volatile compounds undergo additional transformations to yield the final pyrolysis products, referred to as secondary reactions^[7].

Primary transformations mainly involve three major pathways: the formation of char, depolymerization, and fragmentation (as shown in Figure 13). Char is a solid residual product formed during biomass conversion, characterized by aromatic multi-ring structures. The process of char formation involves intra-molecular and inter-molecular rearrangements, primarily including the formation of benzene rings and the combination of aromatic rings in multi-ring structures. These rearrangement reactions often accompany the generation of water or non-condensable gases. Depolymerization refers to the breaking of chemical bonds connecting monomers within polymers, and this reaction continues, leading to a continuous decrease in polymer degree of polymerization until it transforms into volatile small molecules that separate from the system. Typically, this results in the formation of derivative monomers, dimers, and other liquid products at room temperature. Fragmentation involves the breaking of a large number of covalent bonds within polymers at high temperatures, generating small chain molecules such as acids, aldehydes, alcohols, and some pyrolysis gases.

Secondary reactions specifically refer to the cracking or recombination reactions that occur in

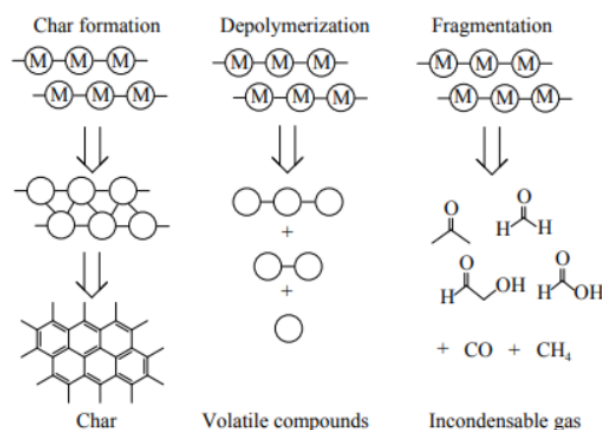


Figure 13 Main mechanism of biomass pyrolysis

the unstable portion of volatile products (such as tar and other aromatic substances). Cracking is the process in which covalent bonds within volatile compounds break to form smaller molecules. During this process, a large number of small molecule pyrolysis gases, such as CH_4 , CO , H_2 , are generated. Recombination involves the combination of volatile substances with each other, leading to the formation of higher-molecular-weight compounds, and this process is also accompanied by gas production. In the secondary reaction stage, cellulose and lignin exhibit somewhat different characteristics.

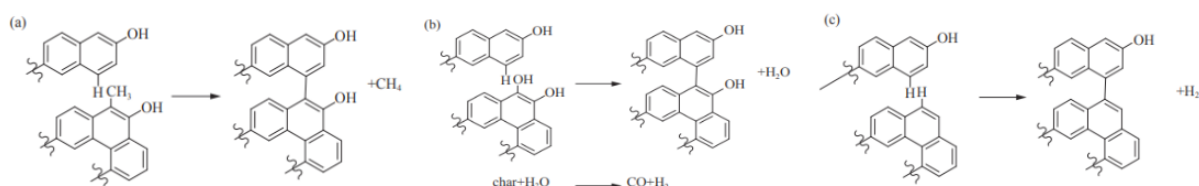


Figure 14 Conversion of substituent group from benzene ring to CH_4 , CO , H_2 and char

8.1.2 Predicted Catalysis Mechanism Analysis

To further analyze the directed catalysis mechanism of desulfurization ash on surrogate reactants cellulose (CE) and lignin (LG), this study, through data arrangement and comparison, elaborately examines the catalytic effects of desulfurization ash on various specific products. It attempts to explain the chemical principles behind these effects. The following is an example of the analysis of the catalytic effects of desulfurization ash at different ratios on the four pyrolysis gases of CE and LG: From Figure (a), it can be seen that the H_2 yield of DFA/CE is significantly greater than that of DFA/LG, and under different desulfurization ash (DFA)/LG mixing conditions, the H_2 yield in the pyrolysis gas is consistently less than 0.8 mL/g. This indicates that the H_2 produced during the pyrolysis of cotton stalks mainly comes from the decomposition of CE in the cotton stalks, and desulfurization ash significantly promotes the

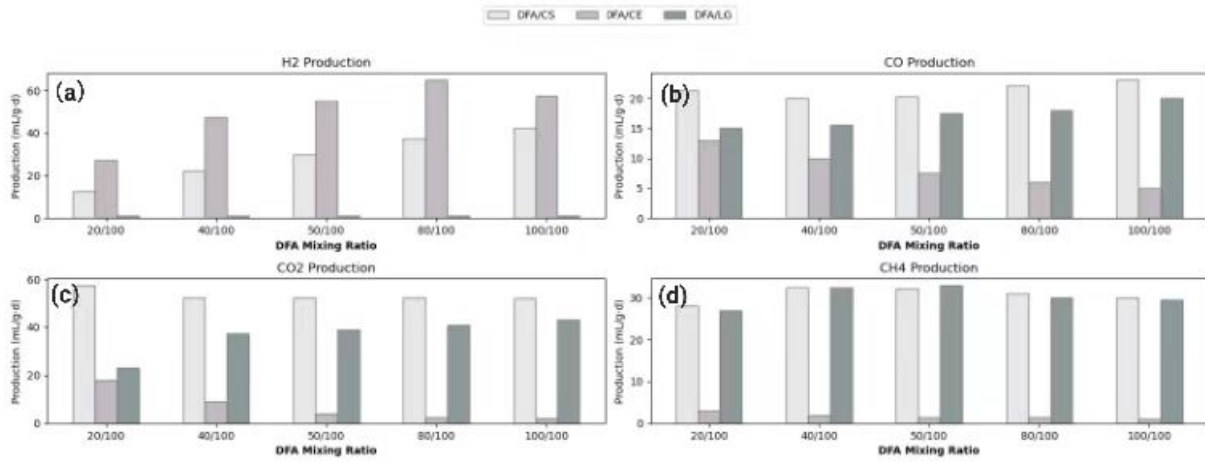


Figure 15 Catalytic effects of different proportions of desulfurization ash on four pyrolysis gases of CE and LG

chemical reaction of hydrogen generation from the free radicals produced during the pyrolysis of CE, resulting in the formation of H₂.

Generally speaking, in the pyrolysis process of lignocellulosic biomass, the cleavage of ether bonds and carboxyl functional groups is the main source of CO and CO₂ in the pyrolysis gas[please add citation here]. From Figures (b) and (c), it can be observed that in the pyrolysis process of cotton stalks, both components CE and LG are important sources of CO and CO₂ in the pyrolysis gas. As the content of desulfurization ash in the pyrolysis mixture sample continues to increase, its catalytic effect inhibits the reaction of CE decomposition to generate CO and CO₂, leading to a continuous decrease in the production of CO and CO₂ in the desulfurization ash/CE pyrolysis gas. Conversely, desulfurization ash promotes the chemical reaction of LG pyrolysis to generate CO and CO₂, resulting in a continuous increase in the production of CO and CO₂ in the desulfurization ash/LG pyrolysis gas.

From Figure (d), it can be inferred that the CH₄ component in the pyrolysis gas of cotton stalks mainly comes from the cleavage of methyl ether side chains abundant in LG, while the thermal decomposition of CE can only produce a very small amount of CH₄, and desulfurization ash has a pronounced inhibitory effect on this process.

8.2 Reaction kinetic model

Kissinger, Akahira, and others proposed the isoconversional kinetic method, which can be used to establish kinetic reaction models without a clear understanding of the reaction mechanism. The kinetic model can be simply expressed by the following equation^[8]:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E_{ag}(\alpha)}\right) - \frac{E_a}{RT} \quad (7)$$

In the equation, α represents the conversion rate, T denotes temperature, β represents the heating rate, $g(\alpha)$ stands for the integral expression of the reaction mechanism constant, considered constant at a given conversion value, and R is a constant.

As the experimental temperatures and heating rates are constant in this problem (T and β are fixed values), we are investigating the relationship between activation energy and conversion rate. By transforming the above equation, we can obtain:

$$\alpha = \exp\left(\frac{1}{c_1 \cdot E_a}\right) \cdot \exp(c_2 \cdot E_a) \quad (8)$$

The mechanism of catalyst influence on the chemical reaction involves changing the activation energy of the reaction. We assume that the proportion of the catalyst is linearly related to its ability to reduce activation energy within a certain range. Let the catalyst proportion be denoted as x , then $E_a = kx + b$. The above equation can be simplified to the following form:

$$a = \left(\frac{1}{c_1 \cdot x} + c_2\right) \cdot \exp(c_3 \cdot x) \quad (9)$$

After determining the form of the reaction kinetics equation based on chemical principles, we utilized the curve-fit function from the scipy library in Python to solve the parameters of the reaction kinetics equation. Firstly, we defined the Dynamical-model(x , c_1 , c_2 , c_3) function, where x represents the independent variable matrix, and c_1 c_3 are the parameters to be solved. The function returns $\left(\frac{1}{c_1 \cdot x} + c_2 - 2\right) \cdot \exp(c_3 - 3 \cdot x)$. Subsequently, we applied the Dynamical-model function, the independent variable (desulfurization ash ratio), and the dependent variable (yield or production rate of pyrolysis products) to the curve-fit function for parameter estimation, obtaining the reaction kinetics equations for various pyrolysis products. Due to space limitations, we present the reaction kinetics parameters for four pyrolysis products:

Substance	First parameter	Second parameter	Third parameter
Parameter_tar	6.07E+04	1.69E-01	-8.96E-01
Parameter_water	2.670937	0.136637	-0.81211
Parameter_char	1.49E+04	5.76E-01	-8.58E-03
Parameter_syngas	2.877523	0.064104	-1.37297

Figure 16 Reaction Kinetic Parameters of Four Pyrolysis Products

9. Model establishment and solution of question 5

This study constructed two mathematical prediction models to forecast the yield or rate of pyrolysis products across the entire range of desulfurization ash ratios from 0 to 100.

Model	Mean Absolute Percent Error	r2_score
Dynamical_model	2.887996370930983	0.9764485474181241
Quadratic_model	6.035249653304552	0.9241613426277608

The reaction kinetics equations obtained in the fourth question were chosen as the mathematical prediction models. The ash ratio was expanded from a discrete set of points (0.1, 0.2, ...) to a complete continuous space of 0 to 1.0. These values were then input into the models to predict the yields or rates of various pyrolysis products. Due to space limitations, we present here the predicted results for the rates of the four pyrolysis products, as shown in Figure X.

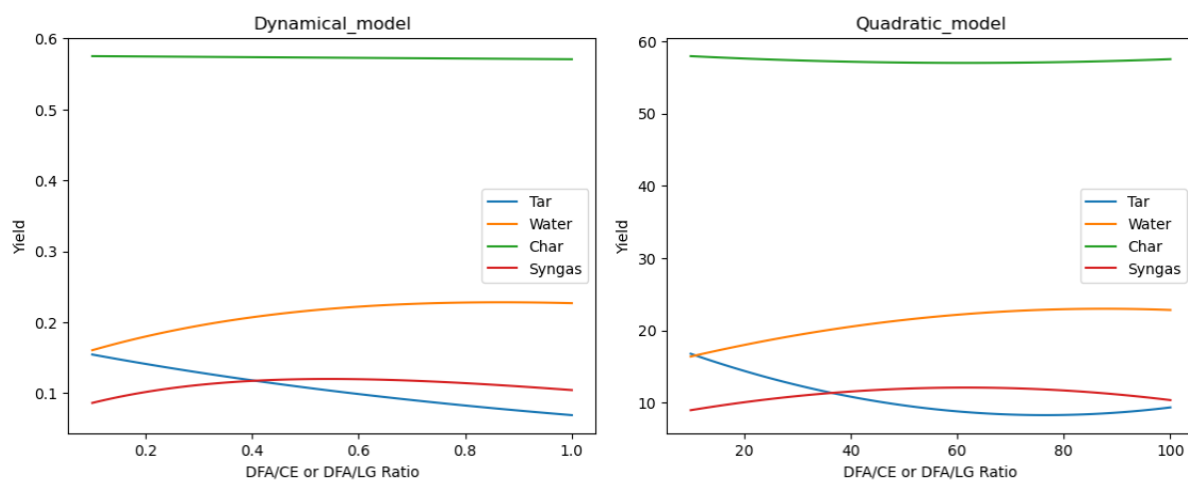


Figure 17 Prediction results of pyrolysis product yield

To assess the performance of the prediction models, we employed a comparative experimental approach and re-established a quadratic prediction model (as shown in Figure X). As observable in the graph, the predictions of Dynamical-model and Quadratic-model are nearly identical, with only slight differences in the prediction of Tar yield. Further, we calculated the average absolute percentage error and correlation coefficient for both models (as shown in the table below). The results indicate that Dynamical-model performs superiorly, demonstrating the accuracy and effectiveness of our modeling of the kinetic equation.

The formula for calculating the average absolute percentage error is as follows:

$$\text{MAPE} = (1/n) * \sum(|(\text{Actual value} - \text{predicted value}) / \text{Actual value}|) * 100\% \quad (10)$$

10. Model evaluation and improvement

10.1 Model Advantages

(1) In the data preprocessing stage, this model takes full account of the characteristics of compositional data constraints. By using centralized log transformation, the original data is transformed to alleviate the constraints imposed by compositional nature, rendering the regression results more reasonable.

(2) In the analysis of the relationship between DFA proportion and pyrolysis product yield in the first question, a stepwise progressive approach is employed. Initially, preliminary discussions on the relationship are conducted through visual methods such as chord diagrams and nested pie charts. Subsequently, correlation coefficients are calculated to scientifically assess the existence of relationships between variables. Finally, ridge regression modeling is performed for pyrolysis products exhibiting correlation, enabling a quantitative analysis of the relationships. This layered and in-depth analytical method enhances logical coherence in the analysis and facilitates a more thorough and comprehensive exploration of relationships.

(3) In the modeling process of the first question, careful consideration is given to the potential data singularity issue arising from the small data size. Therefore, ridge regression is employed by introducing penalty terms to mitigate the impact of the data itself, resulting in a model with superior descriptive and predictive capabilities.

(4) In the differential analysis of the third question, preliminary experiments such as normality tests and homoscedasticity tests are conducted on the data. Based on an understanding of the data characteristics, appropriate analysis approaches are chosen, ensuring the rationality of the differential analysis.

(5) In constructing the reaction kinetics model, domain knowledge of pyrolysis reactions is incorporated. A suitable kinetic model is established based on the mechanism of cotton stalk pyrolysis reactions. Through model comparisons, the effectiveness of our modeling approach is demonstrated.

10.2 Model Limitations

During the construction of the reaction kinetics model, it is assumed that the activation energy is linearly related to the desulfurized ash mixing ratio. Although this assumption has a certain degree of biological and chemical rationale, it lacks empirical evidence due to constraints in data and time.

10.3 Model Improvement

For Question Four, considering the collection of relevant data, an analysis of the correspondence between desulfurized ash mixing ratio and activation energy in different combinations of pyrolysis reactions can be conducted. By regressing and building a model, a more accurate mapping relationship between desulfurized ash mixing ratio and activation energy can be obtained. This improvement aims to enhance the scientific validity of the constructed reaction kinetics model, enabling more accurate predictions of the yield of various pyrolysis products under different catalyst input ratios.

11. Sensitivity Analysis

In chemical production, changes in environmental factors or the state of the substances can significantly impact the yield of products. A reasonable chemical reaction kinetics model should not only fit the existing data well but also be able to adjust the output results sensibly in response to various changes. Therefore, it is necessary to perform sensitivity analysis on the model obtained in this question. This involves altering model parameters to simulate changes in the state of the target product or environmental conditions. The sensitivity of the model is measured by assessing the differences in yield before and after parameter changes.

As the regression models for the yields of various substances are consistent, this study selects Tar in pyrolysis products and H₂ in pyrolysis gases as representatives for analysis (DFA=1.0). For the kinetic model $\alpha = \exp\left(\frac{1}{c_1 \cdot E_a}\right) \cdot \exp(c_2 \cdot E_a)$, the parameter c_2 is adjusted by $\pm 5\%$ in each iteration. The changes in substance yield and the differences from the initial values after each adjustment are calculated. The results are as follows:

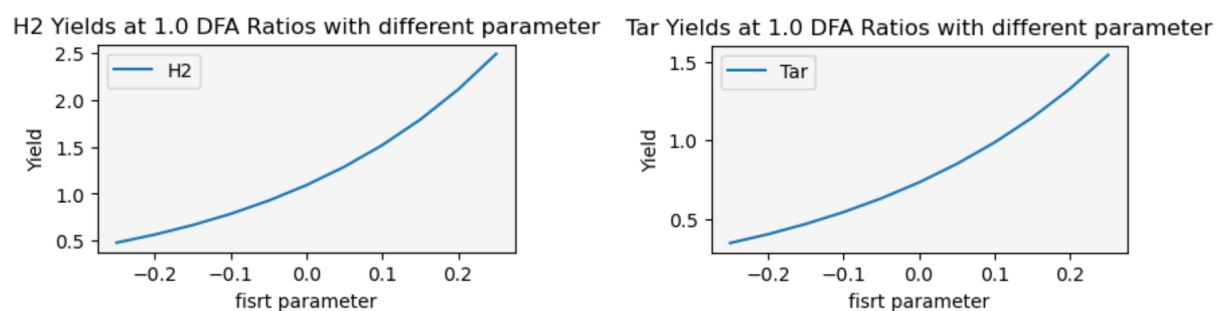


Figure 18 Changes in material yield after treatment and differences from initial values

Taking H₂ as an example, we conducted a detailed analysis of the sensitivity of the reaction kinetics model. Numerically, as the parameter c_2 increases, the yield of H₂ shows a clear upward trend, indicating that the reaction kinetics model we established exhibits good sensitivity. From a slope perspective, as the parameter c_2 increases, the rate of increase in H₂ production also accelerates, reflecting the chemical mechanism of the reaction.

In summary, the model demonstrates good sensitivity, ensuring stability while making reasonable adjustments to changes in external factors.

References

- [1] IEA (2023), World Energy Outlook 2023, IEA, Paris <https://www.iea.org/reports/world-energy-outlook-2023>, License: CC BY 4.0 (report); CC BY NC SA 4.0 (Annex A)
- [2] <https://www.intechopen.com/chapters/68053>
- [3] Energy Fuels (IF 5.3) Pub Date : 2018-01-22 00:00:00 , DOI: 10.1021/acs.energyfuels.7b03078 Hayat Bennadji 1, 2 , Lavrent Khachatryan 2 , Slawomir M. Lomnicki 1
- [4] Aitchison, J., Barceló-Vidal, C., Egozcue, J.J., et al. (2002) A Concise Guide to the Algebraic-Geometric Structure of the Simplex, the Sample Space for Compositional Data Analysis. Proceedings of IAMG, 2, 387-392.
- [5] Scientific Platform Serving for Statistics Professional 2021. SPSSPRO. (Version 1.0.11)[On-line Application Software]. Retrieved from <https://www.spsspro.com>.
- [6] The nature of statistical learning theory.[J] . Cherkassky V.IEEE transactions on neural networks . 1997 (6)
- [7] Zou, J.; Hu, H.; Xue, Y.; Li, C.; Li, Y.; Yellezuome, D.; He, F.; Zhang, X.; Rahman, M. M.; Cai, J., Exploring kinetic mechanisms of biomass pyrolysis using generalized logistic mixture model.Energy Conversion and Management, 258 (2022):115522.
- [8] Citation: LI Cheng-yu, ZHANG Jun, YUAN Hao-ran, WANG Shu-rong, CHEN Yong. Advance on the pyrolytic transformation of cellulose[J].Journal of Fuel Chemistry and Technology, 2021, 49(12): 1733-1751.doi:10.1016/S1872-5813(21)60134-2

Appendix

Inspection value	number	average	Standard deviation	t	P	Inspection value	number	average	Standard deviation	t	P
34.42	8	42.082	3.764	5.758	0.001***	27.42	8	19.262	3.759	-6.139	0.000***
Tar_yield						Water_yield					
Inspection value	number	average	Standard deviation	t	P	Inspection value	Number	average	Standard deviation	t	P
24.17	8	24.065	1.141	-0.26	0.802	16.73	8	14.59	1.271	-4.763	0.002***
Char_yield						S_yield					

Figure 19 The model compound is CE

Inspection value	number	average	Standard deviation	t	P	Inspection value	number	average	Standard deviation	t	P
18.06	8	11.3	3.207	-5.962	0.001***	15.3	8	20.435	2.539	5.721	0.001***
Tar_yield						Water_yield					
Inspection value	number	average	Standard deviation	t	P	Inspection value	number	average	Standard deviation	t	P
57.46	8	57.336	0.373	-0.939	0.379	10.69	8	10.929	1.153	0.586	0.577
Char_yield						S_yield					

Figure 20 The model compound is LG

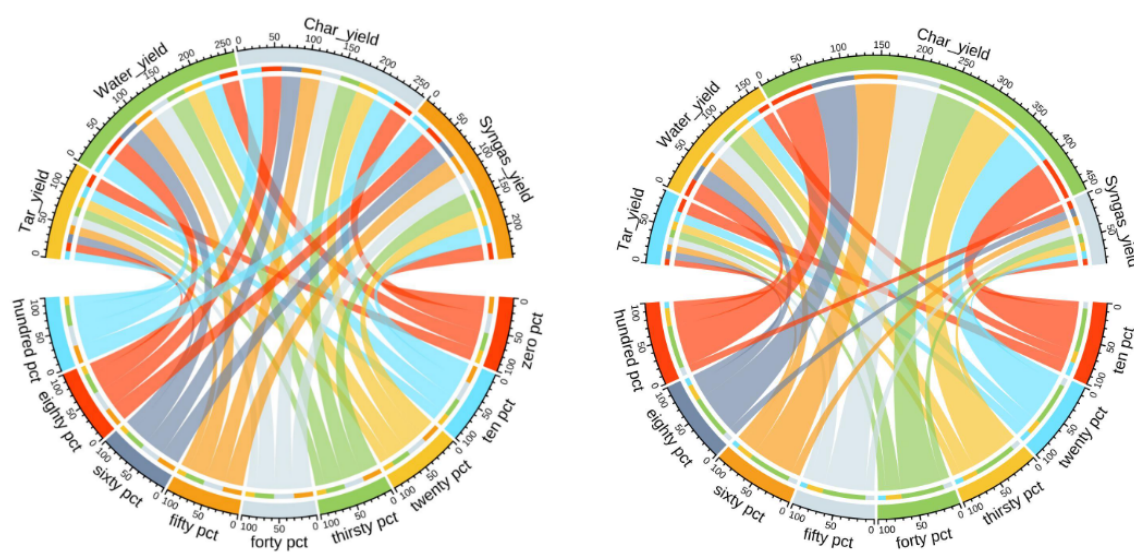


Figure 21 The model compound is CE

There is no relationship between char yield and mixing ratio under this combination.

Under this combination, there is no significant relationship between char, syngas yield, and mixing ratio.

Substance	Redge regression model results
Tar	yield=-0.114+0.233*proportion
Water	yield=0.172-0.353*proportion
S	yield=-0.0-0.292*proportion
Model compound	CE

Figure 22 The model compound is LG

Substance	Redge regression model results
Tar	yield=-0.114+0.233*proportion
Water	yield=0.172-0.353*proportion
S	yield=-0.0-0.292*proportion
Model compound	CE

Figure 23 Left:CS Right:LG