Optimization of the Preparation of C4 Olefins by catalytic Coupling of Ethanol

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Abstract: C4 olefins play an important role in the production of chemical products and pharmaceuticals, and are important basic chemical raw materials. The combination of catalysts and temperature will affect the chemical reaction process of ethanol coupling to prepare C4 olefins. In this paper, through the establishment of function fitting analysis model, legend analysis model, variance analysis model, neural network model, etc., and with the help of Matlab software, the influencing factors in the process of ethanol catalytic coupling to prepare C4 olefins under the condition of ethanol as the platform compound were analyzed, and Interrelationships between factors. It is concluded that the optimal absorption rate of C4 olefins is 26.4894% under the condition that the temperature is 412 degrees and the catalyst combination is 200mg1wt%Co/SiO2-200mgHAP-ethanol concentration of 0.9ml/min. Through the design of different influencing factors, it provides a reference for selecting catalysts to design optimal performance reactions, and has certain application value for exploring the preparation of C4 olefins by ethanol coupling.

Keywords: C4 olefins; fitting analysis model; variance analysis model; neural network model

1. Introduction

In recent years, C4 olefins have been widely used in the production of petrochemical products and pharmaceutical intermediates [1]. C4 olefins play an important role in the production of chemical products and pharmaceuticals, and are important basic chemical raw materials [2]. Among them, the production of C4 alkenes is mainly through ethanol-catalyzed coupling, and the catalyst combination and temperature will affect the chemical reaction process of ethanol coupling to prepare C4 alkenes. Studies have shown that in the process of preparing C4 olefins by ethanol coupling, the selectivity and absorption rate of C4 olefins are affected by catalyst combination and temperature [3]. Therefore, it is of great significance and value to explore the process conditions for the preparation of C4 by catalytic coupling of ethanol [4].

2. Ethanol Conversion and Selectivity Function Fitting

2.1 Preprocessing of Experimental Data

First, the experimental data of 21 groups of catalyst combinations are preprocessed, and the specific processing methods are as follows:

(1) On the basis of the experimental data, the components of the catalyst combination are disassembled and subdivided, and discussed separately.Different catalyst combinations can be disassembled and refined into four parameters: Co/SiO2 content, HAP content, Co/SiO2 and ethanol concentration.

(2) Calculate the values of Co loading, HAP (quartz sand) content, and Co/SiO2 to HAP (quartz sand) loading ratio under different catalyst combinations.

After the above data processing, a statistical table of the preprocessing results of the catalyst combination experimental data is sorted out, and some data are shown in Table 1.

Table 1. Statistical table of experimental data preprocessing results for some catalyst combinations

renumbering	Co/SiO2 content (mg)	Co loading (wt%)	…	Co/SiO2 and HAP (quartz sand) charging ratio	Co:SiO2:HAP (quartz sand) mass ratio
1	200	1	…	1.00	1:100:101
2	200	1	…	1.00	1:100:101
3	200	1	…	1.00	1:100:101
4	200	1	…	1.00	1:100:101
5	200	1	…	1.00	1:100:101
6	200	2	…	1.00	1:50:51
7	200	2	…	1.00	1:50:51
8	200	2	…	1.00	1:50:51
9	200	2	…	1.00	1:50:51
10	200	2	…	1.00	1:50:51

From the analysis of the data in the table, it can be clearly seen that as the temperature increases, the ethanol conversion and C4 olefin selectivity under different catalyst combinations have a relatively obvious growth trend [5], as shown in Figure 1 and Figure 2:

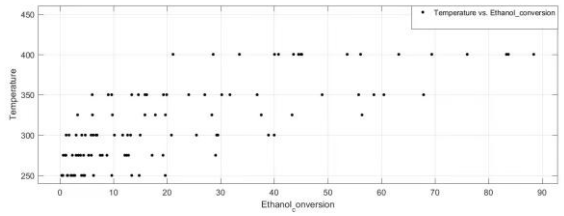

Figure 1. Scatter plot of the relationship between ethanol conversion rate and temperature

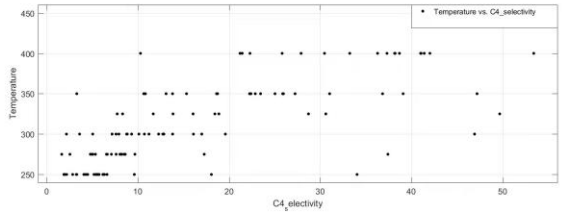

Figure 2. Scatter plot of the relationship between C4 olefin selectivity and temperature

Integrate the relationship between temperature, ethanol conversion and C4 olefin selectivity under different catalyst combinations in Annex 1, and draw the relationship between the three [6], as shown in Figure 3:

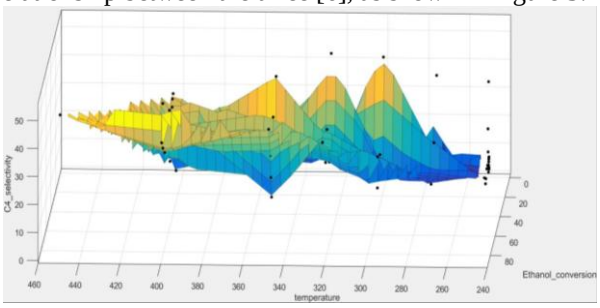

Figure 3. Plot of temperature, ethanol conversion and C4 olefin selectivity

2.2 Building a Function Fitting Model

According to the experimental data of three variables of temperature, ethanol conversion and C4 olefin selectivity, the experimental data of groups A1~B7 were analyzed respectively. According to 21 catalyst combinations, a function fitting model was constructed for the relationship between ethanol conversion, C4 olefin selectivity and temperature for each group [7].

he relationship between ethanol conversion, C4 olefin selectivity and temperature was analyzed sequentially, and Fourier and Power functions were used for fitting [8].

Fourier function: f(x) =a0 + a1*cos(x*w) + b1*sin(x*w)

Power function: f(x) = a*xb

Obtain the ethanol conversion rate and temperature fitting data table, as shown in Table 2:

Table 2. Ethanol conversion rate and temperature fitting data table

Catalyst combination	Function: Fourier1				
	I(T) = a0 + a1*cos(T*w) + b1*sin(T*w)				
	The coefficient of				R
	a_0	a_1	b_1	w	
A1	3.595e+0	-	11.54	0.02528	0.999
	8	3.595e+0 8			3
A2	35.23	-31.24	11.54	0.02528	0.999 3
A3	49.84	31.01	22.17	0.01554	0.987
A4	48.4	48.3	-15.75	0.01326	0.998 7
A5	4.999e+1 0	- 4.999e+1 0	- 4.669e+0 6	3.576e-07	0.994
A6	49.8	-3.695	37.18	0.01873	0.998 4
A7	27.14	-77.8	16.85	0.00504 6	0.999 8
A8	56.62	41.03	-29.01	0.01022	0.999 8
A9	2.467e+0 8	- 2.467e+0 8	3.017e+0 5	-4.45e-06	0.990 3
A10	5.401e+0 7	- 5.401e+0 7	1.21e+05	-8.155e-06	0.994
A11	4.072e+0 8	- 4.072e+0 8	3.814e+0 5	-3.341e-06	0.987 1
A12	8.893e+0 8	- 8.893e+0 8	- 4.613e+0 5	2.069e-06	0.999 1
A13	6.458e+1 0	- 6.458e+1 0	- 4.588e+0 6	2.637e-07	0.996 5
A14	7.54e+07	-7.54e+07	- 1.425e+0 5	7.6e-06	0.997 2
B1	1.348e+0 9	- 1.348e+0 9	5.672e+0 5	-1.672e-06	0.998 9
B2	1.146e+0 9	- 1.146e+0 9	6.519e+0 5	-2.094e-06	0.991 3
B3	4.433e+0 8	- 4.433e+0 8	3.08e+05	-2.502e-06	0.991 5
B4	1.946e+0 8	- 1.946e+0 8	2.456e+0 5	-4.597e-06	0.987
B5	5.987e+0 8	- 5.987e+0 8	- 4.686e+0 5	2.891e-06	0.991 4
B6	9.097e+0 8	- 9.097e+0 8	- 5.809e+0 5	2.487e-06	0.990 2
B7	1.655e+0 9	- 1.655e+0 9	- 8.596e+0 5	1.99e-06	0.996 6

It can be seen from the above function results that the goodness-of-fit index (R value) of the two function fittings floats around 0.99, which proves that the Fourier function is used to fit well. In the fitting process, the A1 to A8Fourier functions have the best fitting effect, and there is no fitting function with similar results. Starting from A9, using the Power function for fitting can get the approximate effect of the Fourier function. In some cases, the fitting degree of the Power function is better than that of the Fourier function, and there are even cases where the Power function is completely fitted (the R value is 1).

Therefore, the power function is used to verify the evaluation of each group's fitting effect as shown in Table 3:

Table 3. Validation table of ethanol conversion rate and temperature fitting data

catalyst combination	Function: Power1		
	$I(T) = a*T^b$		
	coefficient		R
	a	*b*	
A9	1.854e-19	7.817	0.9974
A10	1.852e-22	8.912	0.9993
A11	3.216e-26	10.38	1
A12	1.041e-15	6.393	0.9986
A13	5.356e-19	7.638	0.9998
A14	1.234e-14	6.01	0.9994
catalyst combination	Function: Power1		
	$I(T) = a*T^b$		
	coefficient		R
	a	*b*	
B1	8.265e-16	6.427	0.9988
B2	1.836e-17	7.067	0.9963
B3	1.09e-23	9.334	0.9995
B4	4.586e-22	8.786	0.9986
B5	3.74e-18	7.332	0.9981
B6	5.321e-15	6.177	0.9963
B7	4.392e-15	6.225	0.9988

In the same way, the C4 olefin selectivity versus temperature was analyzed [8]. The data table listing the C4 olefin selectivity and temperature fitting function is shown in Table 4.

Table 4. C4 olefin selectivity and temperature fitting function data table

catalyst combination	Function: Fourier1				
	$C(T)= a_0 + a_1*\cos(T*w) + b_1*\sin(T*w)$				
	coefficient				R
	a_0	a_1	b_1	w	
A1	42.16	6.189	5.481	0.04071	0.9909
A2	30.58	-4.786	-13.58	0.02781	0.9914
A3	29.57	7.831	23.34	0.01805	0.9978
A4	25.1	-15.22	7.574	0.02151	0.9989
A5	4.47e+08	-4.47e+08	-2.23e+05	2.24e-06	0.9905
A6	1.799e+08	-1.799e+08	-2.492e+05	4.95e-06	0.9454
A7	48.03	20.86	-36.75	0.008251	1
A8	49.55	-5.915	-46.18	0.007096	0.9997
A9	23.84	19.47	5.144	0.01525	1
A10	6.57e+08	-6.57e+08	2.768e+05	-1.458e-06	0.9785
A11	6.48e+08	-6.48e+08	8.972e+04	-7.518e-07	0.9994
A12	36.09	20.34	-22.17	0.009728	0.9999
A13	16.38	-0.5601	11.56	0.01999	0.9998
A14	85.22	-23.51	-79.9	0.004998	0.9995
B1	29.49	22.79	4.235	0.01355	1
B2	28.25	25.07	0.401	0.0129	1
B3	6.111e+07	-6.111e+07	4.814e+04	-3.954e-06	0.9763
B4	14.87	-7.26	6.258	0.01976	0.9858
B5	26.29	14.19	-17.19	0.009524	0.9988
B6	17.29	-11.31	6.735	0.02212	0.9993
B7	25.1	20.07	-10.74	0.01208	0.999

It can be seen from the above function results that the goodness-of-fit index (R value) of the two function fittings floats around 0.99, which proves that the model fits well. Similar to the above case, after the A5 combination, the Power function also has a good fitting effect. However, the fitting effect of combined Power functions such as A9, A13, B4, B6, B7 is poor. Therefore, the Power function is used for the fitting evaluation of discrete partial combinations, as shown in Table 5:

Table 5. C4 olefin selectivity and temperature fitting data validation table

catalyst combination	Function: : Power1		
	$C(T) = a*T^b$		
	coefficient		R
	a	*b*	
A5	4.275e-12	4.977	0.9934
A6	2.27e-16	6.611	0.9442
A7	2.43e-10	4.279	0.9955
A8	1.864e-09	3.979	0.9959
A10	1.797e-14	5.665	0.9141
A11	1.398e-13	5.288	0.9875
A12	2.298e-09	3.92	0.9984
A14	2.47e-14	5.748	0.9973
B1	1.234e-09	4.046	0.9947
B2	9.373e-12	4.852	0.9905

B3	1.258e-09	3.932	0.9763
B5	8.954e-10	4.021	0.9972

3. Analysis of the Effect of Catalyst Combination and Temperature on Ethanol Conversion and C4 Olefin Selectivity

Firstly, the data is preprocessed, and it is found by analyzing the data that at 350 degrees Celsius, with the progress of the catalytic coupling reaction, the ethylene selectivity, methylbenzaldehyde and methylbenzyl alcohol have little effect. However, it has obvious effects on ethanol conversion, C4 olefin selectivity, acetaldehyde selectivity, carbon number 4-12 fatty alcohol and C4 olefin yield. Therefore, fitting functions of ethanol conversion, C4 olefin selectivity, acetaldehyde selectivity, carbon number of 4-12 aliphatic alcohol and C4 olefin yield at a constant temperature of 350 degrees Celsius and time were established respectively.

At a fixed temperature of 350 degrees Celsius, the Fourier function and the Power function were also used to fit the data of the ethanol conversion, C4 olefin selectivity, C4 olefin yield, acetaldehyde selectivity and carbon number of 4-12 fatty alcohols for different catalyst combinations.

3.1 Fourier Function and Power Function Fitting Model Establishment And Solution.

(1) Analysis of ethanol conversion rate

I(t) =a0 + a1*cos(t*w) + b1*sin(t*w)

The fitting function is shown in Figure 4:

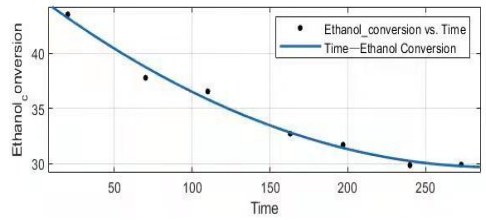

Figure 4. Plot of temperature, ethanol conversion and C4 olefin selectivity

The fitting function is as follows:

$$I(t)=1.169\times10^{7}-1.169\times10^{7}\cos(5.508\times10^{-6}t)-1.908\times10^{4}\sin(5.508\times10^{-6}t)$$

It can be seen from the calculation results and the fitted graph that the conversion rate of ethanol gradually decreases with the progress of the experiment. The goodness of fit index R is greater than 0.9, which proves that the model has a high degree of fit.

(2) Selectivity analysis of C4 olefins

C(t) =a0 + a1*cos(t*w) + b1*sin(t*w)

The fitting function is shown in Figure 5:

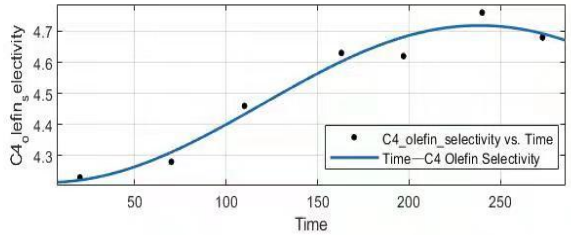

Figure 5. Fitting function graph for C4 olefin selectivity

The fitting function is as follows:

$$C(t)=4.466-0.2524\cos(0.01325t)-4.488\times10^{-3}\sin(0.01325t)$$

It can be seen from the calculation results and the fitting diagram that the selectivity of C4 olefins increases in the range of 0~240min as the experiment is carried out; however, the selectivity of C4 olefins gradually decreases after the experiment is carried out for 240min. The goodness of fit index R is greater than 0.9, which proves that the model has a high degree of fit.

(3) Analysis of the yield of C4 olefins

Y(t) = a*tb

The fitting function is shown in Figure 6:

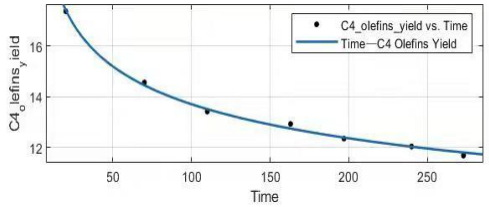

Figure 6. Fitted analytical model for C4 olefin yield

The fitting function is as follows:

$$Y(t)=27.23t^{-0.149}$$

It can be seen from the calculation results and the fitting diagram that the yield of C4 olefins shows a decreasing trend with the progress of the experiment. The goodness of fit index R is greater than 0.99, which proves that the model has a high degree of fit.

3.2 Preparation of C4 Alkenes by Ethanol-Catalyzed Coupling Based on Neuronal Network Method

The neural network can use the high-speed computing level of the computer to determine the relationship between two things [9]. When the relationship between two things is known, the value of one parameter can be used to predict the value of another parameter. Therefore, it is mainly through the establishment of a neural network model to analyze and solve it.

Combined with the analysis of the previous conclusions, it can be seen that under the A3 catalyst combination, the C4 yield gradually decreases with the increase of the temperature to 450 degrees Celsius. Since the temperature of the remaining 20 groups are all below 400 degrees Celsius and the fitted function curves show an increasing trend. Therefore, the optimal solution at this time is: under the condition that the temperature is 412 degrees Celsius and the catalyst combination is 200mg1wt% Co/SiO2-200mgHAP-ethanol concentration of 0.9ml/min, the optimal C4 olefin yield is 29.9650%. The relationship between C4 olefin absorption rate and temperature under A3 catalyst combination is shown in Figure. 7.

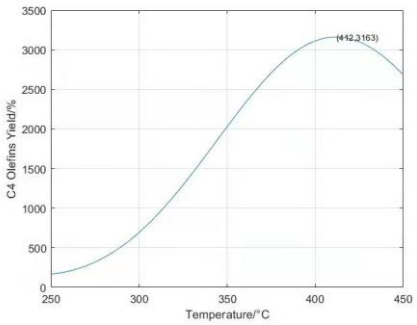

Figure 7. Relationship between C4 olefin yield and temperature under A3 catalyst combination

On the basis of the obtained 412 degrees Celsius, one parameter was selected as the output layer for the C4 olefin yield, Co loading, Co/SiO2 charging ratio, and ethanol concentration, and the other three parameters were used as the hidden layer to establish a neural network model [10].

Taking the absorption rate of C4 olefin as the output layer as an example, the model results are analyzed, and the results are shown in Figure 8:

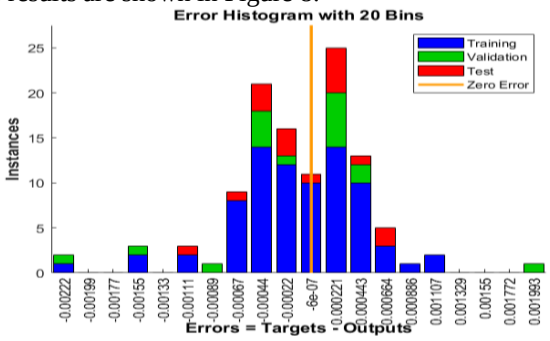

Figure 8. The training result of the test neuron network

The above figure represents the training result of the neuron network with the C4 olefin yield as the output layer. Mes indicates that the smaller the mean square error, the better, but because the network has fewer training samples, the regression curve can be stabilized without too many training times, because the neural network adopts iterative convergence to approximate the analytical formula, it is impossible to achieve zero error in training, and the relative error of the predicted value of the RBF network will be large due to the above reasons. As shown in Figure 9:

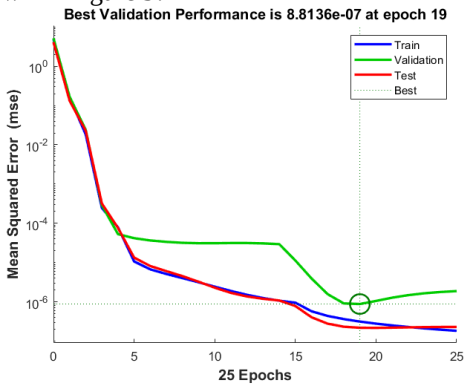

Figure 9. Error view of neural network

The above figure represents the error view of the neuron network with the C4 olefin yield as the output layer. The three colored solid lines represent the performance of the MSE indicator in the BP training process in each generation, and the MSE indicator in the BP cross-validation process in each generation. The performance of the MSE indicators of the BP test process in each generation. The red line of Test indicates the training result of BP calculation, and the dotted line of Best indicates that the training result is optimal when the BP grid is trained to the 19th generation. According to the above algorithm, using the neural network model, the remaining parameters are calculated as the optimal solution of the output layer, as shown in Table 6:

Table 6. Optimal solutions under different catalyst conditions

variable name	RBF network predictions	RBF network relative error (%)	BP network prediction value
C4 Absorption Rate	26.4895	52.4787	26.5210
Co load	1.0000	2.7944×10^{-7}	0.9963
Co/SiO2 to HAP charging ratio	1.0000	1.5000	1.0000
Ethanol concentration	0.9000	1.3000	0.8998

To sum up: under the temperature of 412 degrees Celsius and the catalyst combination of 200mg1wt%Co/SiO2-200mgHAP-ethanol concentration of 0.9ml/min, the optimal C4 olefin yield is 26.4894%.

Since the sample size with a temperature above 350 degrees Celsius is relatively small, it will have a slight impact on the regression curve fitting of machine learning after being eliminated, and even the expected reduction will increase after training, resulting in low reliability of the results and large errors. Therefore, the optimal selection removes the sample points at 350 degrees Celsius, and only retains the sample points at and below 325 degrees Celsius, constructs a neural network model, performs machine learning, and draws a summary table of optimal solutions under different catalyst conditions, as shown in Table 7:

Table 7. Optimal solutions under different catalyst conditions

variable name	RBF network predictions	RBF network relative error (%)	BP network prediction value
C4 yield	3.8611	2.9475	3.2831
Co load	1.0958	1.4521	0.9977
Ethanol concentration	0.8334	2.4779	0.8996
temperature	323.8509	324.0035	324.9739

To sum up: when the temperature is 323.8509 degrees Celsius and the catalyst combination is 200mg1wt%Co/SiO2-200mgHAP-ethanol concentration of 0.8334ml/min, the optimal C4 olefin yield is 3.8611%.

4. Conclusion

C4 olefins play an important role in the production of chemical products and pharmaceuticals, and are important basic chemical raw materials. In this paper, function

fitting analysis model, legend analysis model, variance analysis model, and machine learning algorithm were established to discuss and analyze the reaction performance of ethanol coupling to prepare C4 olefins under different catalyst combinations, so as to provide reference for selecting catalysts to design optimal performance reactions. It is hoped that it can play a positive role in the production of C4 olefins.

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