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Study on Catalyst Combination and Yield of Ethanol to C4 Olefins Based on Regression Analysis

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Abstract: *Catalyst combination and temperature will have a certain impact on the selectivity and yield of C4 olefins. This paper first analyzes the relationship between the products and the reaction mechanism, so as to find out the main products. Then, according to the time-varying trend, regression analysis is carried out. The specific expression and error are obtained by solving the correlation results of the products with strong significance, and the relevant conclusions are obtained by qualitative analysis of the results of the products with weak significance. Then the specific catalyst combination is inferred by distance discrimination method. Finally, the grey correlation analysis is used to verify the curve fitting results in the above two questions.*

Keywords: *Regression Analysis, Grey Correlation Analysis, Catalyst Combination*

1. Introduction

C4 olefins are widely used in the production of chemical products and medicine, and ethanol is the raw material for the production of C4 olefins. In the preparation process, the catalyst combination and temperature will have an impact on the selectivity and yield of C4 olefins. Therefore, it is of great significance and value to explore the process conditions for the preparation of C4 olefins by ethanol catalytic coupling through the combination design of catalysts. This paper analyzes the test results of a given catalyst combination at different times of an experiment when the temperature is set to 350 degrees. In this regard, we first analyze the relationship between the products and their reaction mechanism, and find out the main products. Then, according to the time-varying trend, regression analysis is carried out. By solving the results of products with strong significance, the relevant expressions and errors are obtained, and the results with weak significance are qualitatively analyzed. Moreover, in order to judge the catalyst combination used in the experiment, this paper infers the specific catalyst combination by distance discrimination method.

2. Model Establishment and Solution

2.1. Grey Relational Analysis [1]

2.1.1. Determination of Analysis Sequence

Determine the reference sequence reflecting the characteristics of system behavior and the comparison sequence affecting system behavior. The data sequence reflecting the behavior characteristics of the system is called the reference sequence. The data sequence composed of factors affecting system behavior is called comparison sequence.

(1) The reference sequence (also known as parent sequence) is $Y = Y(k) \mid k = 1,2 \ldots n;$

(2) The comparison sequence (also known as subsequence) is $X_i = X_i(k) \mid k = 1,2 \ldots n, i = 1,2 \ldots m$。

2.1.2. Dimensionless of Variables

Because the data in each factor column in the system may have different dimensions, it is not easy to compare or it is difficult to get a correct conclusion during comparison. Therefore, in the grey correlation analysis, the dimensionless processing of data is generally necessary. There are two main methods:

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(1) Initial value processing: $x_i(k)=\frac{x_i(k)}{x_i(1)}, k=1,2\ldots n; i=0,1,2\ldots m$

(2) Mean processing: $x_i(k)=\frac{x_i(k)}{\overline{x_i}}, k=1,2\ldots n; i=0,1,2\ldots m$

Where k corresponds to a time period and I corresponds to a row (i.e. a feature) of the comparison sequence.

2.1.3. Calculation of Correlation Coefficient

$$\xi_i(k)=\frac{\min\limits_i\min\limits_k\left|y(k)-x_i(k)\right|+\rho\max\limits_i\max\limits_k\left|y(k)-x_i(k)\right|}{\left|y(k)-x_i(k)\right|+\rho\max\limits_i\max\limits_k\left|y(k)-x_i(k)\right|}$$

Let $\Delta_i(k)=\left|y(k)-x_i(k)\right|$, then

$$\xi_i(k)=\frac{\min\limits_i\min\limits_k\Delta_i(k)+\rho\max\limits_i\max\limits_k\Delta_i(k)}{\Delta_i(k)+\rho\max\limits_i\max\limits_k\Delta_i(k)}$$

$\rho\in(0,\infty)$, it is called resolution coefficient. The smaller ρ, the greater the resolution. Generally, the value range of ρ is (0,1), and the specific value can be determined according to the situation. When $\rho\le 0.5463$, the resolution is the best, usually $\rho=0.5$.

2.1.4. Calculation of Correlation Degree

Because the correlation coefficient is the correlation degree value of the comparison sequence and the reference sequence at each time, it has more than one number, and the information is too scattered to facilitate the overall comparison. Therefore, it is necessary to compare each time the correlation coefficient of is concentrated into one value, that is, the average value is calculated as the quantitative expression of the correlation degree between the comparison series and the reference series. The correlation degree formula is as follows:

$$r_i=\frac{1}{n}\sum_{k=1}^{n}\xi_i(k), k=1,2,\Lambda,n$$

2.1.5. Relevance Ranking

The correlation degree is sorted by size. If $r_1<r_2$, the reference sequence y is more similar to the comparison sequence x_2. After calculating the correlation coefficients of $X_i(k)$ series and $Y(k)$ Series, calculate the average value of various correlation coefficients. The average value r_i is called the correlation degree of $Y(k)$ and $X_i(k)$.

2.2. Problem Solving

2.2.1. Preliminary data processing

Firstly, this paper processes the data given, and draws the relationship between product selectivity and time change. Observing the change trend of each product in the figure with time, it is found that the selectivity of fatty alcohol decreases and the selectivity of acetaldehyde increases. Therefore, it can be inferred that acetaldehyde participates in the formation of fatty alcohol. Because C4 olefins can be obtained after fatty alcohol dehydration, acetaldehyde is speculated as the intermediate product of ethanol catalytic coupling to prepare C4 olefins.

After consulting literature [2], it is found that the selectivity of c4-c12oh decreases and the selectivity of acetaldehyde increases, indicating that acetaldehyde participates in the formation process of c4-c12oh. At higher residence time, with the increase of C4 olefin selectivity, the selectivity of acetaldehyde and c4-c12oh gradually decreases, indicating that acetaldehyde also participates in the formation process of C4 olefins. The relevant mechanism is shown in Figure2, which verifies the above conjecture in this paper.

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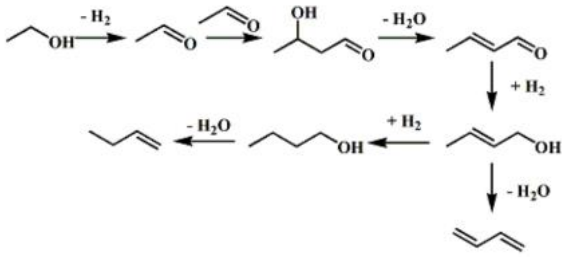

Figure 1: Formation mechanism of C4 olefins

2.2.2. Regression analysis

(1) Selection of main factors

According to the above conclusions, this paper proposes a new definition: "C4 + ethylene selectivity", which means the sum of C4 olefin selectivity and ethylene selectivity of a group.

Because ethanol conversion, C4 olefin selectivity, C4 olefin yield, acetaldehyde selectivity and C4 + acetaldehyde selectivity have the most obvious effects on the results, the above factors are considered as the main factors in this paper. Accordingly, the selectivity of fatty alcohol, methylbenzaldehyde and methylbenzyl alcohol and other products with carbon number of 4-12 were the secondary factors.

(2) Regression analysis solution

Using time as independent variable and ethanol conversion as dependent variable, the scatter diagram was drawn by SPSS. Taking group A1 as an example, the time scatter diagram of ethanol conversion is as follows:

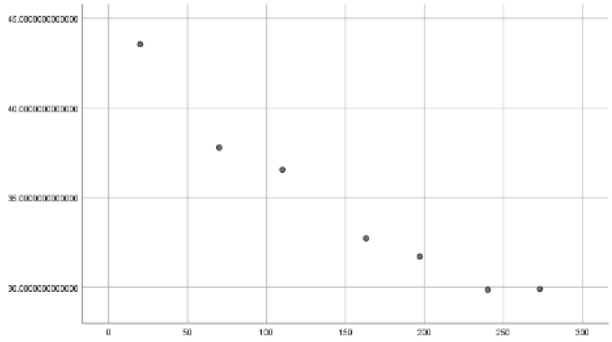

Figure 2: time scatter diagram of ethanol conversion

According to the data change trend shown in the scatter diagram, this paper selects relevant mathematical models to calculate the above data by SPSS. The data results of each group are as follows:

Table 1: Fitting results of main factors

Major Factor	*Relationship*	R^2
Ethanol conversion	*Quadratic*	*0.988*
C4 olefin selectivity	*Quadratic*	*0.241*
Acetaldehyde selectivity	*Quadratic*	*0.968*
C4 olefin yield	*Logarithm*	*0.997*
C4 + acetaldehyde selectivity	*Quadratic*	*0.671*

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From the above data, it can be seen that the fitting degree of C4 olefin yield, ethanol conversion and acetaldehyde selectivity is high, which can be analyzed quantitatively, while the fitting degree of C4 olefin selectivity and C4 + acetaldehyde selectivity is low, which is not suitable for quantitative analysis. Therefore, this paper will use qualitative analysis method to analyze these two groups of data and secondary factors and get relevant conclusions.

(3) Quantitative analysis

In this paper, the correlation expressions and errors of the three groups of data of C4 olefin yield, ethanol conversion and acetaldehyde selectivity are solved. The results of the correlation data expressions and errors are as follows:

Table 2: Quantitative analysis results

Catalyzer	*Nonstandard expression*	*Nonstandard expression*	*Error*
Ethanol conversion	$y = -0.105x + 45.249$	$y = 0.986x^2 - 1.924x$	*150.48*
Acetaldehyde selectivity	$y = -(2.120E-5)x^2 - 0.22x + 4.499$	$y = -0.405x^2 - 1.373x$	*12.751*
C4 olefin selectivity	$y = -215.267ln(x) + 2375.609$	$y = -0.998ln(x)$	*232625.78*

(4) Qualitative analysis

The selectivity of C4 olefins decreased with time at 0-160 minutes, and fluctuated at about 39.5% after 160 minutes.

The selectivity of C4 + acetaldehyde decreased with time at 0-160 minutes, and fluctuated at about 48.0% after 160 minutes.

The selectivity of fatty alcohols with carbon number of 4-12 decreased with time.

The selectivity of methylbenzaldehyde and methylbenzyl alcohol increased with time at 0-160 minutes, fluctuated slightly after 160-240 minutes, and decreased with time after 240 minutes.

The selectivity of other products increased with time at 0-160 minutes, and fluctuated at about 11.0% after 160 minutes.

2.2.3. Solution of catalyst combination

Since the ethanol conversion rate is equal at 240 minutes and 273 minutes, it is considered that the chemical reaction has reached equilibrium, that is, the ethanol conversion rate has reached dynamic equilibrium.The average value is taken according to the relevant data at 240 minutes and 273 minutes, so as to calculate the selectivity of each substance at the end of the reaction. The calculation results are as follows:

Table 3: Standard values of equilibrium state

Catalyst combination (%)	*Ethanol conversion (%)*	*Ethylene selectivity (%)*	*C4 olefin selectivity (%)*	*Acetaldehyde selectivity (%)*	*Fatty alcohol selectivity with carbon number of 4-12 (%)*	*Selectivity of methyl benzaldehyde and methyl benzyl alcohol (%)*	*Selectivity of other products (%)*
Standard value	*29.9*	*4.72*	*39.68*	*8.605*	*31.61*	*4.215*	*11.17*

According to the Euclidean distance method [3], the difference between the selectivity of each

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substance at 350 ℃ and the selectivity of each substance at the end of the reaction is calculated by MATLAB. It can be seen that the minimum Euclidean distance is 20.5167, that is, the most similar catalyst combination is A3, that is, "200mg 1wt% Co / sio2-200mg HAP ethanol concentration 0.9ml/min".

2.3. Model Analysis

In this paper, the grey correlation analysis method is used to analyze the test results of a given catalyst combination at 350 ℃ at different times of an experiment, and the correlation between the selectivity of each product and time is obtained. The results are shown in Table 4 (the larger the value is, the stronger the representative correlation is):

Table 4: Correlation between selectivity of each product and time

Ethanol conversion	*Ethylene selectivity*	*C4 olefin selectivity*	*Acetaldehyde selectivity*	*Fatty alcohol with carbon number of 4-12*	*Methyl benzaldehyde and methyl benzyl alcohol*	*Other products*
0.5489	*0.6244*	*0.6154*	*0.7056*	*0.5678*	*0.6101*	*0.614*

It can be seen from the above table that acetaldehyde selectivity has the highest correlation with time, which once again shows the correctness of the above ideas in this paper.

3. Model Evaluation

The model is designed and solved by using MATLAB, SPSS and other software, and the accuracy is good. The relevant data are visualized, easy to understand and easy to analyze. However, the influence of practical operation and other factors on the reaction process was not considered in detail. And there are few reference data, resulting in some errors in the model.

The model and algorithm have good generalization, and the core algorithm is simple and easy to understand, which can be used for relevant data analysis. At the same time, the model can be refined to improve the accuracy of the model and algorithm by increasing the number of experiments, catalyst combination, temperature gear and other external factors.

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