Research based on optimization model of C4 olefins preparation

Yingchen Liu*, Yuanhao Wang, Xiaoyi Liu

School of Mathematics and Computer Science, Northwest Minzu University, Lanzhou, 730124,China

* Corresponding Author Email: liuyingchen0918@163.com

Abstract. In this paper,through the design of catalyst combination and temperature control,a mathematical model was established to explore the process of ethanol catalytic coupling to produce C4 olefins.Firstly,according to the data in the attachment,temperature was taken as the main variable,and ethanol conversion rate and C4 olefins selectivity were taken as dependent variables to solve the binary regression function. Then,ethanol conversion rate and C4 olefins selectivity were imported into the model as master columns.It was found that temperature had the greatest influence on ethanol conversion and C4 olefins selectivity.Then the BP neural network model was constructed,and different catalyst combinations and temperature data were substituted.Through analysis,the maximum yield of C4 olefin was 53.58%,the filling ratio was 0.49,the Co loading was 2,the ethanol adding rate was 0.3,and the temperature was 450℃.Finally,considering the highest C4 olefin yield as the starting point,additional control experiments were set from the perspectives of whether to use HAP-ethanol,adjacent temperature,ethanol addition rate,Co loading capacity and charging ratio,respectively,to verify the rationality of the neural network model.

Keywords: Catalyst; Multiple regression; Neural network; Control experiment

1. Background

In the production of chemical products and medicine,C4 olefins are often widely used.In recent years,with the global economic recovery after the financial crisis and the wide use of downstream derivatives,the demand for C4 olefin is increasing year by year[1].Ethanol is an essential raw material for the production and preparation of C4 olefins.The selectivity and yield of C4 olefin are affected by catalyst combination and temperature.Therefore,it is of great significance and value to explore the technological conditions for the preparation of C4 olefin by ethanol catalytic coupling through catalyst combination design[2].

2. Modeling and solving of problem 1

2.1. Model Establishment

Let the random variable y and m independent variables $x_0, x_1, \ldots\ldots x_{m-1}$,given n set observations$(x_{0k}, x_{1k}, \cdots\cdots, x_{m-1k}, y_k)$ (k=0,1,……,n-1),using linear expression :

$$y = a_0x_0 + a_1x_1 + \cdots + a_{m-1}x_{m-1} + a_m \tag{1}$$

The observed data were analyzed by regression analysis.According to the principle of least squares:

$$q = \sum_{i=0}^{n-i}[y_i - (a_0x_{0i} + a_1x_{1i} + \cdots + a_{m-1}x_{m-1,i} + a_m)]^2 \tag{2}$$

To minimize the value of q,the regression coefficients $a_0, a_1, \ldots\ldots, a_m$ should satisfy the following equations:

$$CC^T)\begin{bmatrix}a_0\\a_1\\a_2\\\vdots\\a_{m-1}\\a_m\end{bmatrix}=C\begin{bmatrix}y_0\\y_1\\a_0\\\vdots\\y_{n-2}\\y_{n-1}\end{bmatrix}\qquad C=\begin{bmatrix}x_{00}&x_{01}&x_{02}&\cdots&x_{0,n-1}\\x_{10}&x_{11}&x_{12}&\cdots&x_{1,n-1}\\\vdots&\vdots&\vdots&\vdots&\vdots\\x_{m-1,0}&x_{m-1,1}&x_{m-1,2}&\cdots&x_{m-1,n-1}\\1&1&1&\cdots&1\end{bmatrix}\tag{3}$$

2.2. Model solving and result analysis

After solving by MATLAB[3],the following results are obtained:

Table 1 Results of multiple regression

A1	$Y = 181.037251 + 2.011942 \times X_1 + 2.020738 \times X_2$
A2	$Y = 240.216268 + 1.376756 \times X_1 + 2.020738 \times X_2$
A3	Y=232.479934+2.496887 $\times X_1 - 0.317720 \times X_2$
A4	Y=251.207189+1.954980 $\times X_1 - 0.621688 \times X_2$
A5	Y=263.597594 $-$ 1.819142 $\times X_1$+7.397524 $\times X_2$
A6	Y=241.469818+1.918157 $\times X_1$+0.026816 $\times X_2$
A7	Y=201.055044+2.362432 $\times X_1$+0.577096 $\times X_2$
A8	Y=223.708607 $-$ 3.680536 $\times X_1$+9.273289 $\times X_2$
A9	Y=234.694273+0.190619 $\times X_1$+3.734259 $\times X_2$
A10	Y=328.876368+14.920476 $\times X_1 - 34.471959 \times X_2$
A11	Y=249.182243 $-$ 2.105525 $\times X_1$+27.628140 $\times X_2$
A12	Y=197.820177 $-$ 4.421795 $\times X_1$+10.982397 $\times X_2$
A13	Y=232.567139+0.978040 $\times X_1$+4.564868 $\times X_2$
A14	Y=263.387764+4.153975 $\times X_1 - 3.379548 \times X_2$
B1	Y=221.972208 $-$ 2.309531 $\times X_1$+6.784814 $\times X_2$
B2	Y=247.131227 $-$ 1.544057 $\times X_1$+5.746274 $\times X_2$
B3	Y=230.971840 $-$ 1.640534 $\times X_1$+9.690555 $\times X_2$
B4	Y=261.453250+2.250278 $\times X_1$+3.434362 $\times X_2$
B5	Y=219.714826 $-$ 2.308454 $\times X_1$+11.005408 $\times X_2$
B6	Y=246.295266+0.448020 $\times X_1$+4.188244 $\times X_2$
B7	Y=237.980701 $-$ 0.521564 $\times X_1$+5.187351 $\times X_2$

The binary function of temperature,ethanol conversion and C4 olefin selectivity under different catalyst combinations was obtained,that is,the relationship between temperature,ethanol conversion and C4 olefin selectivity was obtained.Then,scatter plots of ethanol conversion rate and C4 olefins selectivity at different times were made to observe the changing trend of ethanol conversion rate and C4 olefins selectivity,and multiple regression models were also selected.After solving the multiple regression model,the following results can be obtained:

$$Y\text{=0- }8.6575\times X_1+0.0575\times X_2+0.1330\times X_3-0.2790\times X_4-0.0118\times X_5-0.1672\times X_6+0.0693\times X_7\tag{4}$$

3. Modeling and solving of problem 2

3.1. Model Establishment

Grey correlation degree analysis: The correlation degree is a measure of the correlation degree that changes between the factors of two systems at different times or with different objects[7].In the process of system development,if two association analysis method is a method to measure the degree of association between factors according to the degree of similarity or dissimilarity of development trend between factors. Calculation steps:

(1) Determine the reference sequence reflecting the characteristics of the system behavior and the comparative sequence affecting the system behavior,that is,the data sequence reflecting the characteristics of the system behavior and the data sequence composed of the factors affecting the system behavior.

(2) The reference sequence and comparison sequence are dimensionless.Due to the different physical meanings of various factors in the system,the dimensions of data are not necessarily the same,so it is difficult to get a correct conclusion during comparison.Therefore,dimensionless data processing is generally required in grey relational degree analysis.

(3) To determine the grey correlation coefficient of reference sequence and comparison sequence $\xi(X_i)$.The degree of correlation is essentially the degree of difference of geometric shapes between curves,and the difference between curves can be used as a measure of the degree of correlation.For a reference sequence x_0 ,there are several comparison sequences $x_1, x_2, \cdots, x_n$ .The correlation coefficient of the comparison sequence and the reference sequence at each time can be calculated by the following formula:

$$\zeta_i(k) = \frac{\min_i \min_k |x_0(k) - x_i(k)| + \rho \cdot \max_i \max_k |x_0(k) - x_i(k)|}{|x_0(k) - x_i(k)| + \rho \cdot \max_i \max_k |x_0(k) - x_i(k)|} \tag{5}$$

3.2. Model solving and result analysis

Firstly, the scatter diagram of C4 olefin selectivity, ethanol conversion rate and temperature was obtained:

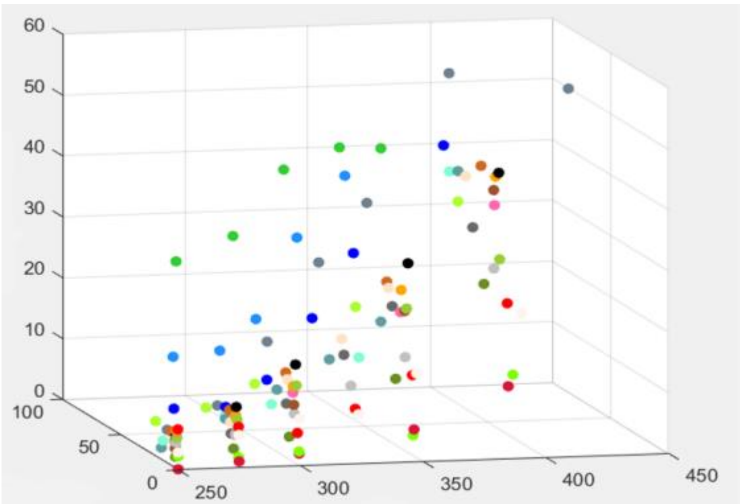

Figure 1 Scatter plot of C4 olefins selectivity, ethanol conversion and temperature

As can be seen in the figure,C4 olefins selectivity and ethanol conversion rate gradually increase with the increase of temperature under the same catalyst condition,indicating that different temperatures and different catalytic converter combinations have a certain impact on C4 olefins selective ethanol conversion rate. The C4 olefins selectivity and ethanol conversion increase with the increase of temperature. At the same time,different catalyst combinations have different effects on the reaction. At the same time,the correlation degree of C4 olefin selectivity,ethanol conversion,temperature and catalyst combination was obtained.

Table 2 Grey correlation degree value

subsequence / principal series	Charging ratio Co/SiO2 to HAP mass ratio	Co load	Ethanol addition rate	temperature
ethanol conversion rate	0.7138	0.72	0.683	0.7408
C4 olefins selectivity	0.7436	0.73	0.7258	0.7766

As can be seen from the table, the larger the gray correlation degree, the greater the influence of catalyst combination and temperature on C4 olefins selectivity and ethanol conversion. For ethanol conversion and C4 olefins selectivity, temperature has the greatest influence on them. The selectivity of C4 olefins was more obviously affected by catalyst combination than ethanol conversion.

4. Modeling and solving of problem 3

4.1. Model Establishment

BP neural networks process[4] information by constructing structures similar to synaptic connections in the brain.The basic steps of realizing BP network are as follows:

(1) Data preprocessing

It is necessary to preprocess the data before training the neural network,so the normalized processing method is chosen.Data normalization is to map data to [0,1] or [-1,1] interval or smaller interval.Because the units of input data are different,the range of some data may be particularly large,resulting in slow convergence and long training time of neural network.Input with large data range may play a larger role in pattern classification,while input with small data range may play a smaller role.So we need to normalize the data.The essence of normalization algorithm is linear transformation algorithm.The conversion formula is:

$$y = (x - min)\,/(max - min) \tag{6}$$

Where min is the minimum value of x,Max is the maximum value of x,the input vector is x,and the normalized output vector is Y.The above formula normalized the data to the interval [0,1].

(2) Build BP neural network

Taking the three-layer perceptron as an example, when the network output is different from the expected output, there is an output error E, which is defined as follows:

$$E = \frac{1}{2}(d - O)^2 = \frac{1}{2}\sum_{k=1}^{\ell}(d_k - o_k)^2 \tag{7}$$

Expand the above definition of error to the hidden layer:

$$E = \frac{1}{2}\sum_{k=1}^{\ell}[d_k - f(net_k)^2] = \frac{1}{2}\sum_{k=1}^{\ell}\left[d_k - f(\sum_{j=0}^{m}\omega_{jk}\, y_j)\right]^2 \tag{8}$$

Further expand to the input layer:

$$E = \frac{1}{2}\sum_{k=1}^{\ell} d_k - f\left[\sum_{j=0}^{m}\omega_{jk}\, f(net_j)\right]^2 = \frac{1}{2}\sum_{k=1}^{\ell} d_k - f\left[\sum_{j=0}^{m}\omega_{jk}\, f(\sum_{j=0}^{n} \upsilon_{jk}\chi_i)\right]^2 \tag{9}$$

(3) Inverse normalization and error calculation of prediction results,and comparison between the real value and predicted value of the verification set.

4.2. Model solving and result analysis

Different catalyst combinations and temperature data were substituted into the trained neural network, and the following figure was obtained:

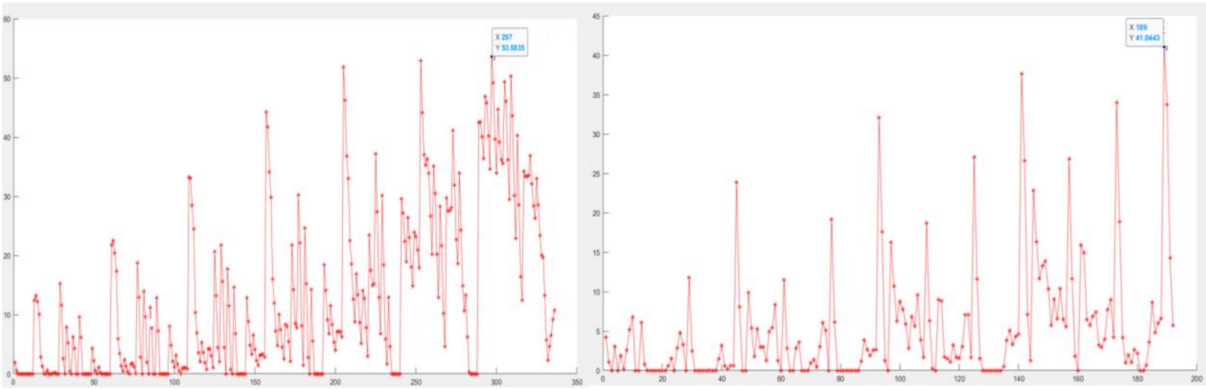

Figure 2 Prediction value of C4 olefin yield (temperature above and below 350 ℃)

The figure represents the maximum yield of C4 olefin obtained by substituting the input layer into the neural network model. The maximum yield of C4 olefins was 53.5835%,the filling ratio was 0.49,the loading capacity of Co was 2,the ethanol addition rate was 0.3,and the temperature was 450 degrees Celsius.

The input layer was substituted into the neural network model to obtain the maximum predicted value of C4 olefin yield below 350 ℃ after removing the data of temperature above 350 ℃ in the test layer.At this time,the yield of C4 olefin was 41.0442%,the charging ratio was 2.03,the loading capacity of Co was 5,the ethanol addition rate was 0.3,and the temperature was 325 degrees Celsius.

5. Solving of problem 4

5.1. Problem analysis

If allow increased 5 times in the experiment,or thinking of C4 olefin yields as high as possible as the starting point,set up additional control experiment,the validity and the rationality of the three model validation issues,respectively from whether to use HAP - ethanol,the speed of adding ethanol,Co load and loading than a few aspects,experimental design and interpretation is as follows:

(1)The catalyst combination of A11 is 90mg quartz sand-ethanol,but not HAP-ethanol.Therefore,90mgHap-ethanol is set as the control variable and other conditions are not changed.

(2)Taking A1 as an example,the temperature range is 250-350,but the temperature division interval is 25,which is not precise enough.Therefore,the temperature interval is set as 5,and other conditions remain unchanged,and the control group is set.

(3)Based on the catalyst combination of A1,the temperature was 300,and the speed of adding ethanol was 1.68 mL /min.The effect of adding ethanol speed on C4 olefin yield was not obvious.Therefore,two control groups were added,and the speed of adding ethanol was set to 0.84 mL /min to 3.33 mL /min,respectively.The velocity change of each group was 0.1 mL /min,and other conditions remained unchanged.

(4)As can be seen from Attachment 1,the Co load is vacant between 2-5,so a control group should be set up with 0.5 as the division,so that the Co load increases from 2 to 5.The selected catalyst combination is temperature 300,Co /SiO2 / HAP charging ratio 1,and ethanol addition rate 1.68.

(5) The maximum value of Co /SiO2 and HAP charging ratio in Appendix 1 is 2,while the interval greater than 2 is not considered.Therefore,a control experiment is set up,and the selected catalyst combination is 300 temperature,ethanol adding rate 1.68,and Co loading rate 1.

5.2. Result analysis

5.2.1 The experiment of 1

The experimental results are shown in the table:

Table 3 Hap-ethanol was compared with and without haP-ethanol

condition	No HAP - ethanol	Have HAP - ethanol
C4 olefin yield (%)	0.00	0.00
	0.01	0.04
	0.03	3.27
	0.36	9.00
	2.58	13.25

The analysis results showed that the overall yield level of C4 olefin with HAP-ethanol increased,and the increase amplitude increased with the increase of temperature.Therefore,it is suggested to replace quartz sand-ethanol with HAP-ethanol,and the experimental effect will be better.

5.2.2 The experiment of 2

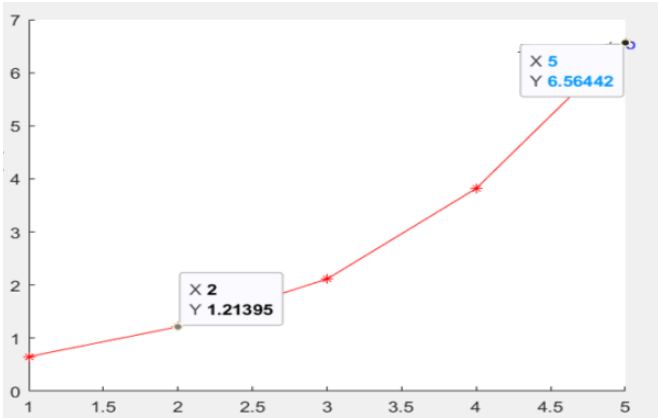

Figure 3 Unrefined temperature interval

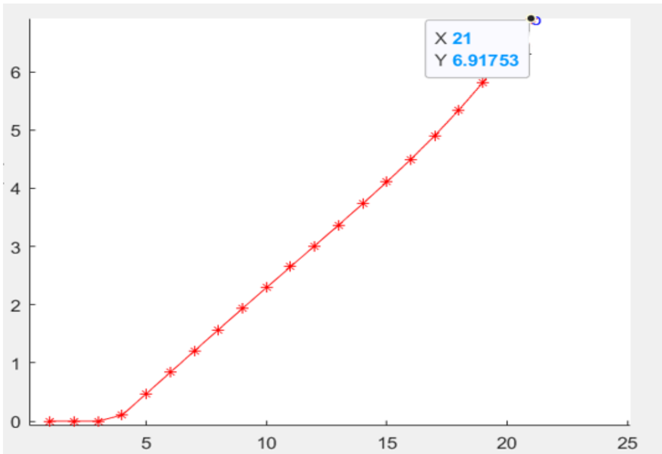

Figure 4 has refined the temperature range

The experimental results are shown in the figure.After the temperature range is refined,the curve is smoother.From the fifth group of experimental data,that is,from 270 ℃ to 350 ℃,the yield growth rate of C4 olefin is a stable value,that is,the yield of C4 olefin is in a linear relationship with the temperature growth[6].

5.2.3 The experiment of 3

The experimental results are shown in the figure.After expanding the range of ethanol addition rate and narrowing the interval interval of each group,it is found that the yield of C4 olefin does not decrease blindly with the increase of ethanol addition rate,but increases first and then decreases.However,this point is not reflected in the data given in Annex I.According to the figure,the yield of C4 olefin is the highest when the ethanol adding rate is 1.14.When the rate of ethanol addition is greater than 2.34,the yield of C4 olefin is close to 0,so the rate of ethanol addition should not be too high,which may cause negative effects on the experiment.

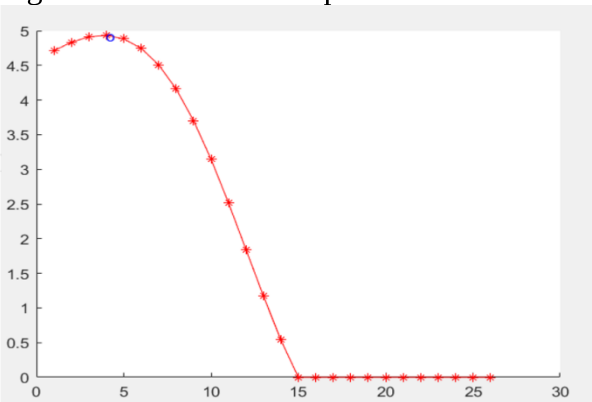

Figure 5 Yield curve of C4 olefin with increasing rate

5.2.4 The experiment of 4

According to the experimental results, with increasing Co loading, the yield of C4 olefin showed a step downward trend, indicating that the effect of Co loading on the yield of C4 olefin was the same within a certain range. At the same time, Co loading should not be too high, otherwise it will reduce the yield of C4 olefin.

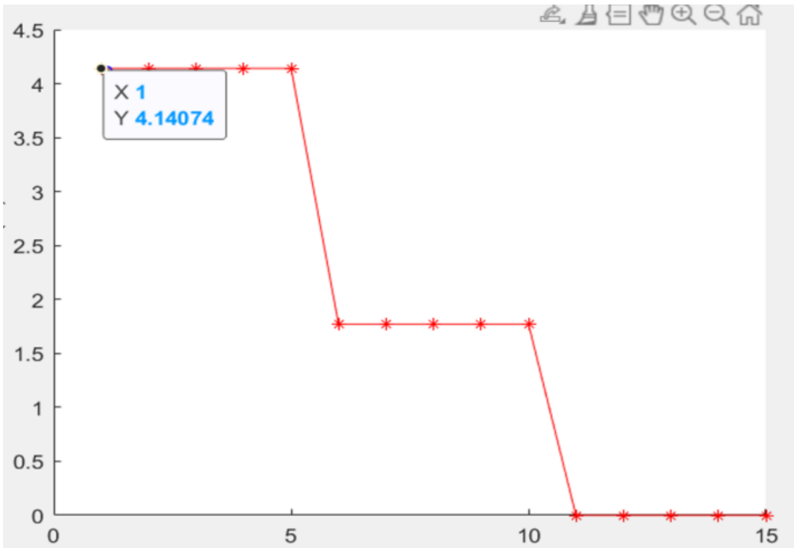

Figure 6 Change curve of C4 olefin yield as Co loading increased

5.2.5 The experiment of 5

As shown in the figure,the yield of C4 olefin reaches a maximum value in the second set of data,which explains why most data sets in Annex 1 have a charging ratio of 1,while annex 1 lacks data when the charging ratio is greater than 2.In the figure,when the charging ratio is greater than 2,the yield of C4 olefin keeps increasing. Therefore,it can be considered to increase the value of charging ratio to improve the effect of the experiment.

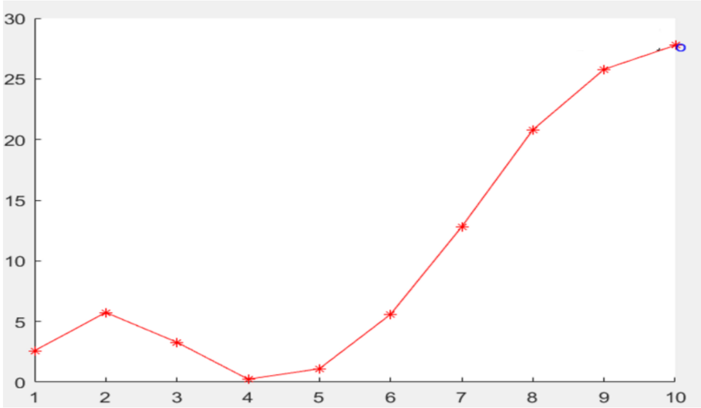

Figure 7 Variation curve of C4 olefin yield when the charge ratio is greater than 2

6. Evaluation of Model

6.1. Advantages

(1)Using multiple regression model,as long as the same model and data are adopted,the only result can be obtained through standard statistical methods.

(2)Grey correlation analysis has no excessive requirements on sample size,and does not require typical distribution rules.Besides,the calculation amount is relatively small,and the results are quite consistent with the qualitative analysis results.

6.2. Disadvantages

(1)In multiple regression analysis,the choice of factor and the expression of the factor is only a kind of speculation,which affects the diversity of factors and the unpredictability of some factors,so that the regression analysis is limited in some cases.

(2)The whole theoretical system of grey correlation analysis is not perfect at present,and its application is subject to some restrictions,so it is more suitable for the analysis of practical problems.

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