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Study on the Optimal Catalytic Conditions for Ethanol Coupling to C4 Olefins based on Miv-Bp Neural Network

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Abstract

As an important chemical raw material, C4 olefins are widely used in the production of chemical products and pharmaceutical intermediates, and ethanol is an important raw material for the preparation of C4 olefins. In order to improve the yield of C4 olefins, we studied the effects of relevant catalyst combination, temperature and time on ethanol conversion and C4 olefin selectivity, and established relevant mathematical models. According to the experimental data provided by the 2021 National College Students' mathematical modeling competition, the influencing factors of ethanol conversion and C4 olefin selectivity are discussed, and five groups of additional experiments are listed according to the existing conclusions, so as to further explore the best combination to improve C4 olefin yield.

Keywords

BP Neural Network; MIV Value; Ethanol Conversion; C4 Olefin Yield.

1. Introduction

At present, C4 olefins are widely used in the production of chemical products and medicine. In terms of chemical products, the production capacity and economic benefits of petrochemical industry can be effectively improved by using C4 olefin products. Therefore, we can vigorously develop the resource utilization of C4 olefins [1]. As the raw material for producing C4 olefins, ethanol is a large chemical product with relatively low price, and can be prepared by microbial fermentation, which is in line with the sustainability and regeneration in the concept of sustainable development. It is not only environmentally friendly, but also cost-effective [2]. Therefore, different catalyst combinations and reaction temperatures are designed to compare the catalyst combinations and temperatures with better catalytic performance for the conversion of ethanol to C4 olefins, which are used for the preparation of C4 olefins from ethanol to prepare C4 olefins with high yield.

The catalyst combination and temperature were selected to make the C4 olefin yield as high as possible under the same experimental conditions. If the temperature is lower than 350 ℃, select the catalyst combination and temperature to make the C4 olefin yield as high as possible. Add 5 experiments and give detailed reasons.

2. Problem Analysis

First, select the catalyst combination and temperature to make the C4 olefin yield as high as possible and analyze under the same experimental conditions. Second, if the temperature is lower than 350 ℃, select the catalyst combination and temperature to make the C4 olefin yield as high as possible. On the basis of the original model, the variable data after splitting the parameters of the catalyst combination is used as the input to obtain the influence degree of each variable on the yield of C4 olefins. The variables with complex linear relationship are optimized to reduce their value range and the numerical value of some relevant variables, and then trained for many times to obtain the highest fitting degree curve, which is obtained in combination with the control variable method, Under the same experimental conditions, some of the most favorable variable values for improving the yield of C4 olefins. When the temperature is lower than 350 ℃, it is analyzed as an extreme value, and the model is BP neural network model.

Five more experiments are added. According to the existing data analysis conclusions, several variables that are most favorable for C4 olefin yield are selected to design five experiments to further obtain the optimal value of each variable. By analyzing these new test data and the original data, the number of possible best combinations is reduced to the greatest extent and the efficiency of analyzing the best combination is improved.

Model assumptions:

Ignoring the influence of environmental variables other than catalyst combination and temperature, it is considered that all experiments given in the annex are carried out in the same ideal environment.

(Note: the following is the symbol description)

Table 1. Symbol description

Symbol	meaning
ET	Ethanol conversion
T	temperature
C	C4 olefin selectivity
A	Loading mode I
B	Loading mode II

3. Establishment and Solution of Model

3.1. Problem Solving

3.1.1. Combination of Catalyst and Temperature

This section will analyze the influence degree of variables based on the MIV algorithm in neural network. In the previous section, six independent variables have been determined. This section will continue the independent variables in the previous section. First, take the variable data in the performance table as the input and use the model for training, so as to obtain the influence degree of each variable on C4 olefin yield. Figure 1 shows the BP neural network training curve of the selectivity of their variables to C4 olefins.

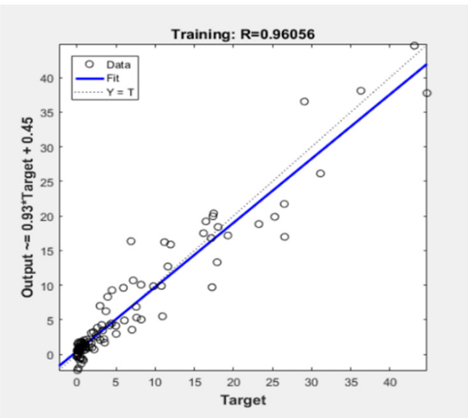

Figure 1. C4 olefin yield of each variable

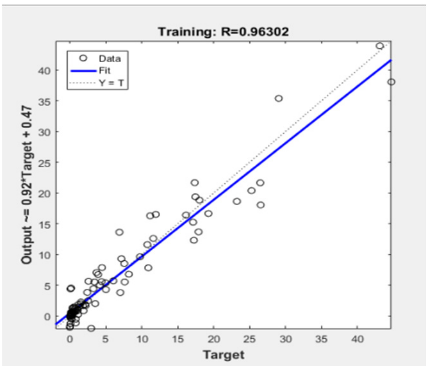

Figure 2. Effect of Co loading on C4 olefin yield

The training data, i.e. the influence degree of each variable on C4 olefin selectivity, are shown in Table 2.

Table 2. MIV values of various variables for C4 olefin selectivity

variable	MIV value
temperature	8.8484
Co load	-0.2433
HAP quality	1.6743
Co / SiO2 mass	-0.4695
Ethanol addition rate	-0.0819
Loading mode	0.1536

It is obvious from the data in Table 2 that temperature has the greatest impact on C4 olefin yield, and the higher the temperature, the greater the C4 olefin yield. The influence of CO loading, HAP quality, Co / SiO2 quality and ethanol addition speed is small, which is not enough to draw a specific scheme, so further optimization training will be carried out below.

According to the data analysis of the independent variable Co load, when the co loading is 2wt%, the C4 olefin yield is the highest. When the co loading is 0.5wt% and 5wt%, the C4 olefin yield is too low, and the co loading in the data sample does not have a simple linear relationship with the C4 olefin yield data. Therefore, the effect of directly using all data for MIV evaluation is poor, so the data corresponding to the co loading of 0.5wt% and 5wt% need to be discarded. After multiple optimization training on the influence degree of CO load, a relatively accurate MIV can be obtained. Figure 2 shows the BP neural network training curve of the influence relationship between optimized co load and C4 olefin yield with the highest fitting degree after multiple training.

The MIV obtained from this training is equal to -0.5230, and its absolute value is less than 1, indicating that the influence of CO loading on C4 olefin yield is very small. Therefore, in order to make C4 olefin yield as high as possible, further selection should be made between 1wt% and 2wt% of CO loading.

The independent variable ethanol addition rate is analyzed, when the ethanol addition rate is 0.3ml/min and 0.9ml/min, the C4 olefin yield is large and close.

After analysis, when the ethanol addition rate is 0.9ml/min, the C4 olefin yield corresponding to the Co / SiO2 mass of 200mg is much higher than that when the Co / SiO2 mass of 50mg. Therefore, it is concluded that the influence of CO / SiO2 mass (50mg, 200mg) on C4 olefin yield is greater than that of ethanol at 0.3ml/min and 0.9ml/min. In addition, when the mass of CO / SiO2 is 50mg, the velocity relationship is relatively clear, so the data corresponding to the mass of CO / SiO2 is 200mg is given priority for the next analysis.

It follows that when the mass of CO / SiO2 is 200mg, the C4 olefin yield corresponding to the ethanol addition rate of 0.3ml/min is much lower than that corresponding to 1.68ml/min, while the C4 olefin yield corresponding to the ethanol addition rate of 0.9ml/min is very close to that corresponding to 1.68ml/min, so in order to optimize the data, Discard the data corresponding to the ethanol addition rate of 0.3ml/min.

It can be guessed from the above analysis that when the mass of CO / SiO2 is 200mg, due to the increase of catalyst volume, considerable reaction contact area can be obtained when ethanol is added quickly, and there is sufficient time for reaction. When ethanol is added too slowly, the contact area is limited, so the yield of C4 olefins is reduced. When the mass of CO / SiO2 is 50mg, the contact area decreases obviously, and the fast addition of ethanol will lead to short contact time and insufficient reaction.

It is known from the experimental data, when the ethanol addition rate is 1.68ml/min, the C4 olefin yield corresponding to 75mg Co / SiO2 mass and 50mg is similar, and its influence degree is less than that of 50mg and 200mg Co / SiO2 mass. Therefore, the data of loading mode B is also discarded, and only the data corresponding to 200mg Co / SiO2 mass is retained.

After the above data optimization, the corresponding C4 olefin selectivity data excluding the ethanol addition rate of 0.3ml/min and the Co / SiO2 mass of 200mg are trained for many times. Figure 3 is the optimized BP neural network curve with the highest fitting degree after many times of training.

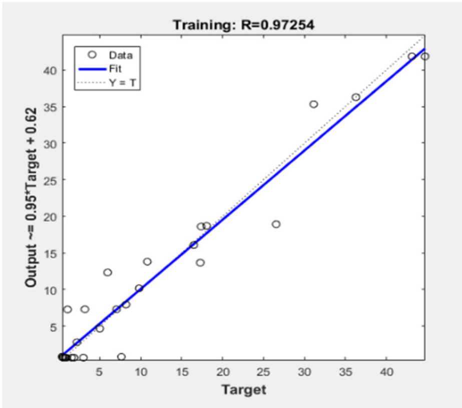

Figure 3. Effect of Ethanol Addition Rate on C4 Olefin Yield

The MIV obtained from the training is equal to - 03959, and its absolute value is less than 1, indicating that the influence of ethanol addition rate on C4 olefin yield is very small. Therefore, in order to make C4 olefin yield as high as possible, the ethanol addition rate should be further selected between 0.9ml/min and 1.68ml/min.

Data analysis is carried out for the independent variables Co / SiO2 and HAP loading ratio and quality. Firstly, the relationship between Co / SiO2 and HAP loading ratio and C4 olefins is analyzed, the Co / SiO2 and HAP loading ratio (i.e. 1:1) corresponding to catalyst combination A12 has the best performance in catalyzing the conversion of ethanol to C4 olefins. At the same time, according to the data [3], when the Co / SiO2 and HAP loading ratio is 1:1, the C4 olefin yield is the highest. Therefore, the following analysis will be carried out under the condition that the Co / SiO2 and HAP loading ratio is 1:1.

When the mass of CO / SiO2 and HAP is 50mg, 75mg and 100mg, the C4 olefin yield is high and the value is close, and when the mass of CO / SiO2 and HAP is 10mg and 25mg, the C4 olefin yield is low and the value is close.

When the loading mode is A, the data of A1 and A12, A3 and A8 are used as the control group to explore the effect of the quality of CO / SiO2 and HAP on the yield of C4 olefins when the loading ratio is 1:1.

It can be concluded that the ethanol conversion rate when the mass of CO / SiO2 and HAP is 200mg is significantly higher than that when the mass is 50mg, and the influence of ethanol addition speed on the yield of C4 olefins is very small.

To sum up, in order to improve the C4 olefin yield as much as possible, when other conditions are close, the loading ratio of CO / SiO2 and HAP is 1:1, the temperature is high (400 ℃), and the loading method is a. if the mass of CO / SiO2 and HAP is 200mg, the ethanol addition rate is 0.9ml/min and 1.68ml/min; If the mass of CO / SiO2 and HAP is 50mg, ethanol is added at a rate of 0.3ml/min. As for the co loading amount, since there is no data with the temperature of 400 ℃ in the key combination, the data with the loading amount of 0.5wt% and 5wt% can only be discarded for analysis according to the existing data, so the loading amount of 1wt% and 2wt% shall be selected as far as possible (the MIV value obtained from these two groups of data is close to 0, and the C4 olefin yield in the existing data is significantly higher than 0.5% and 5%), It is necessary to wait for the fourth question to add the experimental data before making a specific analysis of each co load. For the mass of components with the charge ratio of CO / SiO2 and HAP of 1:1, when the charge mode is a and the ethanol speed is not 0.3ml/min, the mass is 200mg, and when the charge mode is B, the mass is preferred to 75mg.

3.1.2. Combination of Catalyst and Temperature(Below 350 Degrees)

In this section, the influence degree of variables will be analyzed based on the MIV algorithm in the neural network. Firstly, the variable data in the performance table will be used as the input. In principle, based on the requirements of this topic, the data with the temperature of 350 ° C should be eliminated, but the data with the temperature of 350 ° C can be analyzed as the extreme value to improve the accuracy of the experimental conclusion. The model was trained to obtain the influence degree of each variable on the yield of C4 olefins. Figure 4 shows the BP neural network training curve of C4 olefin selectivity of respective variables below 350 degrees.

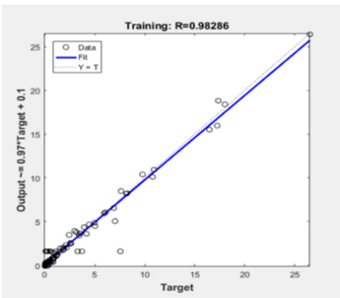

Figure 4. Selectivity of each variable to C4 olefins

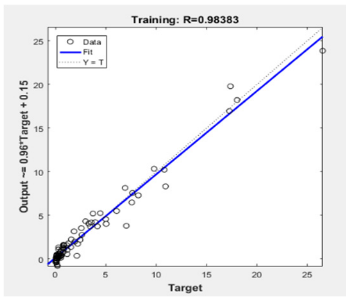

Figure 5. Effect of Co loading on C4 olefin yield

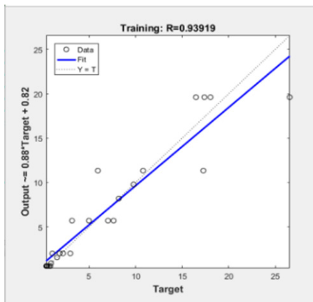

Figure 6. Effect of Ethanol Addition Rate on C4 Olefin Yield

The data obtained from training optimization, i.e. the influence degree of each variable on C4 olefin selectivity, are shown in Table 3.

Table 3. MIV values of various variables for C4 olefin selectivity

variable	MIV value
temperature	3.6306
Co load	-1.5270
HAP quality	-18.4421
Co / SiO2 mass	21.3397
Ethanol addition rate	1.3196
Loading mode	0.1775

Further optimization analysis is conducted for the co load in Table 3. The data optimization will continue the data in the previous section and carry out multiple optimization training for the co load. Figure 5 shows the optimized BP neural network training curve with the highest fitting degree.

The MIV obtained from the training is equal to 0.2093, and its absolute value is less than 1, indicating that the influence of CO loading on C4 olefin yield is very small. Therefore, in order to make C4 olefin yield as high as possible, the co loading should be further selected between 1wt% and 2wt%.

Further optimization analysis is conducted for the ethanol addition speed in Table 3. The data optimization will continue the data in the previous section and carry out multiple optimization training for the ethanol addition speed. Figure 6 shows the optimized BP neural network training curve with the highest fitting degree.

The MIV obtained from the training is equal to -0.0752, and its absolute value is less than 1, indicating that the influence of ethanol addition rate on C4 olefin yield is very small. Therefore, in order to make C4 olefin yield as high as possible, the ethanol addition rate should be further selected between 0.9ml/min and 1.68ml/min.

To sum up, in order to improve the C4 olefin yield as much as possible, when other conditions are close, the loading ratio of CO / SiO2 and HAP is 1:1, the temperature is high, and the loading method is a. if the mass of CO / SiO2 and HAP is 200mg, the ethanol addition rate is 0.9ml/min and 1.68ml/min; If the mass of CO / SiO2 and HAP is 50mg, ethanol is added at a rate of 0.3ml/min. For the co load, the data with the load of 0.5wt% and 5wt% can only be discarded for analysis according to the existing data. Therefore, the data with the load of 1wt% and 2wt% shall be selected as much as possible (the MIV value obtained from these two groups of data is close to 0, and the C4 olefin yield in the existing data is significantly higher than 0.5% and 5%). It is necessary to wait for the fourth question to add the experimental data before making a specific analysis of each co load. For the mass of components with the charge ratio of CO / SiO2 and HAP of 1:1, when the charge mode is a and the ethanol speed is not 0.3ml/min, the mass is 200mg, and when the charge mode is B, the mass is preferred to 75mg.

3.2. Add Five Groups of Experiments

3.2.1. Unified Cause of Local Variables

（1）Variable 1: temperature: select 400 ℃ for consistent temperature

reason:

i. According to the analysis, there is an obvious positive correlation between temperature and C4 olefin yield at and below 400 ℃.

ii. According to data analysis and literature review, it is found that the catalyst can achieve the best catalytic effect at 400 ℃.

iii. Most catalyst combinations have 400 ℃ data, which is convenient for comparative analysis of control variables.

(2)Variable 2: loading mode; Unified as class A

reason:

iv. According to the model, set the values of class A and class B as 1 and 0 respectively, and the corresponding MIV value is positive, and the linear relationship during the period is obvious, indicating that class a loading method is better.

v. In Experiments 4 and 5, the mass of catalyst components is 75mg. There is only one group of data in the given data, which can not form a perfect relationship between the mass of catalyst components and the rate of ethanol addition. Although it is classified as class B and can analyze a group of data and relationships in combination with B6, it is required that the loading mode of the optimal combination should be changed to class A for experiments. At this time, the maximum number of experiments required for the optimal combination is greater than that unified as class A.

(3)Variable 3: Co / SiO2 and HAP loading ratio: unified as 1:1

reason:

When the loading ratio of CO / SiO2 and HAP is 1:1, C4 olefin selectivity is the largest.

(4) Variable 4: mass of catalyst components: 200mg and 75mg

reason:

The optimal mass of catalyst components in loading mode A and B are 200mg and 75mg respectively, and there are too few data sets with a mass of 75mg. Supplementary analysis is needed to obtain the optimal impact of catalyst component quality and ethanol addition rate on improving C4 olefin yield.

3.2.2. Five New Experimental Data

Table 4. Data of five new experiments

	temperature(℃)	Loading mode A(Ⅰ)/B(Ⅱ)	Co/SiO2(mg)	HAP (mg)	Co load (wt%)	Ethanol addition rate(ml/min)
1	400	A	200	200	1	1.68
2	400	A	200	200	2	1.68
3	400	A	200	200	1	2.1
4	400	A	75	75	1	0.9
5	400	A	75	75	1	0.3

3.2.3. Reasons for Selecting Combinations in Each Experiment

3.2.3.1. Experiment 1 and Experiment 2

For the analysis of CO loading, due to incomplete data, it is impossible to analyze the relationship between each co loading and C4 olefin yield at 400 ℃, while Experiment 1 and Experiment 2 can combine A4 and A6 to analyze the best co loading. And the best combination of CO loading can be compared with A7 data to infer the best combination of catalyst when the mass of CO / SiO2 and HAP is 50mg (it has been determined that the most suitable ethanol addition speed is 0.3ml/min when the mass of CO / SiO2 and HAP is 50mg), and a better combination can be obtained by comparison with it.

3.2.3.2. Experiment 3

It can be concluded that when the mass of Catalyst Co / SiO2 and HAP is 200mg, the data results of ethanol addition rate of 0.9ml/min and 1.68ml/min are not different. In this case, the experimental data lack the data of ethanol addition rate of 2.1ml/min, which makes it difficult to exclude the data and join the neural network for analysis.

According to the conjecture on the relationship between speed and component quality, it can be inferred that under the condition of component quality of 200mg catalyst, there is the best speed among the three ethanol addition speeds, so the relevant data of 2.1ml/min is very important. According to the data of Experiment 1, Experiment 3 and A3, the best ethanol addition rate when the mass of CO / SiO2 and HAP is 200mg can be obtained. If the mass of Catalyst Co / SiO2 and HAP of the better combination described above is 200mg, the best combination under this condition can be further calculated in combination with the best ethanol addition rate.

3.2.3.3. Experiment 4 and Experiment 5

Under the condition that the mass of catalyst containing 75mg Co / min and SiO2 is 68mg / min, the best yield can be obtained when the mass of catalyst containing 75mg HAP and SiO2 is 68mg / min 0.3ml/min is likely to form a better combination.

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Therefore, combined experiment 4 and Experiment 5 can obtain the potential optimal solution when the mass of Catalyst Co / SiO2 and HAP is 75mg (the small probability is the relevant combination of ethanol addition rate of 1.68ml/min and 2.1ml/min).

3.2.4. Summary

Compared with the previously calculated local optimal combination, the combination obtained from experiments 4 and 5 has a high probability to obtain the optimal catalyst combination. At most two groups of data (the relevant combination of ethanol addition rate of 1.68ml/min and 2.1ml/min when the mass of Catalyst Co / SiO2 and HAP is 75mg) are collected to obtain the results. The five groups of experiments have effectively reduced the range of possible best combination, so that the probability of obtaining the best combination in the secondary data generated by these data is at a high level.

4. Model Evaluation and Improvement

BP neural network is used to train and obtain the most obvious specific data values of each variable for improving C4 olefin yield, and then carry out variable screening based on miv-bp neural network for these values, which can effectively reduce the specific analysis of human data.

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