

# Research on Catalytic Reaction of Cotton Straw Pyrolysis Based on Model Compounds

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**Abstract.** The study starts from the clean conversion of desulfurized ash and biomass resources, based on correlation analysis and Langmuir-Hinshelwood model, studies the components of cotton stalk pyrolysis products and describes the mechanism and effects of desulfurized ash as a catalyst in the pyrolysis process. Regression analysis, support vector machine, and other methods are used to predict the yield or output of pyrolysis products, which is of great significance for the efficient utilization and sustainable development of cotton stalks. The study found that desulfurized ash significantly promoted the thermal decomposition of cotton stalks, increased the pyrolysis gas yield and lower heating value, increased the production of hydrogen-rich gas in the pyrolysis gas, and reduced the production of carbon oxides. Through the study of model compounds, it was found that desulfurized ash has different catalytic effects on the process of cellulose and lignin components in cotton stalks generating pyrolysis gas.

**Keywords:** Catalytic Pyrolysis, Langmuir-Hinshelwood Model, Model Compound, Regression Analysis.

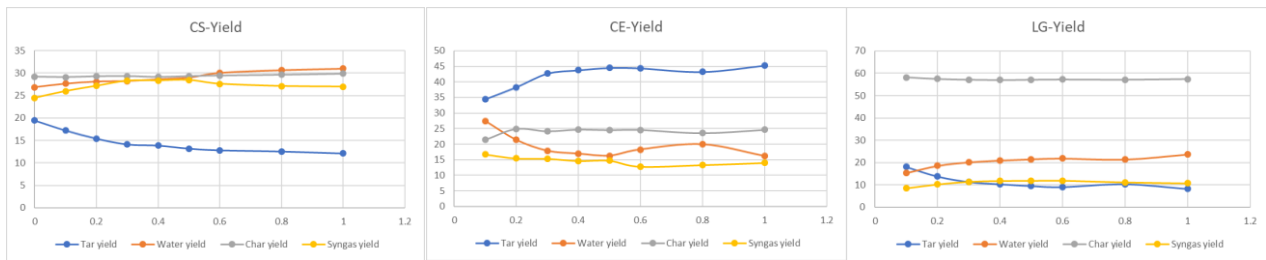
## 1. Introduction

The flue gases generated from the combustion of domestic thermal coal are commonly treated using a semi-dry method. Desulfurization ash (DFA), a byproduct of this process, is energy-intensive, poorly degradable, and subject to secondary pollution. Considering the alkaline-earth metals such as Ca in DFA, it can be used as a catalyst for biomass pyrolysis [1, 2]. In practical applications, for biomasses like cotton stalks (CS), currently, tar and CO<sub>2</sub> reforming [3], production of hydrogen-rich gas through pyrolysis [4, 5], and other methods can be conducted. Theoretical advancements include sophisticated high-temperature catalytic pyrolysis kinetic models [6-9] and well-established pyrolysis mechanism theories for cellulose (CE) and lignin (LG) present in cotton stalks [10]. Due to its fine particle size and low density, desulfurization ash is often directly landfilled, resulting in severe environmental pollution. In light of China's abundant agricultural straw resources and the increasing demand for renewable energy, our research sought to investigate the catalytic pyrolysis of cotton stalks with desulfurization ash. This method has the potential to produce high-calorific value gas and active porous carbon materials, ultimately achieving negative carbon cycle, making it a current research hotspot in the context of the dual carbon constraint. (The pyrolysis reaction experimental data used in this article is sourced from [https://www.nmmcm.org.cn/ad\\_detail/227](https://www.nmmcm.org.cn/ad_detail/227))

## 2. Study on the Yield of Pyrolysis Products and the Mixing Ratio of DFA

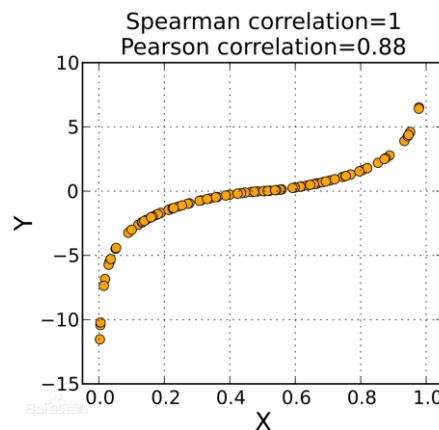
### 2.1. Analysis of Pyrolysis Products Based on Correlation Analysis

First, the paper depicts the relationship between yield and mixing ratio. The graphs are in Fig 1.



**Figure 1.** CS, CE, LG-Yield

There are three common methods for correlation analysis: Pearson, Spearman, and Kendall. Firstly, since the variables in this problem are quantitative variables, they do not fall within the scope of Kendall correlation analysis, which is suitable for handling qualitative variables. Secondly, the data in this problem is small in quantity and may not exhibit a linear relationship, making Pearson correlation analysis unsuitable, as shown in Fig 2. Therefore, the paper ultimately chooses Spearman correlation analysis.



**Figure 2.** Spearman VS Pearson

The paper uses equation (1) to calculate the Spearman correlation coefficients:

$$\rho = \frac{\frac{1}{n} \sum_{i=1}^n (R(x_i) - \bar{R}(x))(R(y_i) - \bar{R}(y))}{\sqrt{\left(\frac{1}{n} \sum_{i=1}^n (R(x_i) - \bar{R}(x))^2\right) \left(\frac{1}{n} \sum_{i=1}^n (R(y_i) - \bar{R}(y))^2\right)}} \quad (1)$$

Fig 3, 4, 5. are the results of our study. The paper assumes that a Spearman correlation coefficient below 0.3 indicates no significant relationship. It can be observed that, for CS, DFA promotes the formation of water and char, inhibits the formation of tar, and promotes the formation of syngas only when the mixing ratio is around 50%; for CE, DFA promotes the formation of tar, inhibits the formation of syngas and water, and has no significant effect on char yield; for LG, DFA promotes the formation of water and syngas, inhibits the formation of tar, and has no significant effect on char yield.

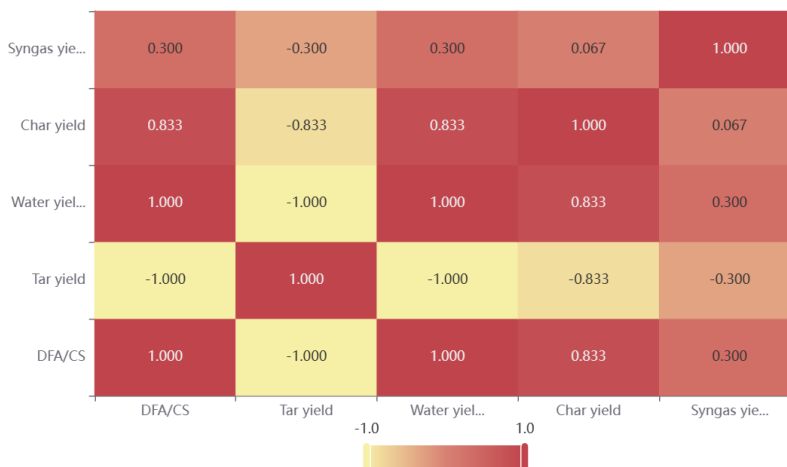


Figure 3. CS-Correlation Coefficients

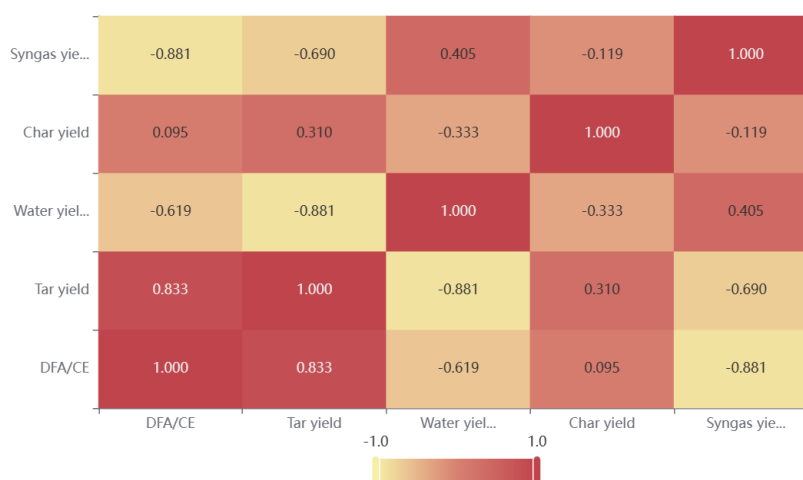


Figure 4. CE-Correlation Coefficients

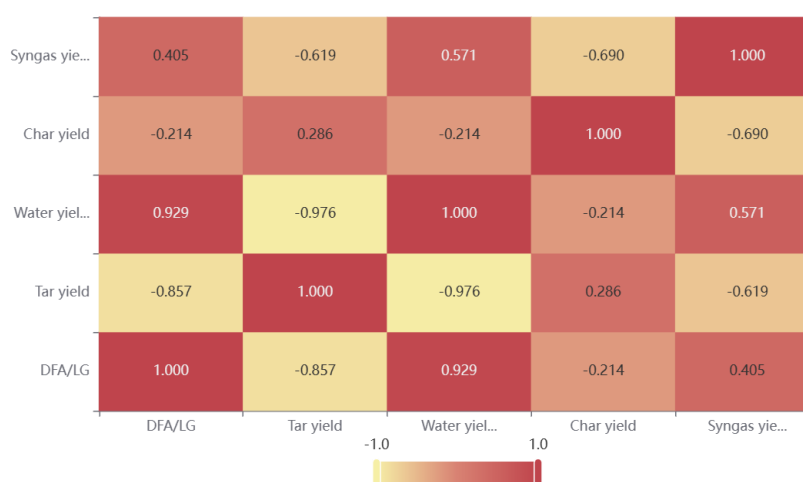


Figure 5. LG-Correlation Coefficients

## 2.2. Linear Regression on the Mixing Ratio of DFA

To better understand the relationship between DFA mixing ratio and cotton stalk pyrolysis products, the paper conducted a linear regression analysis using product yield data for DFA mixing ratios. The analysis of the F-test results reveals that the significance p-values are all less than 0.0001,

indicating significant levels of significance. The model equation based on the above process is as equation (2), and the results are shown Fig 6.

$$r_{CS} = -0.001 - 0.139y_t + 0.036y_w + 0.160y_c - 0.121y_s \quad (2)$$

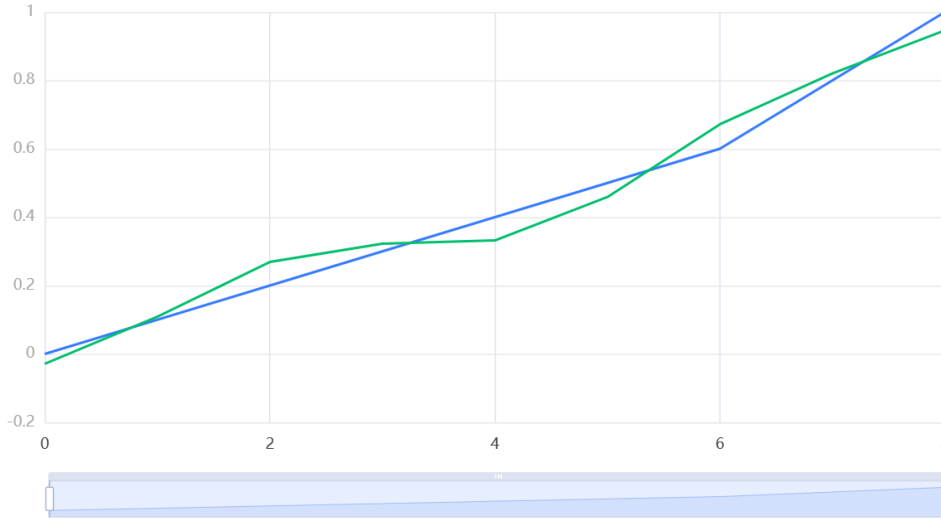


Figure 6. CS-Linear Regression

### 3. Catalytic Reaction Mechanism Model for the Model Compounds (CE and LG)

#### 3.1. Different Catalytic Pyrolysis Processes

Assuming that the desulfurization ash is mainly composed of silicates, sulfates, and sulfites, with calcium (Ca) and magnesium (Mg) being the main metallic elements, and the desulfurization ash can effectively adsorb the C, H, and O atoms in organic compounds. The adsorption process can be described using models such as the Langmuir-Hinshelwood model and the Eley-Rideal model. Subsequently, they react on the surface of desulfurized ash and disintegrate. [1, 2]

Cellulose contains a higher amount of H and O, and a large amount of desulfurization ash is immersed in high-temperature tar. Taking the reaction between tar and water on the surface of desulfurization ash to generate hydrogen as an example, which is shown in Fig 7, the Langmuir-Hinshelwood model is used, assuming that they first combine on the catalyst surface and then react.

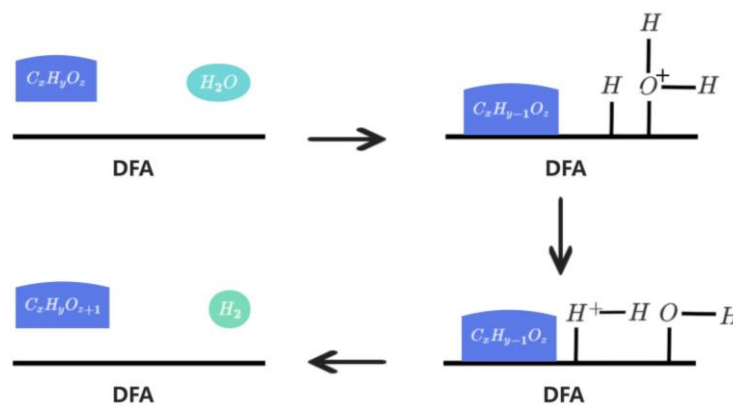
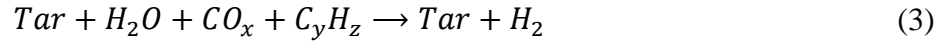


Figure 7. Catalyzed Reaction in CE Pyrolysis

Similarly, tar can also react with hydrocarbons and carbon oxides. In general, a large amount of tar plays a role in carbon fixation, oxygen fixation, and hydrogen release under catalytic conditions. The overall equation is equation (3):



Lignin has a lower content of H and O, making it unable to form much tar. It mainly undergoes reactions with char and other substances. Taking the reaction between char and water on the surface of desulfurization ash to generate carbon dioxide and methane as an example, which is shown in Fig 8, the Langmuir-Hinshelwood model is used, assuming that they first combine on the catalyst surface and then react.

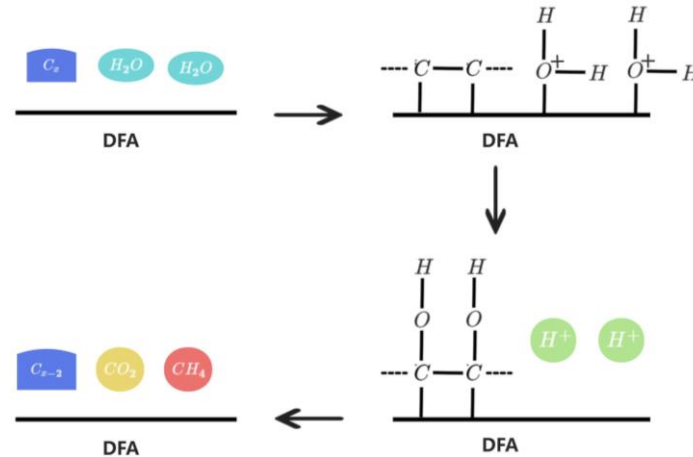
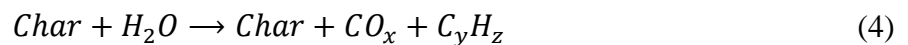


Figure 8. Catalyzed Reaction in LG Pyrolysis

Overall, char forms small molecular gases under desulfurization ash catalysis. The overall equation is equation (4):



### 3.2. Catalytic Reaction Kinetic Model

Regardless of CE or LG, they will first combine with the DFA surface. The reaction mechanism can be represented by formulas (5), (6) and (7), where C<sub>f</sub> represents the active sites on the surface, and C(O) represents the adsorbed surface carbon-oxygen complex.



Based on reaction equilibrium theory, if H<sub>2</sub> is present in the reaction gas, then H<sub>2</sub> can inhibit the reaction by either directly adsorbing on the active sites or promoting the reverse movement of the reaction equilibrium. According to the Langmuir-Hinshelwood reaction mechanism, the reaction rate of CE catalyzed reaction is shown in equation (8), where k<sub>1</sub>(MPa<sup>-1</sup> · s<sup>-1</sup>), k<sub>2</sub>(MPa<sup>-1</sup>), and k<sub>3</sub>(MPa<sup>-1</sup>) are kinetic parameters calculated from experimental data, and p is the gas partial pressure.

$$r_{CE} = \frac{k_1 P_{CO_x}}{1 + k_2 P_{CO_x} + k_3 P_{H_2}} \quad (8)$$

It can be seen that H<sub>2</sub> has an inhibitory effect on the reaction. If there is no H<sub>2</sub> in the reaction gas, the initial gasification reaction rate can be simplified to formula (9), and by transformation, formula (10) can be obtained.

$$r_{CE} = \frac{k_1 P_{CO_x}}{1 + k_2 P_{CO_x}} \quad (9)$$

$$\frac{1}{r_{CE}} = \frac{1}{k_1 P_{CO_x}} + \frac{k_2}{k_1} \quad (10)$$

Similarly, for the Catalyzed Reaction of LG, its reaction rate is as shown in equation (11).

$$r_{LG} = \frac{k_4 P_{H_2O}}{1 + k_5 P_{H_2O} + k_6 P_{CO_x}} \quad (11)$$

Ignore CO<sub>x</sub>, formula (12) and (13) can be obtained.

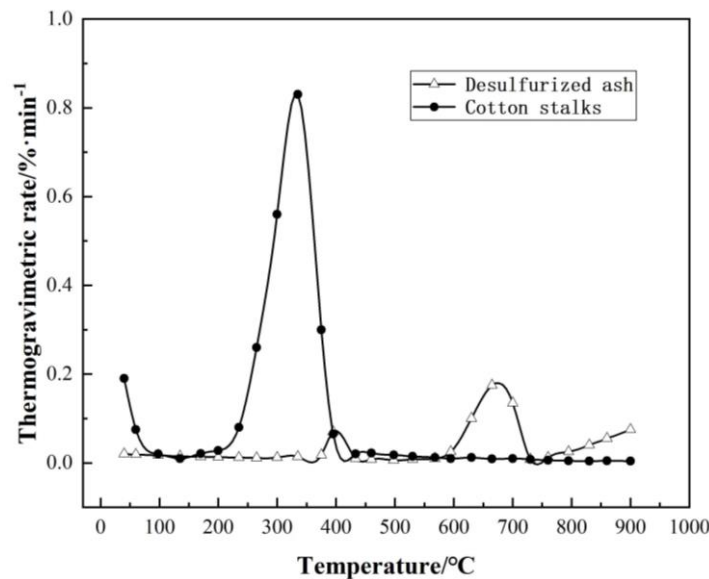
$$r_{LG} = \frac{k_4 P_{H_2O}}{1 + k_5 P_{H_2O}} \quad (12)$$

$$\frac{1}{r_{LG}} = \frac{1}{k_4 P_{H_2O}} + \frac{k_5}{k_4} \quad (13)$$

Analyzing equations (10) and (13), the kinetic parameters k<sub>1</sub> and k<sub>2</sub> can be obtained from the slope and intercept of the curves of 1/r<sub>H<sub>2</sub>O</sub> and 1/P<sub>H<sub>2</sub>O</sub> if there is a good linear relationship between them. Then, the average rate of the entire reaction can be calculated through thermogravimetric analysis, and the kinetic data k<sub>3</sub> can be calculated from formula (8).

This paper uses several model-free is conversional thermogravimetric analysis methods in order to determine the kinetic parameters of decomposition. [7-9]

Analyzing the data of thermogravimetric analysis in Fig 9., the weight is w mg, the heating rate is v K/min, the purge gas is N<sub>2</sub>, the flow rate is V mL/min. The experimental samples are CE and LG with a content of not less than 99% and an average particle size of u μm. The TG/DTG curve of pyrolysis at heating rate v K/min, and the relationship curve of conversion rate with temperature obtained from the decomposition TG curve at different heating rates can be derived.



**Figure 9.** Thermogravimetric Analysis

The paper assumes that at a certain temperature, the thermal decomposition reaction rate of the material is proportional to its conversion rate (the ratio of material mass loss to initial mass) and uses is conversional kinetic methods to calculate the reaction kinetic parameters of the material.

The is conversional kinetic equation can be expressed as equation (14):

$$\alpha = \frac{m_0 - m}{m_0} \quad (14)$$

Where α is the conversion rate, m<sub>0</sub> is the initial mass, and m is the mass at any time. The is conversional kinetic equation can be transformed into equation (15):

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \quad (15)$$

Where k(T) is the reaction rate constant at temperature T, and f(α) is the conversion rate function. By integrating the is conversional kinetic equation, the variation of the material's conversion rate with time can be obtained and then used to calculate the reaction kinetic parameters. Based on this, we establish a reaction kinetic model of CE and LG pyrolysis based on conversion rate.

The kinetic equation describing the pyrolysis reaction is formula (16):

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) \tag{16}$$

Integrating equation (16), the integral form of the kinetic equation is shown in equation (17):

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = kt \tag{17}$$

In equation (17),  $\alpha$  represents the share of the reactant thermally decomposed into products;  $t$  is time;  $f(\alpha)$  and  $G(\alpha)$  are the differential and integral forms of the mechanism functions describing the controlled chemical reaction;  $k$  is the reaction rate constant, usually expressed in Arrhenius form as equation (18) and (19).

$$\ln k_i = \ln A_i - \frac{E_i}{RT} \tag{18}$$

$$k_i = A_i e^{-\frac{E_i}{RT}} \tag{19}$$

By plotting  $\ln(\beta d\alpha/dT)$  against  $1/T$ , the value of  $E$  can be obtained. We use a conversion rate function  $f(\alpha, k)$  regarding the DFA ratio  $k$ , so it is possible to analyze the reaction kinetic models under various catalyst ratios and the influence and role of  $k$  on the reaction model and activation energy  $E$ .

Based on the experimental data and using the least squares method for parameter estimation, we conducted model fitting and validation for the experimental data and model parameters. The results are summarized in the table 1 and 2.

**Table 1.** Results of  $k_i$  at reaction pyrolysis temperature

Pyrolysis reaction	$k_i$	Temperature/K
		873.15
H <sub>2</sub> O pyrolysis	$k_1/\text{MPa}^{-1} \cdot \text{s}^{-1}$	0.032
	$k_2/\text{MPa}^{-1}$	5.467
	$k_3/\text{MPa}^{-1}$	9.809
CO <sub>x</sub> pyrolysis	$k_4/\text{MPa}^{-1} \cdot \text{s}^{-1}$	0.012
	$k_5/\text{MPa}^{-1}$	0.112
	$k_6/\text{MPa}^{-1}$	19.683

**Table 2.** The kinetic parameters of pyrolysis reaction

Parameter	Value
H <sub>2</sub> O pyrolysis	
$E_1/\text{kJ} \cdot \text{mol}^{-1}$	114.87
$A_1/\text{MPa}^{-1} \cdot \text{s}^{-1}$	$11.693 \cdot 10^6$
$E_2/\text{kJ} \cdot \text{mol}^{-1}$	-78.27
$A_2/\text{s}^{-1}$	$2.14 \cdot 10^{-3}$
$E_3/\text{kJ} \cdot \text{mol}^{-1}$	-11
$A_3/\text{s}^{-1}$	$1.337 \cdot 10^{-1}$
CO <sub>x</sub> pyrolysis	
$E_4/\text{kJ} \cdot \text{mol}^{-1}$	344.12
$A_4/\text{MPa}^{-1} \cdot \text{s}^{-1}$	$2.545 \cdot 10^6$
$E_5/\text{kJ} \cdot \text{mol}^{-1}$	-193.32
$A_5/\text{s}^{-1}$	$1.631 \cdot 10^{-10}$
$E_6/\text{kJ} \cdot \text{mol}^{-1}$	-47
$A_6/\text{s}^{-1}$	$9.134 \cdot 10^{-2}$

In conclusion, the Langmuir-Hinshelwood kinetic model of pyrolysis reaction is shown in equations (20) and (21). The L-H kinetic model considers the pyrolysis reaction as composed of several elementary reactions and is derived from the principles of gas adsorption and desorption, providing a certain theoretical basis. The pyrolysis reaction rate with respect to H<sub>2</sub>O and CO<sub>2</sub> partial pressures is

nonlinear, encompassing the effects of H<sub>2</sub> and CO partial pressures on the reaction rate, therefore, the L-H model better corresponds to the essence of coal gasification reactions.

Furthermore, the analysis of the model reveals that activation energy is not a constant value during the decomposition process. With an increase in conversion rate, the activation energy decreases, indicating a change in the reaction mechanism controlling the decomposition process as the reaction progresses.

$$r_{CE} = \frac{11.693 \times 10^6 \exp\left(-\frac{13.816}{T}\right) P_{CO_x}}{1 + 2.14 \times 10^{-3} \exp\left(-\frac{9.414}{T}\right) P_{CO_x} + 1.337 \times 10^{-1} \exp\left(\frac{1.323}{T}\right) P_{H_2}} \quad (20)$$

$$r_{LG} = \frac{2.545 \times 10^6 \exp\left(-\frac{41.389}{T}\right) P_{H_2O}}{1 + 1.631 \times 10^{-10} \exp\left(\frac{23.251}{T}\right) P_{H_2O} + 9.134 \times 10^{-2} \exp\left(\frac{5.653}{T}\right) P_{CO_x}} \quad (21)$$

#### 4. Predictions Based on Mathematical Models

Based on the dynamic model in Part 3, productivity can be predicted. A comprehensive analysis of pyrolysis product yield can be obtained by considering the results of linear and nonlinear fitting and the prediction of the isoconversion kinetic model. The catalytic effect of desulfurized ash on different biomass components can be evaluated by comparing the predicted results under different mixing ratios, and accurate guidance on the trend of pyrolysis product distribution can be provided. The results are shown in Fig 10, Fig 11, Fig 12, Fig 13.

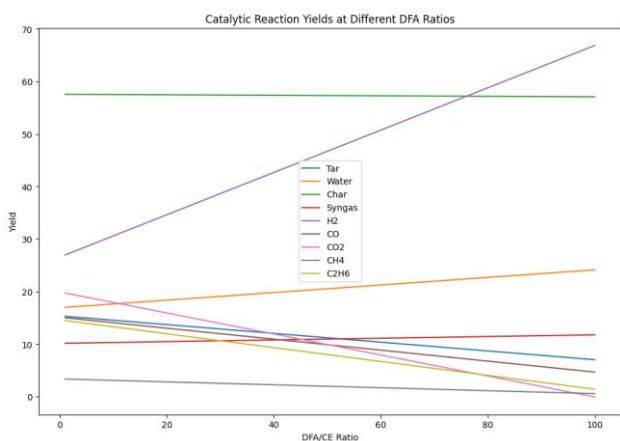


Figure 10. Linear Prediction of CE

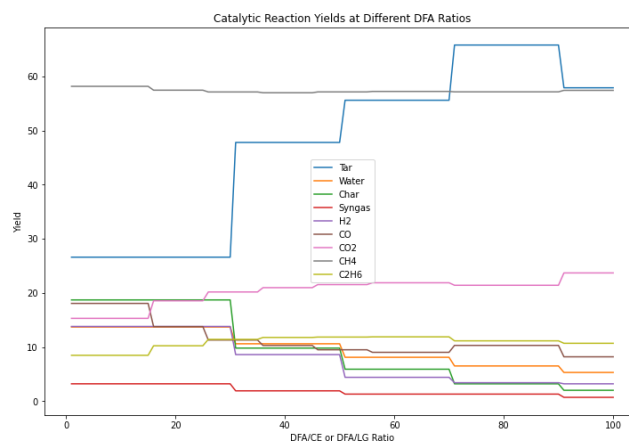


Figure 11. Nonlinear Prediction of CE

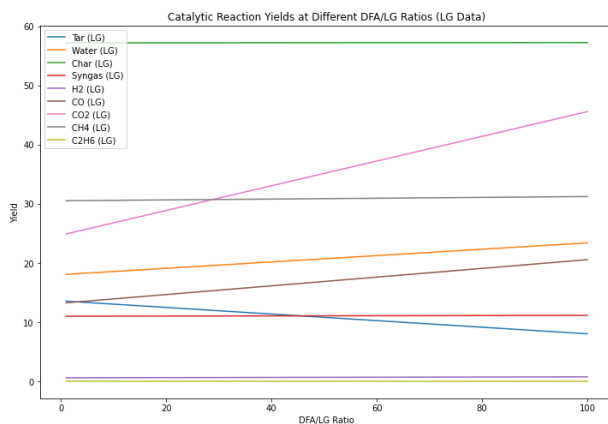


Figure 12. Linear Prediction of LG

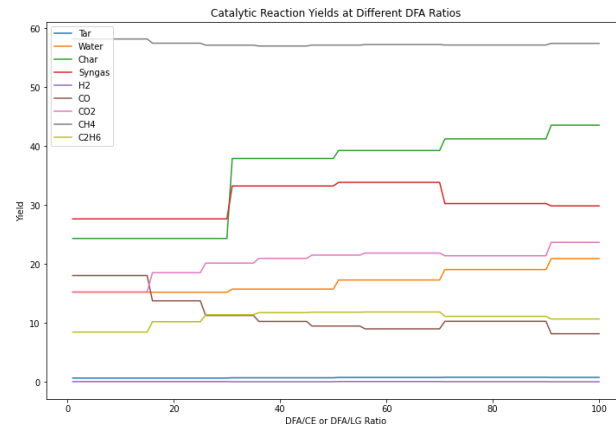


Figure 13. Nonlinear Prediction of LG

Comparing the predicted data with the actual data, it can be seen that our model has good predictive performance, with relatively small errors, fully meeting the requirements.



## 5. Conclusion

The model in this paper is based on abstracting fundamental characteristics from model compounds to simplify complex real-world situations, and allows for a detailed understanding of complex systems while ensuring consistency and reliability. Through our work, we have summarized the complex nonlinear relationship between the proportion of products and the proportion of DFA and obtained reaction equations and kinetic models. We found that cellulose tends to form tar while lignin tends to form coke. From this, we can predict the formation tendency and product proportion of different substances under catalytic conditions. In the future, biomass energy utilization technology is becoming increasingly mature and can be used in fields such as heating, gas supply, and electric power generation. It is one of the most promising technologies for converting biomass into syngas. This technology can not only supplement fossil fuel hydrogen production, but also provide new ideas for high energy consumption and uneconomical traditional hydrogen production.

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