

Modeling and Research on the preparation of C4 olefins based on ethanol coupling

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Abstract. C4 olefin is a chemical material widely used in chemical and pharmaceutical products, and ethanol is the main raw material for the production of C4 olefins. Exploring the process of using ethanol to produce C4 olefins has important practical significance and practical value. In the process of preparing C4 olefins by catalytic coupling of ethanol, the combination and temperature of catalysts have an important impact on the yield and conversion efficiency of C4 olefins. The effects of different catalyst combinations and temperatures on the yield and conversion efficiency of C4 olefins were modeled by function fitting and neural network algorithm. In this paper, the relationship between ethanol conversion, C4 olefin selectivity and temperature is sought through curve fitting method. Firstly, the correlation between ethanol conversion, C4 olefin selectivity and temperature under each group of catalyst combination is analyzed. It is found that the relationship between ethanol conversion and temperature is the best through exponential function curve fitting. When fitting the relationship between C4 olefin selectivity and temperature, for the catalyst combination with peak data, the double exponential function is selected for fitting, and the other combinations are fitted by exponential function. The catalyst combination was divided into four independent variables: total catalyst (mg), CO loading (wt%), Co / SiO₂ and HAP loading ratio and ethanol concentration (ml / min). After normalization combined with temperature, the relationship between the five variables and ethanol conversion and C4 olefin selectivity was obtained through Spearman correlation analysis. Considering that the correlation of some single independent variables to dependent variables is not high, it is considered that the data provided is too dense, and there are few change data for reference, so it is impossible to analyze the real correlation normally. The response surface equation is fitted. When solving the response surface equation, the solution of each coefficient of the equation is obtained by multiple linear regression, so as to obtain the relationship between catalyst combination and temperature and ethanol conversion and C4 olefin selectivity.

Keywords: C4 olefin response surface faspilman correlation analysis multiple linear regression; BP neural network.

1. Introduction

As an important chemical raw material, C4 olefins are widely used in the production of chemical products and pharmaceutical intermediates. Widely sourced, green and clean ethanol can be used to produce C4 olefins. During the preparation process, it is found that the catalyst combination and temperature have an important impact on the preparation of C4 olefins. Therefore, it is of great value to explore the effect of catalyst combination and temperature on the experiment of ethanol catalytic coupling to prepare C4 olefins.

The images of temperature, ethanol conversion and C4 olefin selectivity were made for 21 groups of experimental data, and the images were analyzed. Fitting curve has become the focus of this paper. In the curve between temperature and ethanol conversion, they are obviously positively correlated. I have used curve of MATLAB Fitting fitted the data. Through the fitting methods of primary function, quadratic function and polynomial function, it was found that the relationship between ethanol conversion and temperature was the best through the exponential function curve. In the temperature and C4 olefin selectivity curve, although it shows an increasing trend, some curves reach the peak and decline. This part of the curve is fitted by double exponential function, and the reason for the decline is analyzed. In this paper, taking time as the independent variable and taking the conditions such as

ethanol conversion, ethylene selectivity, C4 olefin selectivity and acetaldehyde selectivity as the dependent variables, the exponential function and polynomial function fitting are carried out to establish the relationship with the previous experiments, so as to draw a conclusion.

The effects of different catalyst combinations and temperatures on ethanol conversion and C4 olefin selectivity were studied Department. Split the catalyst combination, normalize the data of the five variables through five variables: total amount of catalyst, CO loading, Co / SiO₂ and HAP loading ratio, ethanol concentration and temperature, and analyze the relationship between the five variables and the two through Spearman correlation coefficient. It is found that some single variables have little influence on the dependent variables, but have great influence when combined. By fitting the response surface equation, the coefficients of the surface equation are obtained by multiple linear regression, and the relationship between catalyst combination and ethanol conversion and C4 olefin selectivity is obtained.

2. Curve fitting based on multiple functions

In this paper, the relationship between temperature and ethanol conversion and C4 olefin selectivity is studied. Firstly, different functions are fitted with temperature as the independent variable and ethanol conversion and C4 olefin selectivity as the dependent variable respectively, then the most appropriate function is found out, and finally the relationship between dependent variable and independent variable is studied according to the function. Then, under the given temperature and catalyst combination conditions, analyze the test results at different times of the experiment, take time as the independent variable and the test results as the dependent variable for fitting, find out the functional relationship between the test results and the independent variable, and analyze and draw the corresponding conclusions.

2.1. Explore the relationship between temperature and ethanol conversion

When the first assembly method is adopted, in the process of exploring the temperature and ethanol conversion rate, the dependent variables show a gradual increasing trend with the increase of independent variable-s. The curve fitting toolbox of MATLAB is used for curve fitting, and the fitting degree of the exponential function is the highest. Therefore, the exponential function relationship between temperature and ethanol conversion rate is established for each catalyst combination. Under the condition of loading mode I, The expressions of A1 ~ A14 groups of fitting functions are shown in Table 1.

Table 1. Expression of A1 ~ A7 group fitting function.

A1	$y_{1i} = 0.01391e^{(0.02251x_{1i})}$
A2	$y_{2i} = 0.2377e^{(0.01636x_{2i})}$
A3	$y_{3i} = 3.093e^{(0.007641x_{3i})}$
A4	$y_{4i} = 0.7273e^{(0.01213x_{4i})}$
A5	$y_{5i} = 0.394e^{(0.01313x_{5i})}$
A6	$y_{6i} = 0.7322e^{(0.0119x_{6i})}$
A7	$y_{7i} = 3.728e^{(0.007623x_{7i})}$

Put the function images together for comparative analysis. As shown in Figure 1, it can be concluded that there is a strong relationship between ethanol conversion and temperature under each catalyst combination, and the two are basically positively correlated.

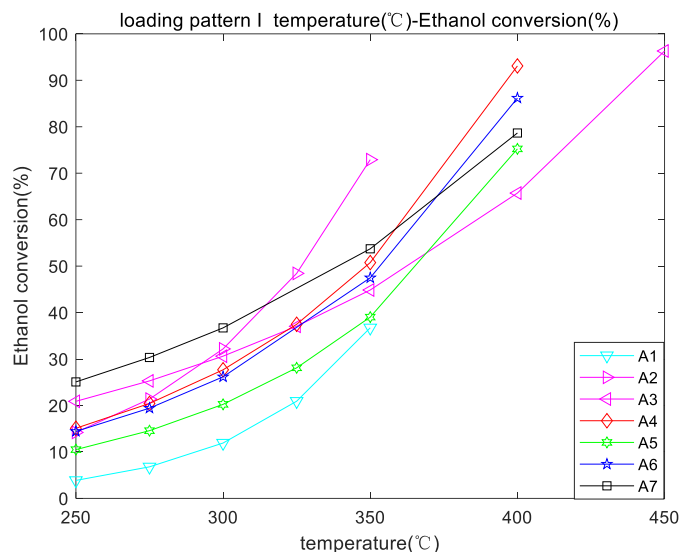


Figure 1. Relationship between ethanol conversion and temperature in loading mode 1.

When loading mode II is adopted, it is found that the change of ethanol conversion rate under the same conditions of loading mode II and loading mode I is very good, and it is concluded that the assembly mode has basically no effect on ethanol conversion rate. Therefore, the exponential function fitting is still used. The fitting function expression is shown in the appendix. The relationship diagram of 7 groups of data fitting is shown in Figure 2.

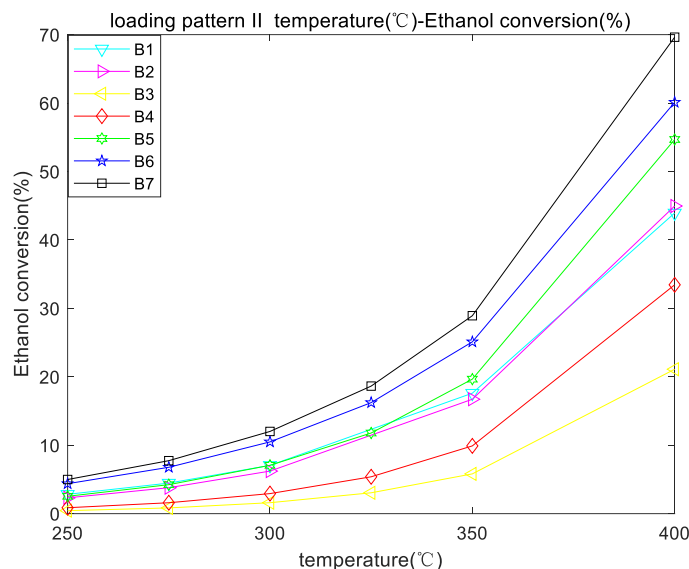


Figure 2. Relationship between ethanol conversion and temperature in feed mode 2.

It can be seen from Figure 2 that the ethanol conversion increases gradually with the increase of temperature, and the ethanol conversion of B7 curve at 400 °C is the highest in this figure.

2.2. Explore the relationship between temperature and C4 olefin selection rate

When the first assembly method is adopted, it is found in the data that there is a gradual increasing relationship between most temperatures and C4 olefin selection rate. In a few data, C4 olefin selection increases first and then decreases with the increase of temperature. For curve fitting in various cases, the fitting degree of exponential function is still the highest for most increasing functions, and for increasing first and then decreasing In rare cases, double exponential functions are used for fitting, and a group of increasing functions have poor fitting effect. Polynomial functions are used for fitting, and the expression of fitting function is shown in the appendix. Fit the data group as shown in Figure 3.

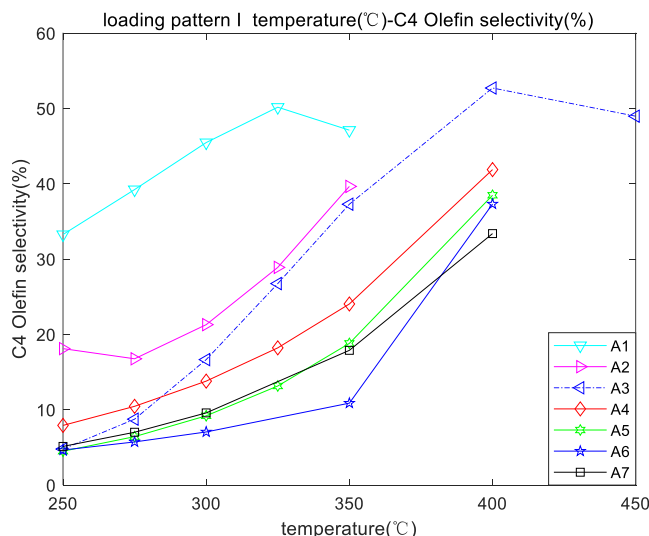


Figure 3. Relationship between temperature of loading mode 1 and selectivity of C4 olefins.

It can be seen from Figure 3 that the selectivity of C4 olefins basically shows a gradual increasing trend with the temperature. For the reason of increasing first and then decreasing in the experiment, by querying the data [3], when the temperature is higher than a certain temperature, the selectivity of other products will gradually increase, resulting in the decrease of C4 olefin selectivity.

When the second assembly method is adopted, in the process of exploring the temperature and C4 olefin selectivity, most of the data show monotonic increase. It is found that the increasing function still uses the exponential function, which has a high degree of fitting. The fitting effect of one group of data using the primary function is better. See the appendix for the expression of the fitting function. The seven groups of data are fitted by function, as shown in Figure 4.

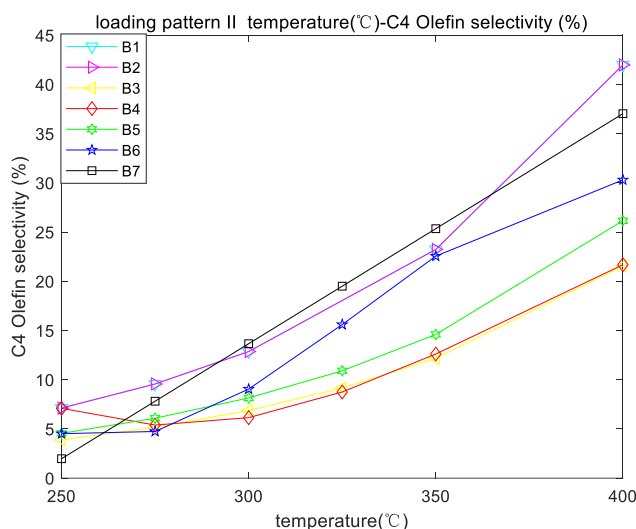


Figure 4. Relationship between temperature of loading mode II and selectivity of C4 olefins.

As can be seen from Figure. 4, for charging mode II, the selectivity of C4 olefins is positively correlated with temperature.

3. Response surface analysis based on multi factors

3.1. Data analysis

Firstly, the effects of catalyst combination and temperature on ethanol conversion and C4 olefin selection rate need to be analyzed. For each group of catalyst combination contains multiple factors,

the factors in the catalyst combination are divided into multiple factors to study the effects of multiple factors and temperature in the catalyst combination on ethanol conversion and C4 olefin selection rate, When the factors in the catalyst combination were separated, it was found that the factors were not unified with the temperature unit, so normalization was required.

3.2. Data processing

The total catalyst loading ratio is Co / O2, the total catalyst loading ratio is Co / SiO2 and the total catalyst loading ratio is SiO2, respectively.

Normalization processing: use the following formula to normalize the five factors.

$$X'_i = \frac{x'_i - x_{\min}}{x_{\max}} \quad (1)$$

Where x'_i, X'_i respectively represent the values before and after normalization, x_{\max}, x_{\min} respectively represent the maximum and minimum values in each factor data. Because there are too many variables used in this paper, it is fixed here for symbolic explanation.

3.3. Establishment and solution of model

For the data in this paper, if each independent variable is analyzed with the dependent variable, it is found that some data have little impact on the dependent variable, but combined with other factors will have a greater impact on the dependent variable. Therefore, the response surface equation [4] is introduced here:

$$Y' = \lambda_0 + \sum_{i=1}^k \lambda_i x_i + \sum_{i=1}^k \lambda_{ij} x_i^2 + \sum_{i<j}^k \lambda_{ij} x_i x_j \quad (2)$$

In this formula, Y' represents the value of the dependent variable, λ_0 represents the constant, λ_i and λ_{ij} represent the coefficients of regression, and x_i is the independent variable.

3.3.1. The relationship model between various factors and ethanol conversion was established Spearman correlation analysis [5].

Firstly, the effects of CO / SiO2 and HAP loading ratio, total amount of catalyst, CO loading, ethanol concentration and temperature on ethanol conversion and C4 olefin selectivity were analyzed. As shown in Table 2.

Table 2. Spearman correlation analysis of various factors and ethanol conversion.

	X1	X2	X3	X4	X5
rho	-0.66	0.434	0.03	-0.378	0.779
Ethanol conversion	0.496	0.000	0.759	0.000	0.000
Significance N	109	109	109	109	109

When the significance is less than 0.05, it indicates that there is a significant correlation between the two variables. According to table 1, the correlation between ethanol conversion rate and Co / SiO2, HAP loading ratio and co loading is very weak. This paper believes that these two factors have little influence on ethanol conversion rate alone, and these single factors with little influence are eliminated.

Establish the corresponding surface equation between ethanol conversion and various factors, the normalized data were imported into SPSS, and the relationship between ethanol conversion rate and various factors was analyzed by multiple regression.

When the significance is less than 0.05, it is considered that the correlation between independent variables and dependent variables is weak. In order to make the regression effect of the final equation better, remove the factors with weak significance and repeat multiple linear regression for many times until the equation with the best regression effect is obtained.

Finally, the expression of ethanol conversion and each independent variable is

$$Y_1 = 0.58X_5^2 + 0.349X_4^2 + 0.618X_2X_4 + 0.572X_2X_5 - 0.322X_2 - 0.821X_4 + 0.068X_5 + 0.379 \tag{3}$$

The regression effect of the model is analyzed

Table 3. Regression effect.

Model	R	Square of R	Adjusted R square	Standard inclination
1	0.957	0.915	0.902	8.19E-002

The regression effect of the model is analyzed and judged by the square of R. according to the square of R in Table 3, the absolute value of this value tends to 1 before and after adjustment, indicating that the effect of multiple linear regression is very strong.

3.3.2. The model of the relationship between various factors and C4 olefin selectivity was established

In the same way as the model for analyzing the relationship between various factors on ethanol conversion, firstly, analyze the effects of five factors: Co / SiO2 and HAP loading ratio, total catalyst, CO loading, ethanol concentration and temperature on C4 olefin selectivity, as shown in Table 4.

Table 4. Spearman correlation analysis of various factors and ethanol conversion.

	X1	X2	X3	X4	X5
rho	0.123	0.316	-0.159	-0.152	0.763
Ethanol conversion	0.202	0.001	0.099	0.115	0.000
Significance N	109	109	109	109	109

When the significance is less than 0.05, it indicates that there is a significant correlation between the two variables. From table 5 above, it can be seen that the selectivity of C4 olefins has a very weak correlation with the three factors of CO / SiO2 and HAP loading ratio, CO loading and flow rate. It cannot be directly considered that these independent variables have no relationship with the dependent variable. Some data have a joint influence on the dependent variable. Therefore, the influence of these three factors on a single variable can be eliminated.

When the significance is less than 0.05, it is considered that the correlation between independent variables and dependent variables is weak, so as to make the regression effect of the final equation better. Remove the factors with weak significance, repeat multiple linear regression for many times, and finally get the equation with the best regression effect.

Finally, the relationship between the selectivity of C4 olefins and several other variables can be obtained:

$$Y_2 = 0.509X_5^2 - 0.080X_2^2 - 0.181X_1X_5 + 0.173X_2X_4 + 0.407X_2X_5 - 0.481X_4X_5 + 0.562X_5 + 0.103X_2 - 0.029 \tag{4}$$

The regression effect of the model is analyzed

Table 5. Regression effect.

Model	R	Square of R	Adjusted R square	Standard inclination
1	0.925	0.856	0.844	1.03E-001

According to the square of R in Table 5, its absolute value tends to 1 before and after adjustment, indicating that the effect of multiple linear regression is good.

4. Maximum prediction of BP neural network model

4.1. Model analysis

Firstly, for this problem, an optimization model should be established to study the relationship between catalyst combination and temperature on ethanol conversion and C4 olefin selectivity. The functional relationship between dependent variable and independent variable is established to obtain the corresponding analysis. In this paper, the most appropriate catalyst combination and temperature are obtained to maximize the final C4 olefin yield. First, the largest C4 olefin yield in the data is found, and the experimental combination is A3, It is found that the C4 olefin yield reaches the maximum when the temperature is 400, and the C4 olefin yield suddenly decreases when the temperature is 450. If multiple linear regression is still used, the rise and fall of this data in this period cannot be detected, because only this group of data has changed in this experiment, and others have gradually increased. As a result, if the maximum value is calculated by function, the higher the temperature is, the higher the C4 olefin yield is, and the optimal value cannot be detected, Therefore, the function is not used to calculate the maximum value.

4.2. Solution of model

Firstly, it is found that when the temperature in the experimental combination A3 is 400, the C4 olefin yield is the highest and the temperature suddenly decreases at 450 degrees. Keep the catalyst combination conditions of this group unchanged and change the temperature range. The value should be selected near 400. In this paper, the temperature range is 390-422. Import the data to calculate the value of C4 olefin yield, as shown in table 6.

Table 6. C4 olefin yield.

temperature	C4 olefin yield
390	0.390431084
393	0.399803354
396	0.407739605
399	0.414028413
402	0.41845097
405	0.420887638
408	0.421471368
411	0.420684339
414	0.419280603
417	0.418047965
420	0.417568671

In order to more intuitively see the maximum yield of C4 olefins, the two aspects are analyzed, as shown in Figure 5.

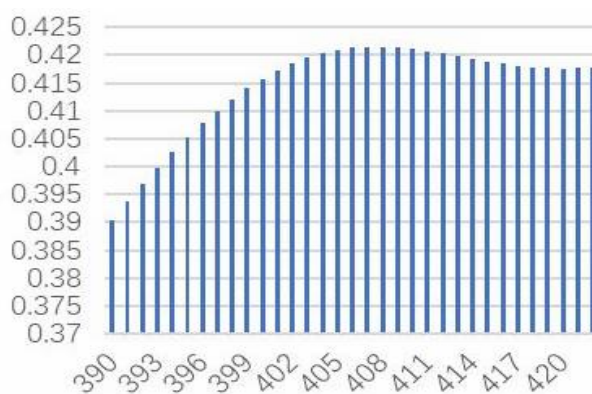


Figure 5. Relationship between temperature and C4 olefin yield.

In Figure 5, the temperature range is obtained when the C4 olefin yield is the maximum. According to the data in the table, it can be concluded that when the temperature is 408, the C4 olefin yield reaches the maximum, and the maximum value is 0.421471368.

Therefore, when the catalyst combination is 200mg 1wt% Co/sio2-200mg HAP ethanol, the concentration is 0.9ml/min, and the temperature is 408.

Since the required temperature is less than 350, the maximum C4 olefin rate is calculated. Firstly, arrange and combine the four factors of the catalyst, select the temperature between 250-350, import the data into Matlab, calculate the C4 olefin yield under each arrangement and combination according to the neural network algorithm, sort according to the calculated value, and finally calculate that the maximum value of C4 olefin yield in the range of temperature less than 350 is 0.275843666. At this time, the catalyst combination is 200mg 2wt% Co/sio2-200mg, and the concentration of HAP ethanol is 2.1ml/min.

4.3. Evaluation of model

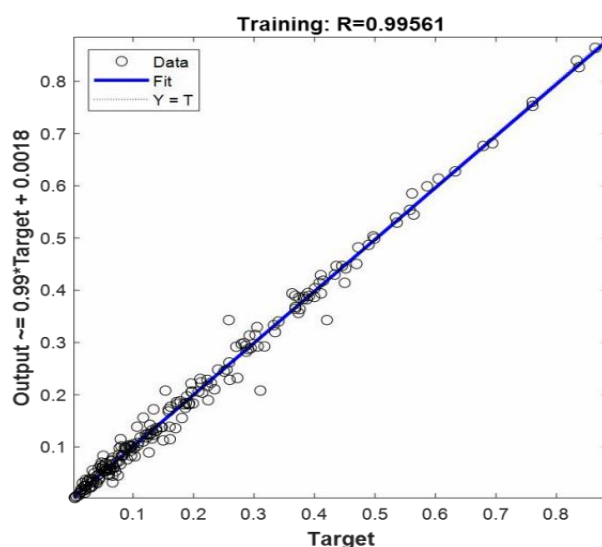


Figure 6. Regression: Regression chart.

As shown in Figure 6, the regression curve $r = 9.99561$, with high accuracy.

5. Conclusion

In the statistical analysis of this paper, various factors are comprehensively considered. The relationship with ethanol conversion and C4 olefin selectivity is obtained from the analysis of five variables: total catalyst amount, CO loading, Co / SiO₂ and HAP loading ratio, ethanol concentration and temperature. In multiple methods of analyzing correlation, based on the actual characteristics of the data, such as the discontinuity of some data, the optimal model is selected to calculate the Spearman correlation coefficient, According to the logical relationship between problems, we can reasonably infer the special value, which is not limited to relying on software to fill in the null value. In terms of analyzing outliers, from the perspectives of numerical range, data variance, correlation between data and so on, screen and exclude outliers, and eliminate the obtained equation for many times and multiple linear regression, so as to obtain the equation with the strongest correlation coefficient.

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