

Cotton stalk pyrolysis reaction: scientific determination of more efficient feed ratio

Summary

With the development of The Times, the demand for energy is increasing rapidly. At the same time, people's awareness of environmental protection is also motivated. The development and utilization of new clean energy is particularly important. Under this circumstances, the research and development of new energy in the laboratory is of great importance. To make scientific determination of more efficient feed ratio, this paper designed reasonable prediction method based on regression analysis algorithm and Friedman algorithm.

For question I, we first sort out and calculate some characteristic values of the given data, compare the difference of the data in each combination, and analyze the data property. By establishing scatter plot and regression model, we make judgment on the trend of data change. Then, Friedman method was used to detect the difference of data sets, and the catalytic action and catalytic effect of catalyst desulfurization ash were described.

For question II, we used line chart and column stack chart to express the trend of the yield of each gas component in different pyrolysis combinations with the change of mixing ratio. Then, the trend of the yield of each gas in the same pyrolysis combination is also analyzed.

For question III, we judged the significant difference of CE and LG pyrolysis product yield and gas component yield respectively. Non-parametric test was conducted on the data given in the question, and 0.05 was selected as the significance level for comparison with p-value. Line chart was made for intuitive analysis to judge the significance of the difference between CE and LG groups.

For question IV, based on the limited data given, the chemical mechanism of cellulose and lignin pyrolysis reaction was speculated respectively. As for cellulose, the pyrolysis reaction mechanism of cellulose was predicted, and the types and yields of products were analyzed by querying the existing data. Then, the kinetic model such as Arrhenius equation is constructed, the parameter values in the equation are fitted, and the equation which is generally applicable to this experiment is deduced by using the idea of regression analysis. As for lignin, we speculated the mechanism of pyrolysis reaction and its products and characteristics through its structure and properties. In addition, we found that different types of products can be obtained by controlling the temperature range.

For question V, based on the available data sets, we use scatter plots and their interpolation curves to perform the characteristics of regression analysis to plot the possible yields of cellulose and lignin pyrolysis products, so as to predict the optimal mixing ratio of pyrolysis reactions and the distribution of pyrolysis products. For the pyrolysis combinations DFA/CE and DFA/LG, the relative benefits reached their maximum when the mixture ratio was 0.84 and 0.28, respectively. In order to ensure the feasibility of the model in this paper, RMSE method was used to evaluate and analyze the sensitivity of the model.

Finally, we provide three sensitivity analysis methods to check the accuracy of the mathematical model. According to our analysis, we believe that the model established in this paper has good practicability.

Keywords: pyrolysis reaction, regression analysis, Friedman test, interpolation curve

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1 Introduction

1.1 Background

With the increasing demand for renewable energy around the world, biomass as a mature renewable energy source has attracted wide attention. Among them, cotton stalk is regarded as an important biomass energy resource because of its rich biomass components such as cellulose and lignin. Although the pyrolysis of cotton stalk can produce various forms of renewable energy, the quality and yield of its pyrolysis products are affected by various factors such as pyrolysis temperature and catalysts. Therefore, it is of great significance to study the mechanism and properties of cotton stalk pyrolysis products (see Appendix for definitions), as well as the mechanism and role of catalysts in the pyrolysis process, for the effective utilization and sustainable development of cotton stalk.

Due to various factors such as cost, the controllability and stability of catalyst desulfurization ash in the reaction and their contribution to cotton stalk pyrolysis should be considered during the pyrolysis and selection of model compounds at different mixing ratios, so as to obtain the best results at the lowest cost.

1.2 Work

(1) Research objective

With the continuous development of The Times, the concept of environmental protection has gradually gained popularity. People increasingly pursue raw materials with low cost, low pollution and high recyclability. Biomass can meet these requirements. However, as an emerging fuel substance, we need to explore its combustion products, and explore the nature, so as to verify the feasibility of our recognition and use. In this paper, through data analysis, mathematical modeling, reasoning and prediction, we seek the best input mixing ratio that can produce the maximum benefit, and make a contribution to the experimental operation or actual industrial production.

(2) Research content

Based on Appendix 1 and Appendix 2, we integrated and analyzed the data given in them, explored the regression properties of discrete data, speculated the mechanism of thermal decomposition of cotton stalk, and established a kinetic model for analysis and verification.

(3) Research Methods

Mathematical models (discrete data feature tables, regression analysis models, etc.), chemical models (chemical reaction mechanism, organic chemical structure simplification, reaction kinetics models, etc.), and conjectures and predictions based on limited data conditions were used.

(4) Research steps

Integrate data → analyze data properties → build model → analyze model → predict results

(5) Expected results

By controlling some conditions in the chemical reaction, we can achieve the initial control effect on the type and yield of pyrolysis products of cotton stalk and predict the distribution of product yield. On the basis of protecting the environment to the greatest extent, we can achieve the greatest positive economic benefits. Reduce the unnecessary trouble caused by potential errors in the optimization of experimental practice operation.

2 Problem analysis

2.1 Data analysis

2.1.1 Description of data

In Appendix 1, the percentages of pyrolysis products generated under different DFA/CS, DFA/CE, and DFA/LG mixing ratios are given, which include tar, water, coke residue, syngas, etc. The specific gas generation distribution in syngas is given in Appendix 2.

2.1.2 Definition of data eigenvalues

In the process of analyzing data group, we often use the methods of maximum value, minimum value, average value, variance, standard deviation and so on to explore the dispersion degree of data or the stability of distribution.

Here, we give the definition of eigenvalue (DE):

A data eigenvalue is a linear group of data used to characterize the data. Data feature values contain ten constants, which are sample size, maximum value, minimum value, mean value, standard deviation, median value, variance, kurtosis, skewness and coefficient of variation (CV).

The above values will be used to analyze the properties of the data group.

2.2 Analysis of Question I

Through the analysis of the question I, we can divide it into two parts to solve respectively. In the first part, we study the effect of mixing ratio on the pyrolysis product. In the second part, the catalytic effect of desulfurization ash on the pyrolysis reaction of cotton stalk will be studied.

The first part requires us to analyze the specific data given in the table and judge the difference of pyrolysis products under different mixing ratios through the analysis results. Before analyzing the data, we can list the characteristic quantities of the given data (such as sample size, maximum value, average value, variance, etc.) to determine the analyzability of the data. Then, we use statistical methods to analyze the relationship between the mixing ratio and the pyrolysis products.

In the second part, we can first judge the nature of the data and ensure that the given data meet the preconditions for relevant analysis. Under the premise that the difference of data is statistically significant, we can analyze the catalytic effect and effect of desulfurization ash on pyrolysis reaction under different conditions.

2.3 Analysis of Question II

Through the analysis of the question raised by the second question, we can divide the

second question into two parts to be solved separately. In the first part, the trend of the yield of each gas component in different pyrolysis combinations with the change of mixing ratio was studied. The second part deals with the variation trend of the fractional yield of each gas in the same pyrolysis combination with the change of the mixing ratio.

For the first part, we can draw intuitive and clear line charts to show the trend of the yield of each gas component in different pyrolysis combinations changing with the change of mixing ratio. Then, comparative analysis was carried out to compare the gas yield changes between different pyrolysis combinations, and to analyze the catalytic effect of desulfurization ash on the pyrolysis process of cotton stalk, fiber and lignin.

For the second part, we plotted the column stack diagram to show the changes in the sub-yield of each gas produced by the same pyrolysis combination under different mixing ratios. Combined with the chemical reaction mechanism and pyrolysis process theory, we inferred the possible reasons for the changes in the yield of different gases.

2.4 Analysis of Question III

Question III requires us to analyze whether there is a significant difference in the yield of CE and LG pyrolysis products and the yield of gas components under the catalysis of the same proportion of desulfurization ash according to the data given in the table. We can use the given data to conduct non-parametric tests and compare with the critical value to determine whether there is a significant difference.

Here, we choose the cutoff value of 0.05, which is commonly used in statistics. A p-value greater than 0.05 would indicate no significance. p-value less than 0.05 will be considered significant.

2.5 Analysis of Question IV

This question requires us to establish the catalytic reaction mechanism of desulfurization ash of CE, LG and other model compounds, and analyze the reaction kinetic model established by them.

As a kind of biomass, cotton stalk is mainly composed of cellulose, hemicellulins, lignin, trace elements and minerals[1]. Among them, cellulose accounted for 40-60%, hemicellulose accounted for 20-40%, and lignin accounted for 10-25%. Thermogravimetric analysis of the model compounds showed that the pyrolysis characteristics of the three polymers were significantly different: the thermal weight loss of cellulose and hemicellulose was between 300-400°C and 200-350°C, respectively, while the thermal weight loss of lignin lasted for a long time and had a wide range of 200-600°C[2].

Since the experimental data are only given for the pyrolysis products of CE and LG, and we know that all reactions are carried out under the same temperature condition by default, we choose the reaction temperature range of 350~400°C. In this temperature range, hemicellulose can be considered as no thermogravimetric process, that is, only cellulose and lignin undergo thermal decomposition reaction, so as to fully meet the feasibility of the given data set treatment.

Therefore, in the subsequent modeling process, we analyzed the pyrolysis products of cellulose and lignin to analyze the pyrolysis mechanism of cotton stalk and establish a kinetic model.

2.6 Analysis of Question V

According to the question, in the data table given in Appendix 1 and Appendix 2, the mixing ratio of desulfurization ash and biomass is 10/100, 20/100, 30/100, 40/100, 50/100, 60/100, 80/100 and 100/100, respectively. The reason for the selection of this mixing ratio is that under these known experimental conditions, the relative error of the parallel experiment is less than or equal to 5%. However, if the mixing ratio is small, it may have a great impact on the experimental results, and even seriously affect the exploration and optimization process of the experiment. Therefore, based on the existing data, we need to integrate and analyze the data set, and establish an appropriate mathematical model to predict the yield or yield of pyrolysis products under limited data conditions (that is, a specific temperature, pressure, etc.), so as to greatly reduce the time needed for experimental optimization, and more accurately describe the change trend of pyrolysis product distribution.

In addition, the combustion of cotton stalk as biomass fuel belongs to the utilization of biomass energy in new energy sources. Compared with traditional wood or coal combustion, it has many advantages, such as recyclability, low pollution, wide distribution, etc. [3]. Here, we take the low pollution of biomass combustion as the main consideration factor for selecting the optimal scheme, and the economic benefits as the secondary consideration factor. Therefore, we need to explore the lowest pollution of pyrolysis products of cotton stalk under a certain mixing ratio, that is, the least polluting gases are generated.

In summary, for the question V, we think that it can be divided into the following two parts.

(1) Optimal scheme prediction model: Through the given data, an appropriate function model is established, and the properties of the function image are used to solve the mixing ratio scheme when the pollution is the lowest.

(2) Prediction of the yield or quantity of pyrolysis products under different mixing ratios: a regression function model was used to predict the yield of pyrolysis products under various mixing ratios.

We will use Matlab2023a to visualize the data, and establish the corresponding mathematical model to solve the problem.

3 Symbol and Assumptions

3.1 Symbol Description

Symbols	Description
<i>Inc.</i>	Data changing show an increasing trend
<i>Dec.</i>	Data changing show an decreasing trend
<i>Std.</i>	Data is basically unchanged and remains stable
H_0	Null hypothesis
H_1	Alternative hypothesis

χ^2	Chi-square Distribution
R_j	Sum of the ranks of all samples under the j th condition
ρ	A certain level of significant level
α	Average value per unit of output of CO and C ₂ H ₆
β	Specific yield of H ₂
γ	Relative benefit

3.2 Fundamental assumptions

Since the data presented in the appendix are too small, we cannot fully consider the various factors that affect the experimental results, such as temperature, pressure or pressure, heating rate, reactant or product concentration, etc. Therefore, we need to make a series of assumptions before modeling to ensure the feasibility of the model we have built. The details are as follows:

- (1) All reactions are carried out at constant temperature and the same temperature;
- (2) In all reactions, the CE concentration is same. Likewise, the LG concentration is the same in all reactions.
- (3) All reactions are carried out under constant pressure and the pressure is the same.
- (4) The catalyst has high activity at the reaction temperature.

4 Models and Test

4.1 Question I: Data visualization Processing

4.1.1 Data eigenvalue

Using the data provided in Annex 1, the top ten eigenvalue tables of the DFA/ cotton stalk (DFA/CS), DFA/CE and DFA/LG pytolysis product yields were presented and compared.

By observing Tables 4.1, 4.2 and 4.3, we can intuitively see the specific characteristic values of the horizontal distribution of the data.

Table 4.1 Yield of Decomposition Products from DFA/CS Pyrolysis

Variable	Sample quantity	Maximum	Minimum	Mean	standard deviation	Median	Variance	Kurtosis	Skewness	Variable coefficient (CV)
Tar yield	9	19.46	12.13	14.5467	2.4309	13.89	5.9091	2.8114	1.0108	0.16711
Water yield	9	31.02	26.84	28.9133	1.4153	28.62	2.0031	1.8567	0.21381	0.04895
Char yield	9	29.87	29.11	29.3789	0.2464	29.33	0.060711	2.7559	0.87259	0.0083868
Syngas yield	9	28.45	24.49	27.1611	1.2786	27.16	1.6348	3.1125	-0.96876	0.047074

Table 4.2 Yield of Decomposition Products from DFA/CE Pyrolysis

Variable	Sample quantity	Maximum	Minimum	Mean	standard deviation	Median	Variance	Kurtosis	Skewness	Variable coefficient (CV)
Tar yield	9	45.28	34.42	42.0825	3.7639	43.51	14.1668	3.1155	-1.2515	0.089441

Water yield	9	27.42	16.14	19.2625	3.7586	18.045	14.1267	3.8139	1.3738	0.19512
Char yield	9	24.91	21.43	24.065	1.1411	24.565	1.3021	4.7334	-1.762	0.047418
Syngas yield	9	16.73	12.75	14.59	1.2708	14.65	1.6149	2.28	0.14065	0.087099

Table 4.3 Yield of Decomposition Products from DFA/LG Pyrolysis

Variable	Sample quantity	Maximum	Minimum	Mean	standard deviation	Median	Variance	Kurtosis	Skewness	Variable coefficient (CV)
Tar yield	9	18.06	8.19	11.3	3.2068	10.29	10.2837	3.4873	1.2692	0.28379
Water yield	9	23.69	15.3	20.435	2.5388	21.19	6.4457	3.2503	-0.95555	0.12424
Char yield	9	58.17	56.98	57.3362	0.37286	57.19	0.13903	4.2594	1.5116	0.0065031
Syngas yield	9	11.88	8.47	10.9287	1.1532	11.275	1.33	3.5862	-1.283	0.10552

4.1.2 Analysis of scatter plot and fit curve

Through the above table, it is difficult to observe the difference of pyrolysis products under different mixing ratios. In addition, the scatter plot can reflect the numerical changes at each time, and the fitting curve can depict the general trend of the scatter distribution. Therefore, the multiple linear (or nonlinear) regression analysis method in statistics was used to draw the scatter plot and fitting curve of the yield of tar, water, coke slag and syngas under the three pyrolysis combinations, as shown below.

(1) DFA/CS

Figure 4.1 (see Annex 1 for image generation code) shows that the fitting curve of pyrolysis recovery rate of each product is linearly correlated with the change of desulfurization ash/cotton stalk (DFA/CS) mixing ratio.

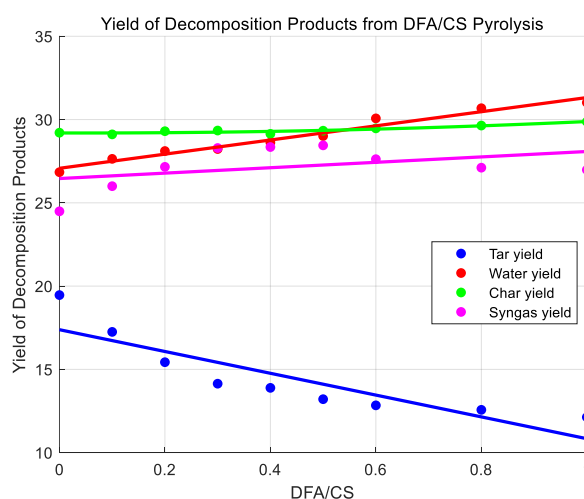


Figure 4.1 Yield of Decomposition Products from DFA/CS Pyrolysis

We further observed and analyzed that with the continuous increase of mixing ratio, the pyrolysis recovery rate of tar decreased, and the pyrolysis recovery rate of water, coke slag and syngas increased, and the pyrolysis recovery rate of water changed most significantly. Comparing the scatter plots, it can be seen that the pyrolysis recovery of tar

and syngas is greatly affected by the fluctuation of mixing ratio, while that of water and coke slag is less affected, and the data is relatively stable.

(2) DFA/CE

Figure 4.2 (see Annex 1 for image generation code) illustrates the mixture ratio of desulfurization ash/cellulose oligosaccharide (DFA/CE).

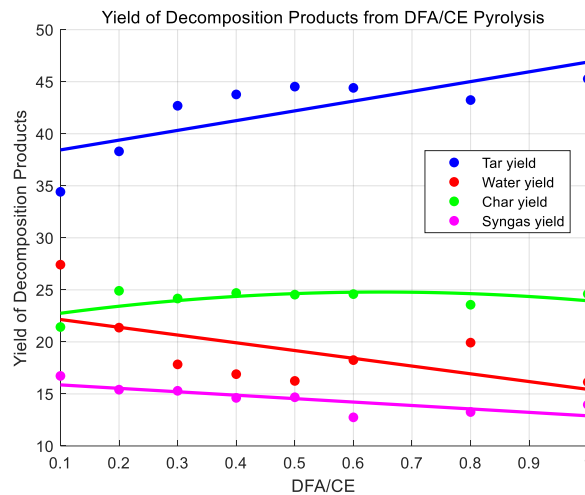


Figure 4.2 Yield of Decomposition Products from DFA/CE Pyrolysis

The fitting curve of the pyrolysis recovery of coke slag has a nonlinear correlation with the increase of the mixing ratio, and there is a change process of first increasing and then decreasing. The recovery of tar, water and syngas showed linear changes, and the recovery of tar showed an increasing trend, while the recovery of water and syngas showed a decreasing trend. Similarly, by comparing the scatter plots, it can be observed that the actual recovery rates of tar and water are more floating and unstable than those of syngas and coke slag.

(3) DFA/LG

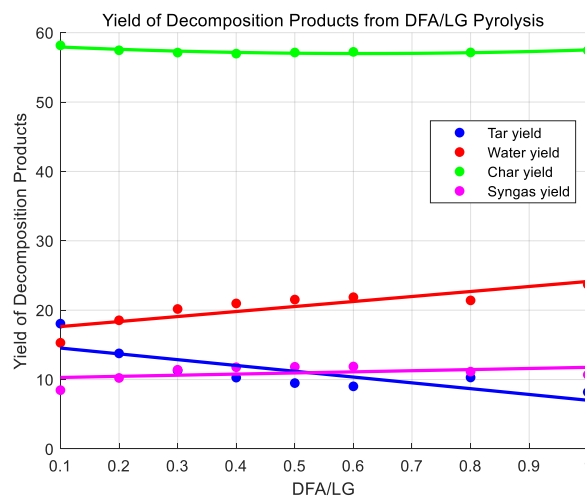


Figure 4.3 Yield of Decomposition Products from DFA/LG Pyrolysis

Figure 4.3 (see Annex 1 for the image generation code) shows that the regression model of pyrolysis recovery of coke slag is nonlinear and stable, while the regression model of pyrolysis recovery of tar, water and syngas is linear when the mixture ratio of de

sulphurization ash/lignin (DFA/LG) changes. Among them, the recovery yield of water and syngas increased with the increase of mixing ratio, and the recovery yield of tar decreased.

By comprehensively comparing the above three figures, we listed the following chart to summarize the relationship between the mixing ratio and the pyrolysis products (tar, water, coke slag and syngas) in each pyrolysis combination.

Table 4.4 Relationship between mixing ratio and pyrolysis products

	Tar yield	Water yield	Char yield	Syngas yield
DFA/CS	Dec.	Inc.	Std.	Inc.
DFA/CE	Inc.	Dec.	I&D.	Dec.
DFA/LG	Dec.	Inc.	Std.	Inc.

4.1.3 Friedman test and analysis of catalytic action of desulfurized ash

Through the previous analysis of the graph, we roughly grasp the relationship between the mixing ratio and the pyrolysis products in the three pyrolysis combinations. In the following, we analyze whether the desulfurization ash has a catalytic effect on the pyrolysis reaction and analyze its catalytic effect.

Considering that biomass pyrolysis, as a heat conversion technology that makes full use of biomass resources, has a more complex reaction process, in fact, a variety of factors will affect the pyrolysis results, specifically reflected in the reaction raw material, mixing ratio, pretreatment, heating rate, termination temperature, pyrolysis atmosphere, pressure pressure and other aspects[4]. Therefore, when we study the catalytic effect of desulfurization ash, we believe that the experiment takes ideal conditions, that is, ignoring the change of some factors that may exist in the reaction process and cause the change of experimental results.

(1) Why Friedman test was selected

Because the sample size of the data given in Appendix 1 is small, not universal, and there is a certain chance error, we use Friedman test to test the data group, which can ensure the rationality and stability of the subsequent data analysis. It can also avoid the possibility of verifying the normality or homogeneity of variance of the data when selecting other methods.

2. Calculate the Friedman statistic

Step 1: Formulate the hypothesis

Zero hypothesis H_0 : In the whole, it is roughly equal under different conditions. Namely, there is no difference.

Alternative hypothesis H_1 : there are at least two conditions in general are not equal. Namely, there are differences.

Step 2: data collection

We divided the data given in Appendix 1 into three data groups according to different pyrolysis combinations, and calculated the Friedman statistic separately.

Step 3: Calculate the rank for each sample

Step 4: Calculate the values

We define N as the total number of samples, k as the number of conditions, R_j as the rank summation of all samples under the j condition. Then, we can get the following

formula:

$$\chi^2 = \frac{12}{N(k+1)} \left(\sum_{j=1}^k R_j^2 - \frac{N^3 - N}{4} \right)$$

Through the above formula, we can draw the χ^2 of the three datasets are 23.13, 22.95 and 20.25, respectively. Furthermore, we run the code shown in Figure 4.4 in Matlab.

```
pValue = 1 - chi2cdf( $\chi^2$ ,3);
disp(['p value:',num2str(pValue)]);
```

Figure 4.4 Matlab code

The p values for the three datasets are shown in Table 4.5.

Table 4.5 Value of Friedman Test

	DFA/CS	DFA/CE	DFA/LG
Approximate value of χ^2	23.13	22.95	20.25
p value of data array (Approximate result)	3.8e-05	4.1e-05	0.0002

Step 5: Draw conclusions

For a given significance level $\rho = 0.05$, the p-value of the three pyrolysis combinations of DFA/CS, DFA/CE and DFA/LG are all less than ρ , so the zero hypothesis can be considered wrong. It means that there is a difference between the groups. In other words, the use of different doses of catalyst (that is, different mixing ratios) will affect the yield of pyrolysis products. That is, it has a catalytic effect.

At the same time, combined with Figure 4.1, Figure 4.2, Figure 4.3 and Table 4.4, we know that the change of the ratio of catalyst (DFA) to three substances (CS,CE,LG) usage has a certain impact on the change of pyrolysis product yield.

4.2 Question II: Variation trends of data

4.2.1 Line chart

Using the data provided in Annex II, we plotted the variation trend of the pyrolytic gas product yield of desulfurization ash/cotton stalk (DFA/CS), desulfurization ash/oligo saccharide cellulose (DFA/CE) and desulfurization ash/lignin (DFA/LG) under different mixture ratios, and gave trend analysis and comparative analysis on the chart.

(1) Trend analysis of the gas yield of each pyrolysis combination

Figure 4.5 shows the trend of the gas yield rate of nine gases, including hydrogen, carbon monoxide, carbon dioxide, methane, ethane, propane, propylene, ethylene and butane, in the desulfurization ash/cotton stalk (DFA/CS) group as the mixing ratio changes.

Through the analysis of the image, we can draw the following conclusions:

(a) Hydrogen: with the increase of mixing ratio, the yield of hydrogen increased continuously.

(b) Carbon monoxide: when the mixing ratio is less than 40/100, the yield decreases.

When the mixing ratio was greater than 40/10, the yield showed an upward trend.

(c) Carbon dioxide: with the increase of mixing ratio, the yield decreased.

(d) Methane: when the mixing ratio is less than 40/100, the yield increases. When the mixing ratio was greater than 40/100, the yield showed a downward trend.

(e) Ethane: the yield first increased and then decreased.

(f) Propane: increasing production.

(g) Propylene: production first increased and then decreased, but basically maintained stability.

(h) Ethylene: production first increased and then decreased.

(i) Butane: production first increased and then decreased.

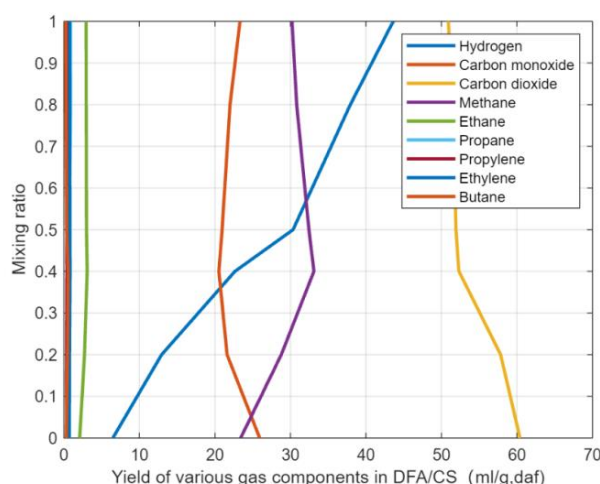


Figure 4.5 The variation trend of DFA/CS gas yield

As can be seen from the figure, hydrogen, carbon monoxide and carbon dioxide are apparently changed, while other gases changed subtly.

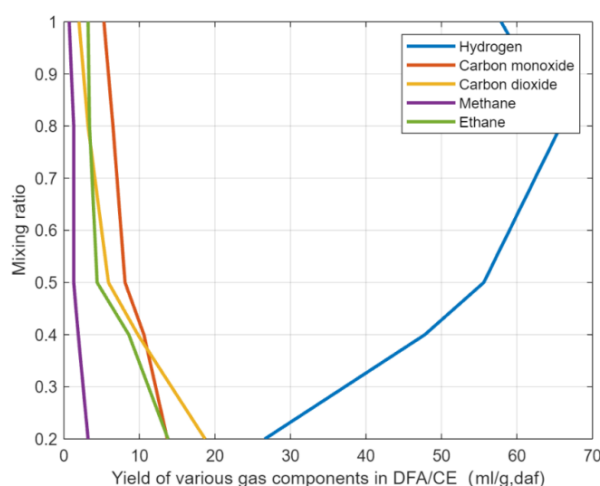


Figure 4.6 The variation trend of DFA/CE gas yield rate

Figure 4.6 shows the variation trend of the yield of five gases, including hydrogen, carbon monoxide, carbon dioxide, methane and ethane, in the desulfurization ash/cellulose oligosaccharide (DFA/CE) group with the change of mixing ratio.

Through the analysis of the image, the following conclusions can be drawn:

(a) Hydrogen: the yield of hydrogen increases with the increase of mixing ratio. When the mixing ratio was greater than 80/100, the yield showed a downward trend.

(b) Carbon monoxide: the overall trend is downward, when the mixing ratio is less than 50/100, the rate of decline is faster. When the mixing ratio was greater than 50/100, the decreasing speed slowed down.

(c) Carbon dioxide: the overall trend of is downward, when the mixing ratio is less than 50/100, the rate of decline is faster. However, when the mixing ratio was greater than 50/100, the decreasing speed slowed down.

(d) Methane: the overall trend is downward, and the decreasing rate was relatively slow;

(e) Ethane: the overall trend was downward, and the rate of decline was faster when the mixing ratio was less than 50/100. However, when the mixing ratio was larger than 50/100, the decreasing speed slowed down.

According to the figure, it can be further concluded that in the desulfurization ash/cellulose oligosaccharide (DFA/CE) group, except for hydrogen, the yield of the other four gases showed a decreasing trend with the increase of the mixing ratio.

Figure 4.7 shows the trend of the yield of the five gases, including hydrogen, carbon monoxide, carbon dioxide, methane and ethane, in the desulfurization ash/lignin (DFA/LG) group as the mixing ratio changes.

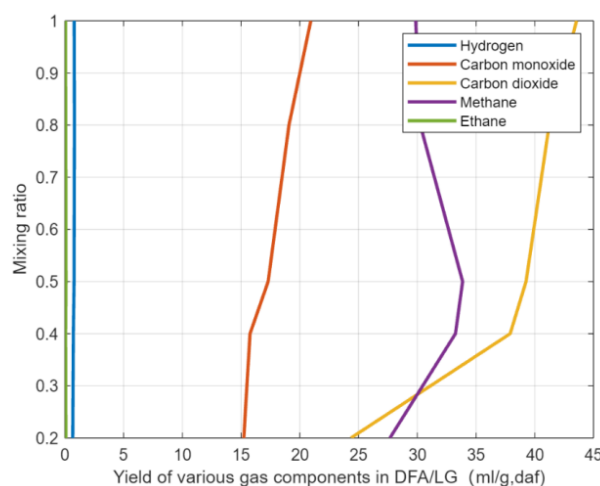


Figure 4.7 The variation trend of DFA/LG gas yield rate

Through the analysis of the image, we can draw the following conclusions:

(a) Hydrogen: with the increase of mixing ratio, there was no significant change in the yield of hydrogen.

(b) Carbon monoxide: the overall trend is upward.

(c) Carbon dioxide: the overall trend is upward. When the mixing ratio is less than 40/100, the increase rate is faster. When the mixing ratio was greater than 40/100, the rising speed slowed down.

(d) Methane: when the mixing ratio was less than 50/100, the yield gradually increased. When the mixing ratio was greater than 50/100, the yield gradually decreased. However, when the mixing ratio was greater than 80/100, the yield remained basically constant.

(e) Ethane: with the increase of mixing ratio, the yield did not change significantly.

From the figure, it can be further concluded that in the desulfurization ash/lignin (DFA/LG) group, the yields of hydrogen and ethane are almost not affected by the mixing ratio,

and the yields of the other three gases show an increasing trend on the whole, except that the yields of hydrogen and ethane have an increasing trend with the increase of the mixing ratio.

(2) Overall analysis of the variation trend of each pyrolysis combination gas

By observing the three line charts as a whole and combining their textual descriptions, we can learn that:

(a) Hydrogen: with the increase of mixing ratio, the increase of hydrogen yield in biomass is mainly affected by the oligosaccharides.

(b) Carbon monoxide: when the mixing ratio is less than 40/100, the yield decreases because the effect of decreasing oligosaccharides exceeds the effect of increasing lignin; When the mixing ratio was greater than 40/100, the increase of yield was due to the effect of the increase of lignin exceeding the effect of the decrease of oligosaccharide.

(c) Carbon dioxide: with the increase of mixing ratio, the yield of carbon dioxide decreased because the effect of cellulose oligosaccharide on the decrease of yield exceeded the effect of lignin on the increase of yield. However, when the mixing ratio was greater than 40/100, the overall yield slowed down because lignin increased the yield faster.

(d) Methane: when the mixing ratio was less than 40/100, lignin had a significant effect on the increase of its yield, which increased the overall yield. However, when the mixing ratio was greater than 40/100, the yields of both the oligosaccharide group and the lignin group decreased, so the overall yield also decreased.

(e) Ethane: there was no significant change in ethane yield as the yield of cellulose oligosaccharide group and lignin group did not change significantly as a whole.

(f) Propane, propylene, ethylene and butane: these four gases were not produced in the oligosaccharides and lignin groups, so the yield change was determined by the cotton stalk group.

4.2.2 Columnar stack diagram

In DFA/CS, it can be seen from Figure 4.8 that with the increase of mixing ratio, the total yield of pyrolysis gas of cotton stalk increases continuously, among which the sub-yield of ethylene increases significantly, while the sub-yield of other gases does not change apparently.

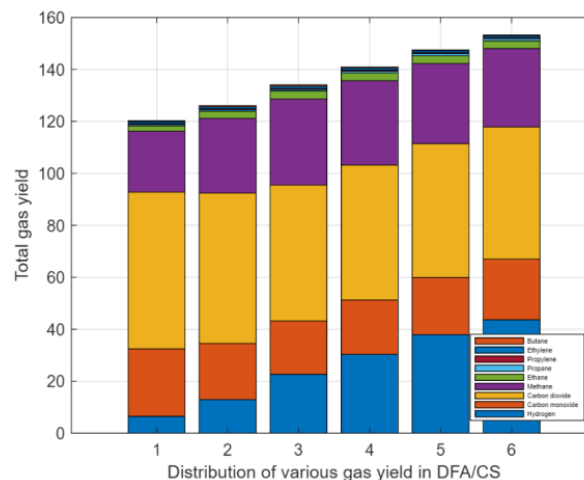


Figure 4.8 Histogram of DFA/CS gas yield rate

In DFA/CE, the total production rate of pyrolysis gas of oligosaccharides fluctuated

with the increase of mixing ratio, but the difference was not large. The sub-production rates of methane, ethane and carbon dioxide decreased significantly, and the sub-production rate of hydrogen increased firstly and then decreased.

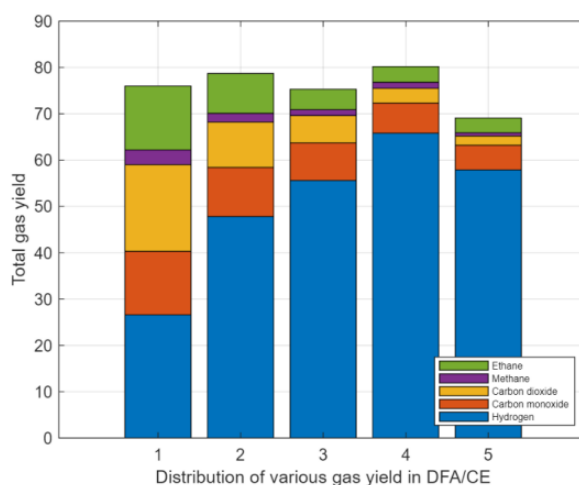


Figure 4.9 Histogram of DFA/CE gas yield rate

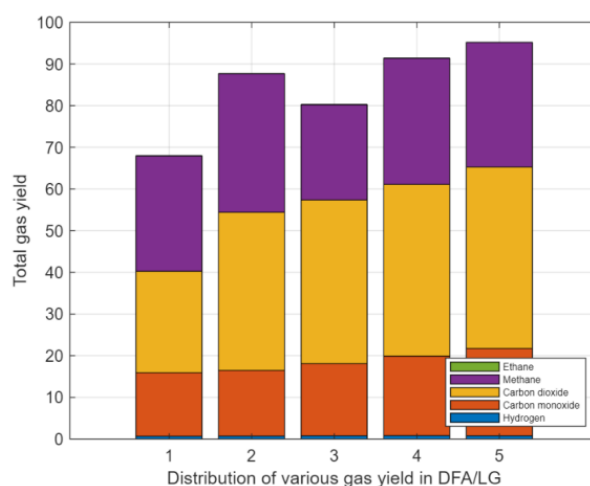


Figure 4.10 Histogram of DFA/LG gas yield rate

As can be seen from Figure 4.10, the total production rate of lignin pyrolysis gas in DFA/LG showed an increasing trend on the whole, with slight fluctuations in the middle, and the sub-production rates of carbon monoxide and carbon dioxide continued to increase.

4.3 Question III: Existence of significance differences

From the previous analysis, we need to perform a non-parametric test on the data. To do this, we used the Friedman test to analyze the data in Appendices 1 and 2 and complete the third question.

4.3.1 Calculation of p-value

(1) Analysis of the yield of pyrolysis products

Here we abbreviate Tar yield as Tar, Water yield as Water, Char yield as Char, Syngas yield as Syngas, and CE pyrolysis product as 1, The product obtained by LG pyrolysis will

be denoted as 2.

In Table 4.6, we observed that the p-values were less than 0.05 except for Water, which was greater than 0.05. Therefore, we can conclude that there was a significant difference in the yield of CE and LG pyrolysis products.

Table 4.6 Determining significant differences Data Table(1)

Rank	Rank mean	test statistics			
		case quantity	χ^2	DOF	Progressive significance
Tar1	2.00	8	8.000	1	0.005
Tar2	1.00				
Water1	1.25	8	2.000	1	0.157
Water2	1.75				
Char1	1.00	8	8.000	1	0.005
Char2	2.00				
Syngas1	2.00	8	8.000	1	0.005
Syngas2	1.00				

(2) Analysis of the yield rate of CE and LG gas components

Here, the products obtained by CE pyrolysis were not labeled, and the products obtained by LG pyrolysis were added with suffix subscript ". " .

Table 4.6 Determining significant differences Data Table(2)

Rank	Rank mean	test statistics			
		case quantity	χ^2	DOF	Progressive significance
H2	2.00	5	5.000	1	0.025
H2.	1.00				
CO	1.00	5	5.000	1	0.025
CO.	2.00				
CO2	1.00	5	5.000	1	0.025
CO2.	2.00				
CH4	1.00	5	5.000	1	0.025
CH4.	2.00				
C2H6	2.00	5	5.000	1	0.025
C2H6.	1.00				

According to Table 4.7, we observed that the p-values of H₂, CO, CO₂, CH₄ and C₂H₆ were all less than 0.05, so we can conclude that there is a significant difference in the yields of CE and LG gas components.

4.3.2 Analysis of line chart

Here, we denote the product obtained by CE pyrolysis as 1, and the product obtained by LG pyrolysis as 2. Line charts were drawn for the variation trend of the yield of desulfurized ash/cellulose oligosaccharide (DFA/ CE) and desulfurized ash/lignin (DFA/LG)

pyrolysis products at different mixing ratios.

From the line chart in Figure 4.11, we can intuitively see that there is a significant difference in the yield of CE and LG pyrolysis products under the same proportion of desulfurization ash.

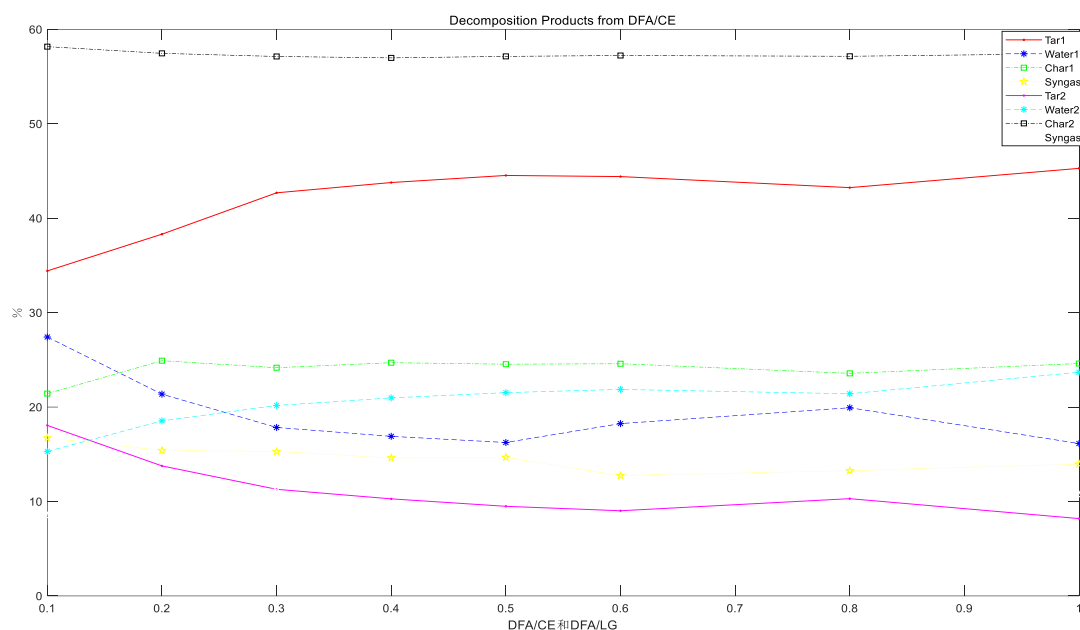


Figure 4.11 CE/LG yield ratio under same ratio DFA

In addition, the products obtained by CE pyrolysis were not marked, and the products obtained by LG pyrolysis were added with "." to make distinction. Line charts were drawn for the variation trend of the pyrolysis gas product yield of desulfurized ash/cellulose oligo saccharide (DFA/CE) and desulfurized ash/lignin (DFA/LG) under different mixing ratios.

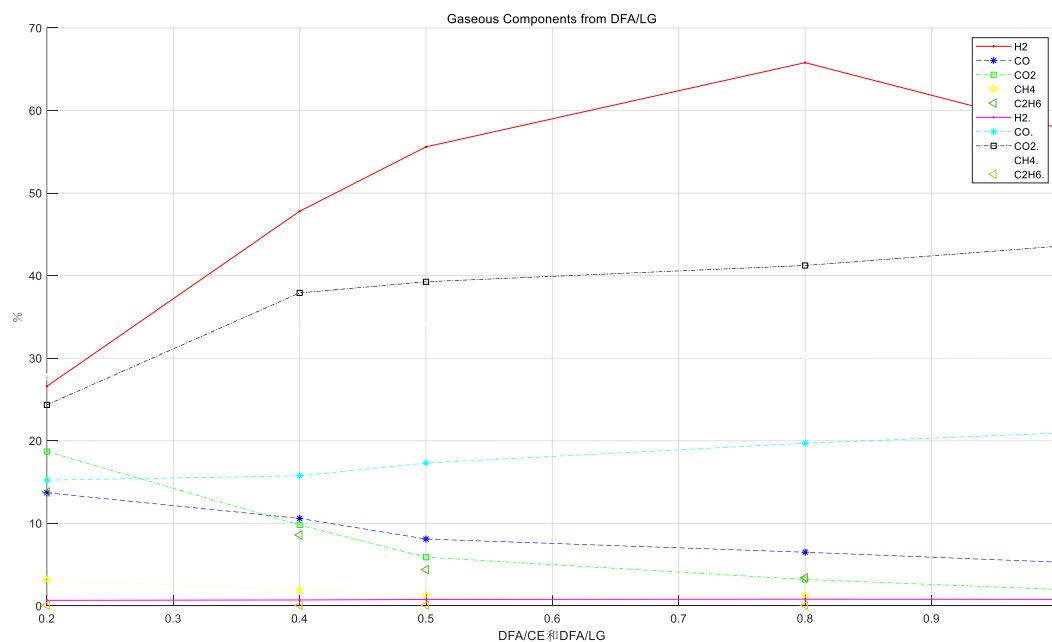


Figure 4.12 CE/LG yield ratio under different mixing ratio

Through the line chart, we can see that under the same proportion of desulfurization ash, there is a significant difference in the yield of CE and LG pyrolysis gas product yield.

In summary, according to the previous analysis of p-values and line charts, we can judge that there are significant differences in the yield of CE and LG pyrolysis products and pyrolysis gas products under the action of the same proportion of desulfurization ash.

4.4 Question IV: Mechanism of pyrolysis reaction and establishment of kinetic models

4.4.1 Pyrolysis mechanism and establishment of kinetic model of cellulose

For discussion, we divided the question into two parts, including the speculation of pyrolysis mechanism and the establishment of kinetic model of cellulose pyrolysis reaction.

(1) The mechanism of cellulose pyrolysis

In the pyrolysis process, cellulose is depolymerized to form different active fragments such as $C_4 \sim C_6$, and glucose is further cleaved. After multiple complex free radical reactions such as dehydroxyl and polymerization, small molecular oxygen-containing compounds such as acetic acid, furan, ketone and aldehyde are finally generated. Through high-temperature pyrolysis gas chromatography-mass spectrometry (GC-MS) and other tests, some scientists found that the pyrolysis process of cellulose as shown in Figure 4.13.

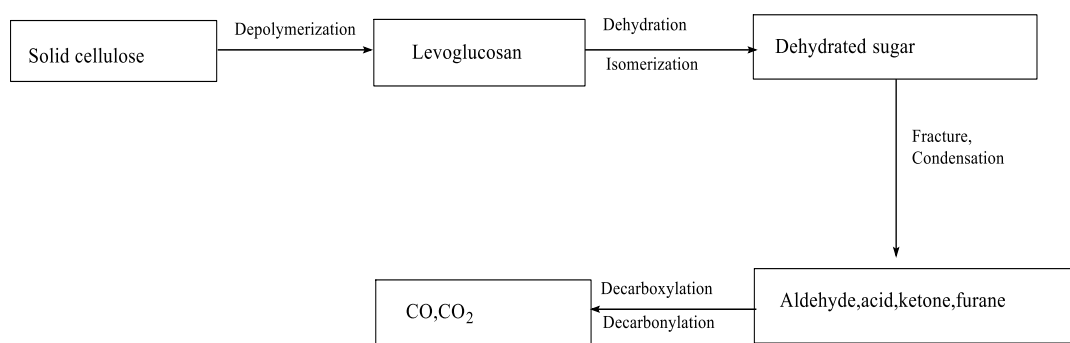


Figure 4.13 Pyrolysis process of cellulose

Under different pyrolysis conditions, cellulose has different evolution paths, and the distribution of generated products is different. Dong C et al. [5] summarized the evolution paths of various pyrolysis reactions of cellulose and prepared pictorial fibers Dimension pyrolysis reaction pathways. It was found that the cellulose unit was depolymerized into two carbon and four carbon fragments, and then the small molecular compounds such as CO were generated by decarbonylation and polymerization.

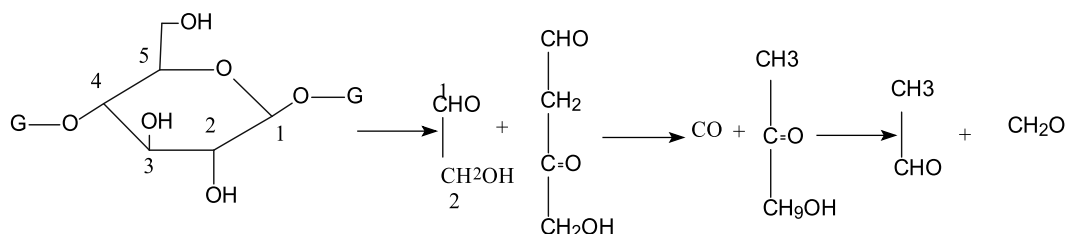


Figure 4.14 Pathway of cellulose pyrolysis reaction

Combined with the fiber pyrolysis reaction route, and the variation trend of each gas yield in the DFA/CE group with the increase of mixing ratio in Annex II, we separated the

cellulose pyrolysis reaction route and guessed the possible chemical equation and reaction mechanism as shown in the Figure 4.15.

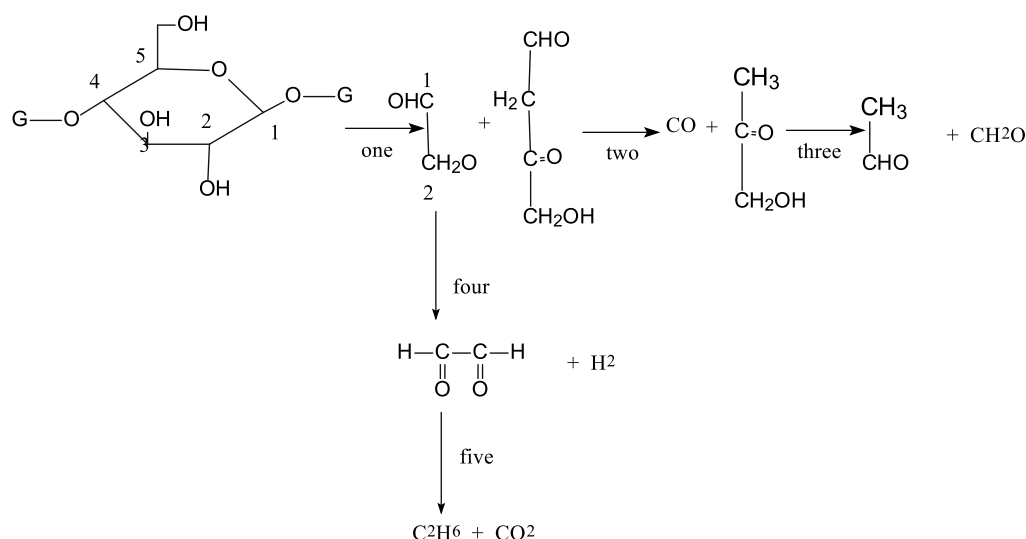


Figure 4.15 Prediction of pathway of cellulose pyrolysis reaction

From the related literature, we can get the X-ray fluorescence spectrum analysis (XRF) results of catalyst desulfurization ash as follows:

Table 4.8 X-ray fluorescence spectrum analysis of desulfurized ash

CaO	SO ₃	SiO ₂	Al ₂ O ₃	MgO	Fe ₂ O ₃	Cl	F	TiO ₂	K ₂ O	Na ₂ O
58.54	21.24	7.77	3.80	2.66	2.16	1.65	1.20	0.36	0.31	0.18

From the table, we conclude that the main components of desulfurized ash are compounds containing Ca^{2+} . Combined with the chemical knowledge we have learned, we know that glyoxal is easy to form complexes with divalent metal ions. That is, glyoxal is easy to combine with desulfurized ash to form complexes. Based on this, we put forward the possible reaction mechanism conjecture about cellulose pyrolysis as follows.

The first reaction occurs in cellulose pyrolysis, which produces 2-hydroxy acetaldehyde and 4-hydroxy-3-oxy-butyraldehyde, and the fourth reaction of 2-hydroxy acetaldehyde produces glyoxal and hydrogen. Since glyoxal is easy to combine with the catalyst desulfurization ash to form a complex, the degree of the fourth reaction is increased, and the production of hydrogen is increased. At the same time, more 2-hydroxy acetaldehyde is consumed. As the result, the content of reactants involved in the second reaction is reduced. It is not conducive to the forward reaction and the production of CO is reduced. For reaction five, because the reactant glyoxal formed a complex with the catalyst desulfurization ash, the reaction was carried out to a smaller extent and less ethane and carbon dioxide were produced.

According to the analysis and conjecture, we can get the conclusion that with the increasing of DFA/CE, the yield of hydrogen increases, the yield of carbon monoxide decreases, and the proportion of ethane and carbon dioxide is relatively small. This is basically consistent with the data in Annex II, so we believe that the guess is reasonable.

(2) Establishment and analysis of the kinetic model of cellulose pyrolysis reaction

In essence, cellulosic biomass pyrolysis involves many complex phenomena, because it is accompanied by the change of chemical composition in biomass. During pyrolysis, many reactions occur simultaneously in a very short period of time. In this regard, we give an overview of the pyrolysis reaction mechanism:



In this regard, we used a simplified apparent kinetic model (AKM) to describe the catalytic reaction of desulfurization ash on model compounds (CE and LG), and considered the effect of temperature through the Arrhenius equation. The specific steps are as follows.

(a) Establish the first-order reaction kinetic model

$$r = k * [CE]$$

Where r is the reaction rate, $[CE]$ is the concentration of CE, and k is the rate constant.

(b) Application of the Arrhenius equation

Relate the rate constant k to temperature:

$$k = A * e^{-\frac{E}{RT}}$$

Where A is the exponential factor, E is the activation energy, R is the ideal gas constant, and T is the temperature.

(c) Overall reaction rate equation

Combining the above two equations, the overall reaction rate equation is obtained as follows.

$$r = A * e^{-\frac{E}{RT}} * [CE]$$

Through the specific experimental data, we can fit and calculate the estimated values of the parameters A and E , and then use the idea of regression analysis to predict the equation that can be widely used in this experiment.

4.4.2 Analysis of lignin's property and prediction of pyrolysis mechanism of lignin

(1) Overview

Lignin is a natural aromatic polymer that is abundant in total amount, second only to cellulose. However, due to its more complex structure and less degradability compared with cellulose and semilignin, the vast majority of biomass conversion platforms cannot make full use of lignin components in raw materials, resulting in serious waste of lignin resources. Therefore, the use of rapid pyrolysis technology to convert lignin has received extensive attention. Here, we will start from the structure of lignin, combined with possible reaction pathways, intermediate products and final products, put forward the possible pyrolysis mechanism of lignin under the action of catalyst.

(2) Structure of lignin

Lignin structure can be divided into three kinds of phenyl propane units with different methoxy content, which are divided into guaiacyl propane unit (G-type lignin), syringyl propane unit (S-type lignin) and p-hydroxyphenyl propane unit (H-type lignin) according to the amount of methoxy base connected by the benzene ring from more to less (Figure 4.16 from left to right).

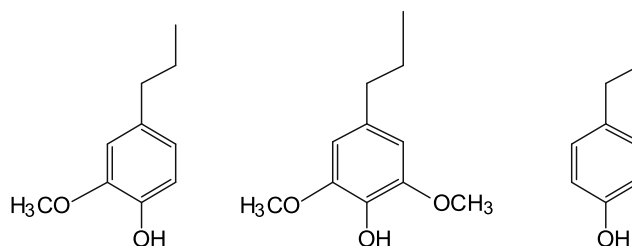


Figure 4.16 Division of Lignin structure

The functional group of a compound and its structure determine the chemical properties of a compound. Therefore, for the study of lignin pyrolysis, we need to understand the functional groups and structural composition of lignin.

For the functional groups of lignin, methoxy group is an important group to distinguish lignin unit, which has strong stability. It requires a strong oxidant to decompose the benzene ring. Phenolic hydroxyl is the main source of intramolecular hydrogen bond of lignin, and its content affects the physical and chemical properties of lignin. The carbonyl group, carbon-carbon double bond and carboxyl group in lignin side chain structure also have a certain impact on the chemical reactivity and physical adsorption of lignin, which leads to the joint action of a variety of functional groups during the reaction. It has a certain complexity.

The unit connection of lignin is mainly coupled by ether bond and C-C bond, and the main connecting bonds include β -O-4, α -O-4, γ -O-4, 4-O-5, β -5, 5-5, β -1, β - β , etc., which are usually complex, as shown[6] in Figure 4.17.

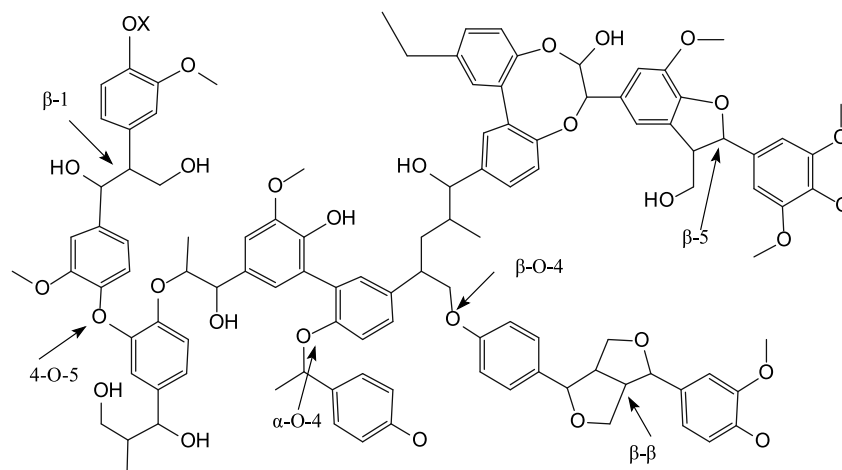


Figure 4.17 Unit connection of Lignin

However, there are usually two structures of lignin, namely acylated structure and cross-linked structure, which limit the separation and utilization of lignin. For different lignin, the degree of acylation and cross-linking is different, which makes it more difficult and complex to study the reaction mechanism of lignin pyrolysis.

(3) The mechanism of lignin pyrolysis

The intermediates produced by lignin pyrolysis are strong hydrogen receptors. Under the condition of rich hydrogen radicals, these intermediates can be used to form phenolic compounds. However, the composition of lignin lacks hydrogen, which leads to the instability of the intermediate, and a series of reactions such as polymerization and

rearrangement have occurred to form oligomers. In general, the pyrolysis process of lignin is very complex, and the reaction temperatures of various linkage bonds and functional groups are quite different.

When the pyrolysis temperature is between 200 °C and 300°C , lignin can be slowly depolymerize, but only β -O-4 and α -O-4 will have C-O fracture. The following figure shows the fracture mechanism of these two bonds. When lignin decomposes, phenolic compounds with structure close to lignin unit are formed, and carbon monoxide, carbon dioxide and water are released.

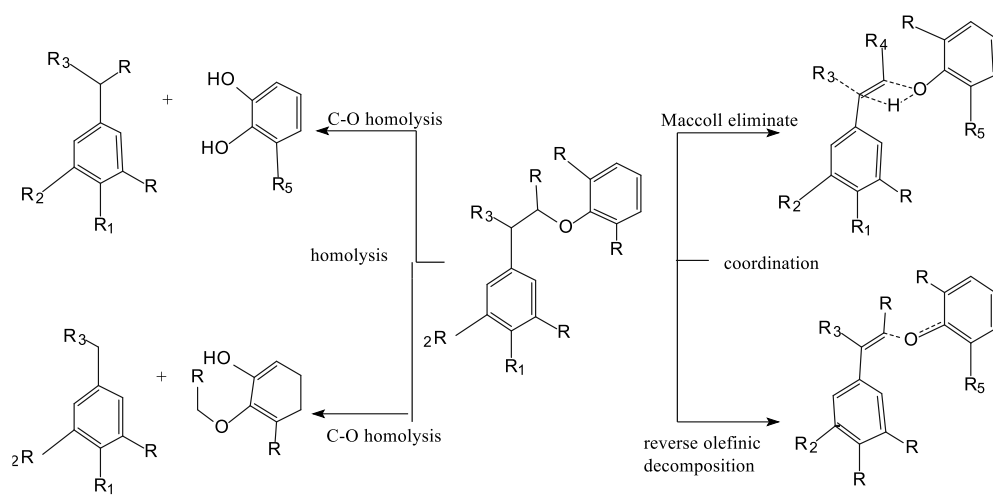


Figure 4.18 β -O-4 bond fracture mechanism

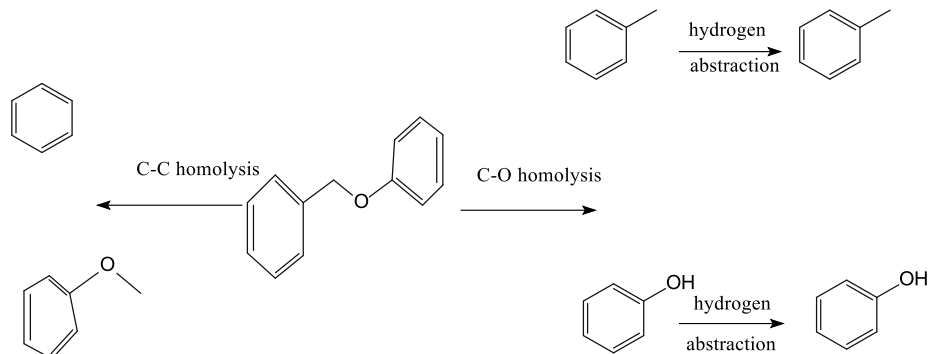


Figure 4.19 α -O-4 bond fracture mechanism

When the temperature is between 300°C and 400°C , most C-C bonds between alkyl chains become unstable and break, and compounds containing 1~3 carbon atoms such as methane, acetaldehyde or acetic acid begin to form. In this temperature range, the decomposition rate of lignin is high[7].

When the temperature is higher than 400°C , the methoxy group becomes active, and the intramolecular rearrangement and alkylation reaction will generate a series of phenolic products and small molecular gases without alkyl side chains. However, different fracture modes of the methoxy group will lead to different products, and the pyrolysis of lignin has a certain degree of uncertainty.

(4) The pyrolysis characteristics of lignin

The lignin structure of different biomass materials is different, so the pyrolysis characteristics are also different. For lignin obtained by different methods, the reaction

activities were different because the methods had significant effects on the chemical structure of lignin after separation. These two kinds of pyrolysis characteristics make it difficult for us to accurately and quantitatively explore the lignin pyrolysis products.

(5) Explanation of the difficulty of establishing a pyrolysis model for lignin

Lignin has rich functional groups and complex structure, and its pyrolysis reaction process has large temperature difference, which is difficult to control and explain. For the intermediate products of the reaction, due to the influence of various factors such as connection mode, temperature, catalyst, etc., it is difficult to speculate the specific reaction pathway and establish a convincing and representative kinetic model for its pyrolysis. Therefore, we only describe the mechanism of lignin pyrolysis without modeling.

4.5 Question V: Predictive models of data

4.5.1 Predictive models for optimal scenarios

Here, we consider low pollution as the main consideration in selecting the optimal mixing ratio. According to appendix 2, we know the CE or LG thermal decomposition of hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4) and ethane (C_2H_6), carbon monoxide and ethane belong to gas pollution. In experiment exploring or actual production process, we need to cut its production as possible, in order to achieve the purpose of protecting the environment. At the same time, due to the high economic value of hydrogen, we should recycle the hydrogen in the product as much as possible to maximize the economic benefits. Respectively, the influence of the output of the other three gases on the optimal mixing ratio is taken into account in DFA/CE and DFA/LG.

(1) For the change of DFA/CE mixing ratio, we find that the proportion of methane that can be recycled is very small, and the economic benefit of recycling is not large. Carbon dioxide is neither polluting nor has significant economic benefits.

We define a set of variables as follows:

α : the average value per unit of production of carbon monoxide and ethane;

β : hydrogen production per unit;

γ : relative benefit, calculated by the difference between β and α , the greater the relative benefit is, the higher the recovery value is, otherwise it is small.

Based on the above, when the optimal mixing ratio occurs, we can easily know that the value of γ should be the largest. We set up a functional relationship with the mixing ratio as the independent variable and the relative benefit γ as the dependent variable.

However, the data presented in Appendix 2 is a discrete group of points, which does not reflect the change process well. We need to use a flat Slippery curves connect them and thus predict the optimal mixing ratio.

Interpolating a curve means interpolating a continuous function to the discrete data such that the curve passes through all the given discrete data points. Interpolation is an important method for approximating a discrete function. It can be used to estimate the approximate value of a function at other points from the value of a function at a finite number of points. The so-called interpolation is used to fill the gaps between pixels during image transformation [8]. Here, we use the interpolation curve to achieve the purpose.

Further, we plot the image shown in Figure 4.20. It shows that when the mixing ratio

is 0.84, the relative benefit value is the largest. That is to say, the gas product pollution of cellulose pyrolysis reaction is relatively small, and the economic benefit is relatively large, which is in line with the actual industrial production demand.

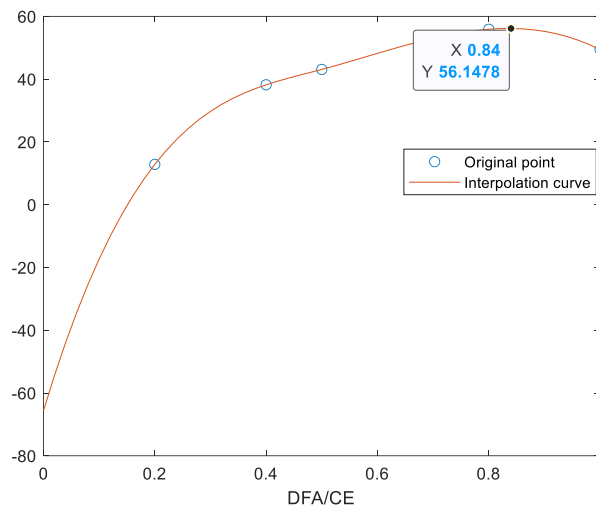


Figure 4.20 DFA/CE scatter graph and interpolation curve

(2) For the change of DFA/LG mixture ratio, we can know from the observation of the data that the amount of hydrogen and ethane produced in the gas product of lignin pyrolysis recovery is very small, which can be ignored compared with the other three gases. For carbon monoxide, carbon dioxides and methane, carbon dioxide is still not considered here because its relative benefit is very small. In addition, we found that the amount of methane produced first increased and then decreased with the increase of the mixing ratio, and the change was not very obvious. Therefore, we do not consider the amount of methane produced.

In DF A/LG, we only need to consider the effect of carbon monoxide production on the recovery of the gas product of lignin pyrolysis. We established the function of carbon monoxide production as a function of DF A/LG mixture ratio. Similarly, an interpolation curve was used to predict the optimal mixing ratio. We can plot the image shown in Figure 4.21.

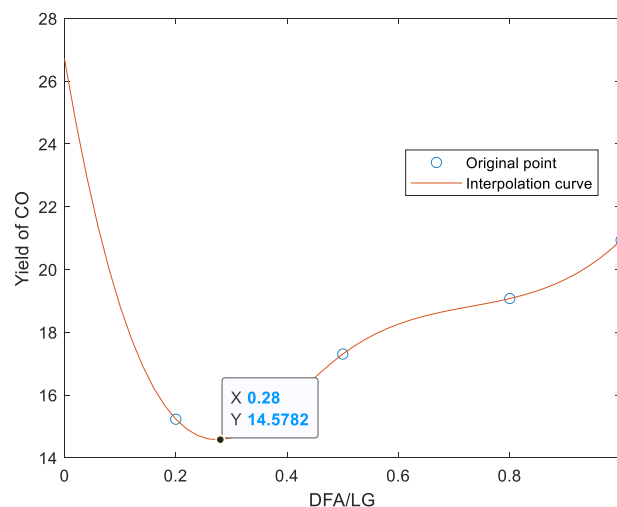


Figure 4.21 DFA/LG scatter graph and interpolation curve

Figure 4.21 shows that when the mixing ratio is 0.28, the production of carbon monoxide is the least. That is, the gas recovery product of lignin pyrolysis is the least polluting at this time.

In particular, it was noted that the production of carbon monoxide tended to increase with the increase of mixing ratio when only scatter points were observed. In other words, the increase of the proportion of desulfurization ash may play a certain role in promoting the production of carbon monoxide. According to the analysis, when the mixing ratio is 0, the pollution of the recovered gas from lignin pyrolysis is the least.

4.5.2 Prediction of yield or quantity of pyrolysis products

Due to the incompleteness of the experimental data, we cannot accurately predict the yield or quantity of pyrolysis products, and can only approximate the prediction results. Specifically, we provide the following steps to make a rough prediction.

(1) Data preparation

We sorted out the available data and determined that the data contained features such as a particular temperature, different mixing ratios, and so on.

(2) Feature selection and normalization

Since it is specified that all reactions are carried out at the same temperature, temperature is considered as an independent variable in the following model. That is, the influence of temperature on the output of pyrolysis products is ignored, and a regression prediction model with mixing proportion as the independent variable is established.

(3) Model selection

Based on the given data, we need to create a scatter plot to visualize the data. The interpolation curve has a good property of predicting the change trend of discrete data, so we still draw the interpolation curve here to fit the change trend of pyrolysis product yield under the change of continuous mixing ratio.

(4) Model evaluation

We used the root mean square error (RMSE) method to determine the accuracy of the interpolation curve in predicting the yield of pyrolysis products. The data in the appendix are not sufficient for us to verify the accuracy of the model, so we provide the code shown in Figure 4.22, which can be evaluated by Matlab2023a software compilation in real operation.

```
1 actual_data = [];
2 interpolated_data = [];
3 rmse = sqrt(mean((actual_data-interpolated_data).^2));
4
```

Figure 4.22 Matlab code of the RMSE

(5) Adjustment and optimization of the model

In the actual production process, we calculate the RMSE through the actual data to select the best parameter model.

(6) Prediction

Under the condition of limited data in this problem, we use the existing multiple discrete points to draw a discrete map, and draw its interpolation curve, and make a simple prediction of the pyrolysis product yield or quantity.

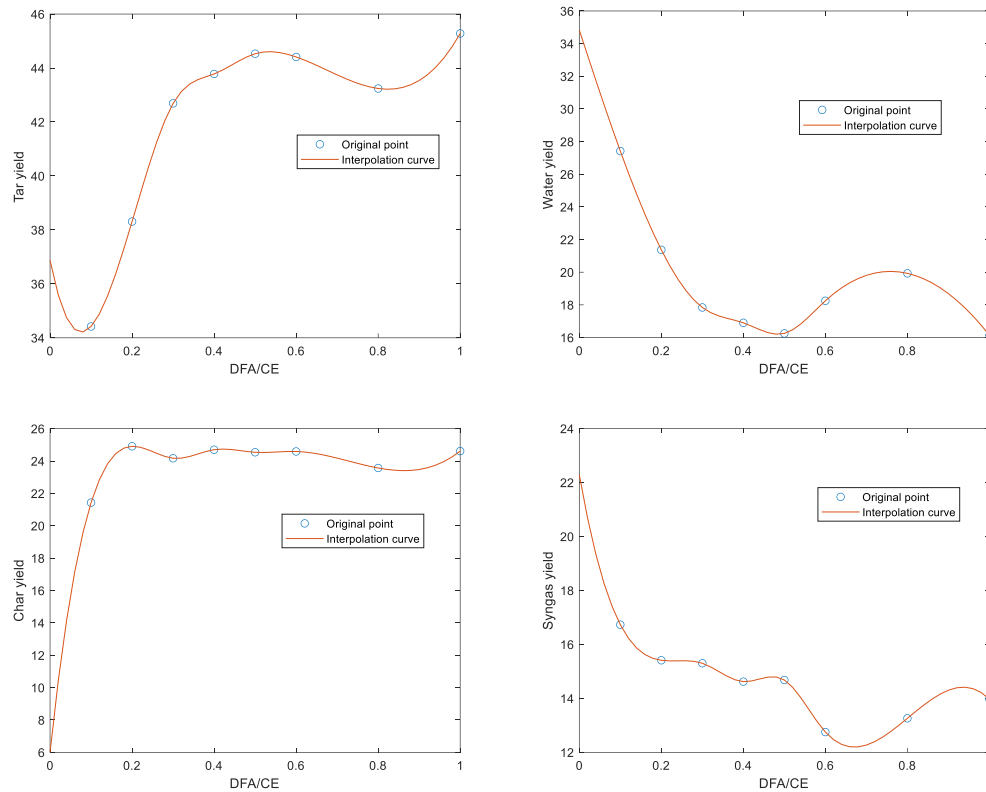


Figure 4.23 Discrete graph of pyrolysis product yield and its interpolation curve for DFA/CE

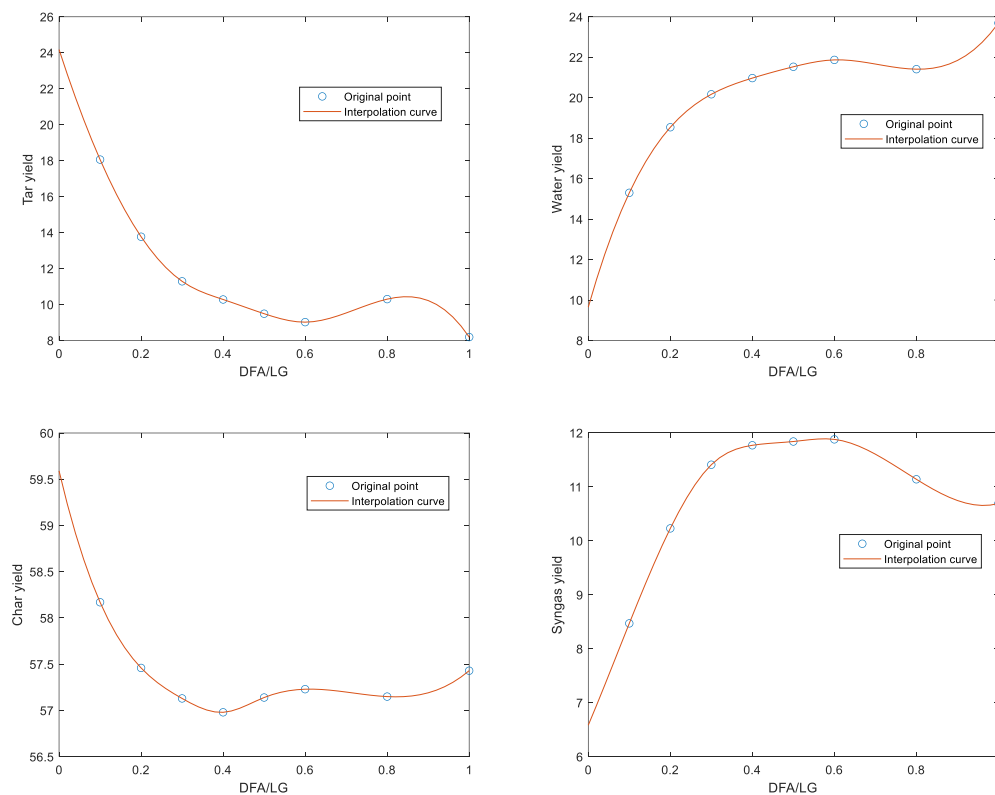


Figure 4.24 Discrete graph and interpolation curve of DFA/LG pyrolysis product yield

As shown in Figure 4.23 and Figure 4.24, we can predict the yield or quantity of cellulose pyrolysis products (Tar, Water, Char, Syn gas) at a certain mixing ratio by reading

the ordinate of a certain point on the curve. Among them, Figure 4.23 and 4.24 show the variation of pyrolysis product yield (or quantity) in DFA/CE combination and in DFA/LG combination, respectively.

(7) Iteration and improvement

If new experimental data are available, we can use the code provided in Figure 4.22 to determine the feasibility of the Interpolation curve model, so as to predict the yield or quantity of pyrolysis products with relatively high accuracy.

5 Sensitivity Analysis

In the mathematical modeling process of the above five questions, we used root mean square error (RMSE), mean absolute error (MAE), coefficient of determination (R-squared) three methods for sensitivity analysis. In the following, we introduce our use of these three methods and their advantages and disadvantages.

5.1 Root-mean-square error(RMSE)

We apply the following steps:

(1) For each observed value, calculate the difference (residual) between the predicted value and the actual value.

(2) Square each residual.

(3) Calculate the average of all squared residuals.

(4) Take the square root of the average to get the RMSE.

In the process of using the root mean square method, we found that it has a strong sensitivity to large errors, because each error is squared in the calculation, which helps emphasize the impact of large errors. However, it also has some limitations and is more sensitive to outliers.

5.2 Mean absolute error(MAE)

The following steps are applied: calculate the mean absolute error between the difference curve and the actual data points, which is the average of the absolute value of the difference between the predicted value and the actual value.

During usage, we found that MAE is less sensitive to outliers because it uses absolute values rather than squares, avoiding excessive influence of large errors on the overall error. Compared with other metrics such as root mean square error (RMSE), MAE is easier to interpret because it directly represents the magnitude of the average prediction error.

5.3 Determination coefficient(R-squared)

We found that (R^2) may increase when unimportant predictor variables are added to the model, making it a weaker penalty for model complexity. Therefore, when evaluating model performance, it is often recommended to incorporate other metrics such as root Mean Square Error (RMSE) or Mean Absolute error (MAE) to get a full picture of how the model is performing.

6 Strengths and Weakness

For Question I: The yield of desulfurization ash/cotton stalk (DFA/CS), desulfurization ash/oligosaccharide cellulose (DFA/CE), and desulfurization ash/lignin (DFA/LG) pyrolysis products were compared and analyzed from ten aspects in the table of ten eigenvalues. The data were comprehensive and objective, and well described multiple indicators. At the same time, the method of multiple linear (or nonlinear) regression analysis in statistics was used to make the fitting curve, and the Friedman test was carried out. However, the sample size of the data may be small, and there are some accidental errors.

For Question II: The use of line chart and column stacked chart makes the analysis of each gas yield data in Annex II more intuitive and clear. It is easy to obtain the variation trend of each gas product yield with the change of mixing ratio and the proportion of each gas component in the total gas component. However, no accurate mathematical model has been established to fit the change trend, which may have some deficiencies in accuracy and subjective factors account for a large proportion.

For Question III: The non-parametric test method was used to analyze the significant differences in the yield of CE and LG pyrolysis products and the composition of irritating gases under the catalysis of the same proportion of desulfurization ash. It was simple and easy to understand, and supported by mathematical analysis. However, this method is only effective for this problem, and its general applicability may be slightly inferior.

For questions IV and V: By reviewing a large number of references, effective kinetic models and prediction models were established. Reasonable conjectures and assumptions were put forward on the pyrolysis mechanism of cellulose and lignin. However, due to the lack of understanding of lignin pyrolysis reaction mechanism, it is impossible to establish an accurate model to predict it. Only the structure and reaction pathways are explained.

7 Conclusion

We draw the conclusions on each of the five questions.

(1) In the DFA/CS combination, catalyst has a large negative correlation effect on tar production; In the DFA/CE combination, the catalyzer had a great promotion effect on the yield of tar. However, in the DFA/LG combination, we found that the catalyst had no significant effect on the four pyrolysis products (tar, water, coke residue and syngas). The specific change trend is shown in the analysis of Table 4.2.

(2) Under the catalysis of the same proportion of desulfurization ash, there are significant differences in the yield of CE yield of each component of pyrolysis gas.

(3) The predicted values are shown in Figure 4.24 and Figure 4.25. In the DFA/CE group, the maximum relative benefit was obtained when the mixing ratio was 0.84. In the DFA/LG group, we divided it into two cases. On the one hand, when the mixing ratio was 0.28, the contamination degree of lignin pyrolysis gas products was the smallest. On the other hand, when the mixing ratio was 0. That is, without catalyst, the contamination degree was the smallest.

References

- [1] LIN Tao.etc,Anatomical Characteristics and Chemical Components of Cotton Stalk[J]. Journal of Northwest Forestry University, 2012, 27(5): 201~206.
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Appendix

Matlab Code

Fig.4.1

```
x1 =[0;0.10;0.20;0.30;0.40;0.50;0.60;0.80;1]';
y1 =[19.46;17.25;15.43;14.14;13.89;13.21;12.84;12.57;12.13]';
x2 =[0;0.10;0.20;0.30;0.40;0.50;0.60;0.80;1]';
y2 =[26.84;27.64;28.11;28.23;28.62;29.01;30.07;30.68;31.02]';
x3 =[0;0.10;0.20;0.30;0.40;0.50;0.60;0.80;1]';
y3 =[29.21;29.11;29.30;29.34;29.14;29.33;29.47;29.64;29.87]';
x4 =[0;0.10;0.20;0.30;0.40;0.50;0.60;0.80;1]';
y4 =[24.49;26.00;27.16;28.29;28.35;28.45;27.62;27.11;26.98]';
figure;
scatter(x1, y1, 'b', 'filled');
hold on;
scatter(x2, y2, 'r', 'filled');
scatter(x3, y3, 'g', 'filled');
scatter(x4, y4, 'm', 'filled');
p1 = polyfit(x1, y1, 1);
p2 = polyfit(x2, y2, 1);
p3 = polyfit(x3, y3, 2);
p4 = polyfit(x4, y4, 1);
x_fit1 = linspace(min(x1), max(x1), 100);
x_fit2 = linspace(min(x2), max(x2), 100);
x_fit3 = linspace(min(x3), max(x3), 100);
x_fit4 = linspace(min(x4), max(x4), 100);
y_fit1 = polyval(p1, x_fit1);
y_fit2 = polyval(p2, x_fit2);
y_fit3 = polyval(p3, x_fit3);
y_fit4 = polyval(p4, x_fit4);
plot(x_fit1, y_fit1, 'b-', 'LineWidth', 2);
plot(x_fit2, y_fit2, 'r-', 'LineWidth', 2);
plot(x_fit3, y_fit3, 'g-', 'LineWidth', 2);
plot(x_fit4, y_fit4, 'm-', 'LineWidth', 2);
title('Yield of Decomposition Products from DFA/CS Pyrolysis');
xlabel('DFA/CS');
ylabel('Yield of Decomposition Products');
legend('Tar yield', 'Water yield', 'Char yield', 'Syngas yield');
grid on;
hold off;
```

Fig.4.2

```

x1=[0.10;0.20;0.30;0.40;0.50;0.60;0.80;1.00]';
y1=[34.42;38.31;42.69;43.78;44.53;44.41;43.24;45.28]';
x2=[0.10;0.20;0.30;0.40;0.50;0.60;0.80;1.00]';
y2=[27.42;21.37;17.84;16.90;16.25;18.25;19.93;16.14]';
x3=[0.10;0.20;0.30;0.40;0.50;0.60;0.80;1.00]';
y3=[21.43;24.91;24.17;24.70;24.54;24.59;23.57;24.61]';
x4=[0.10;0.20;0.30;0.40;0.50;0.60;0.80;1.00]';
y4=[16.73;15.41;15.30;14.62;14.68;12.75;13.26;13.97]';
figure;
scatter(x1, y1, 'b', 'filled');
hold on;
scatter(x2, y2, 'r', 'filled');
scatter(x3, y3, 'g', 'filled');
scatter(x4, y4, 'm', 'filled');
p1 = polyfit(x1, y1, 1);
p2 = polyfit(x2, y2, 1);
p3 = polyfit(x3, y3, 2);
p4 = polyfit(x4, y4, 1);
x_fit1 = linspace(min(x1), max(x1), 100);
x_fit2 = linspace(min(x2), max(x2), 100);
x_fit3 = linspace(min(x3), max(x3), 100);
x_fit4 = linspace(min(x4), max(x4), 100);
y_fit1 = polyval(p1, x_fit1);
y_fit2 = polyval(p2, x_fit2);
y_fit3 = polyval(p3, x_fit3);
y_fit4 = polyval(p4, x_fit4);
plot(x_fit1, y_fit1, 'b-', 'LineWidth', 2);
plot(x_fit2, y_fit2, 'r-', 'LineWidth', 2);
plot(x_fit3, y_fit3, 'g-', 'LineWidth', 2);
plot(x_fit4, y_fit4, 'm-', 'LineWidth', 2);
title('Yield of Decomposition Products from DFA/CE Pyrolysis');
xlabel('DFA/CE');
ylabel('Yield of Decomposition Products');
legend('Tar yield', 'Water yield', 'Char yield', 'Syngas yield');
grid on;
hold off;

```

Fig.4.3

```

x1=[0.10;0.20;0.30;0.40;0.50;0.60;0.80;1]';
y1=[18.06;13.77;11.29;10.28;9.49;9.02;10.30;8.19]';
x2=[0.10;0.20;0.30;0.40;0.50;0.60;0.80;1]';
y2=[15.30;18.54;20.17;20.97;21.53;21.87;21.41;23.69]';
x3=[0.10;0.20;0.30;0.40;0.50;0.60;0.80;1]';
y3=[58.17;57.46;57.13;56.98;57.14;57.23;57.15;57.43]';

```

```

x4=[0.10;0.20;0.30;0.40;0.50;0.60;0.80;1]';
y4=[8.47;10.23;11.41;11.77;11.84;11.88;11.14;10.69]';
figure;
scatter(x1, y1, 'b', 'filled');
hold on;
scatter(x2, y2, 'r', 'filled');
scatter(x3, y3, 'g', 'filled');
scatter(x4, y4, 'm', 'filled');
p1 = polyfit(x1, y1, 1);
p2 = polyfit(x2, y2, 1);
p3 = polyfit(x3, y3, 2);
p4 = polyfit(x4, y4, 1);
x_fit1 = linspace(min(x1), max(x1), 100);
x_fit2 = linspace(min(x2), max(x2), 100);
x_fit3 = linspace(min(x3), max(x3), 100);
x_fit4 = linspace(min(x4), max(x4), 100);
y_fit1 = polyval(p1, x_fit1);
y_fit2 = polyval(p2, x_fit2);
y_fit3 = polyval(p3, x_fit3);
y_fit4 = polyval(p4, x_fit4);
plot(x_fit1, y_fit1, 'b-', 'LineWidth', 2);
plot(x_fit2, y_fit2, 'r-', 'LineWidth', 2);
plot(x_fit3, y_fit3, 'g-', 'LineWidth', 2);
plot(x_fit4, y_fit4, 'm-', 'LineWidth', 2);
title('Yield of Decomposition Products from DFA/LG Pyrolysis');
xlabel('DFA/LG');
ylabel('Yield of Decomposition Products');
legend('Tar yield', 'Water yield', 'Char yield', 'Syngas yield');
grid on;
hold off;

```

Table 4.5

```

data = [19.46 26.84 29.21 24.49;17.25 27.64 29.11 26;15.43 28.11 29.3 27.16;14.14 28.23 29.34
28.29;13.89 28.62 29.14 28.35;
13.21 29.01 29.33 28.45;12.84 30.07 29.47 27.62;12.57 30.68 29.64 27.11;12.13 31.02 29.87 26.98];
p_value = friedman(data);
fprintf('Friedman 检验的 p 值为: %.4f\n', p_value);
if p_value < 0.05
fprintf('拒绝原假设，组之间存在差异。 \n');
else
fprintf('未能拒绝原假设，组之间没有显著差异。 \n');
end
%%

```



```

data = [34.42 27.42 21.43 16.73;38.31 21.37 24.91 15.41;42.69 17.84 24.17 15.3;43.78 16.9 24.7
14.62;
44.53 16.25 24.54 14.68;44.41 18.25 24.59 12.75;43.24 19.93 23.57 13.26;45.28 16.14 24.61 13.97];
p_value = friedman(data);
fprintf('Friedman 检验的 p 值为: %.4f\n', p_value);
if p_value < 0.05
fprintf('拒绝原假设, 组之间存在差异。 \n');
else
fprintf('未能拒绝原假设, 组之间没有显著差异。 \n');
End
%%
data = [18.06 15.3 58.17 8.47;13.77 18.54 57.46 10.23;11.29 20.17 57.13 11.41;10.28 20.97 56.98
11.77;
9.49 21.53 57.14 11.84;9.02 21.87 57.23 11.88;10.3 21.41 57.15 11.14;8.19 23.69 57.43 10.69];
p_value = friedman(data);
fprintf('Friedman 检验的 p 值为: %.4f\n', p_value);
if p_value < 0.05
fprintf('拒绝原假设, 组之间存在差异。 \n');
else
fprintf('未能拒绝原假设, 组之间没有显著差异。 \n');
End

```

Fig.4.24

```

x = [0.2,0.4,0.5,0.8,1.0];
y = [13.75,9.6,12.5,9.9,8.5];
z = [26.6,47.8,55.6,65.8,57.9];
a = z-y ;
xi = 0:0.02:1;
ai = interp1(x, a, xi, 'spline');
plot(x, a, 'o', xi, ai, '-')
legend('Original point', 'Interpolation curve');
xlabel('DFA/CE');
ylabel('Relative benefit  $\gamma$ ')
max=max(ai)
min=min(ai)

```

Fig.4.25

```

x = [0.2,0.4,0.5,0.8,1.0];
y = [15.23,15.76,17.305,19.075,20.935];
xi=0:0.02:1;
yi=interp1(x,y,xi,'spline');
plot(x,y,'o',xi,yi,'-');
legend('Original point','Interpolation curve');
xlabel('DFA/LG');

```

```
ylabel('Yield of CO');  
max=max(xi);  
min=min(yi)
```