Study on C4 olefin production by ethanol coupling based on multiple regression model

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Abstract. In this paper, the influencing factors of ethanol conversion, C4 olefin selectivity and C4 olefin yield in the experiment of ethanol coupling preparation were analyzed, and then quantified modeling was carried out, and the combination design of catalyst was carried out, so as to make the above three variables reach the optimal value.Using the experimental data, professional and statistical analysis methods were used to analyze the correlation and regression of the possible influencing factors.On the basis of the experimental data given in the research background, the optimal catalyst combination and temperature for the above targets in the process of preparing C4 olefin were obtained.

Keywords: ethanol conversion, C4 olefin selectivity, C4 olefin yield, multiple linear regression

1. Introduction

With the shortage of fossil energy production and the aggravation of the impact on the environment, the supply of energy gradually tends to be diversified, and the development of new clean energy becomes more and more urgent. In chemical products and pharmaceutical production, C4 olefin is widely used. The source of ethanol is wide, green and clean. Using ethanol as raw material, C4 olefin is prepared by catalytic coupling. Therefore, the preparation of olefin is of great significance in chemical industry. In the process of preparation, the combination design of catalysts has very important value for the process conditions of C4 olefin preparation by ethanol catalytic coupling [1]. At present, the common catalysts in use are roughly composed of Co loading, Co/SiO2 and HAP loading ratio and ethanol concentration. These catalysts and temperature will have different effects on the selectivity of C4 olefin and the yield of C4 olefin. This paper mainly analyzes the ethanol conversion rate of each catalyst and the relationship between temperature and C4 olefin selectivity and temperature, and carries on the quantitative analysis, and the test results of the given catalyst combination at 350 degrees in a different time of an experiment were analyzed[2].Then, the factors and temperature in the catalyst combination were selected as variables to solve the influence of catalyst factors and temperature on ethanol conversion and C4 olefin selectivity.

2. Data preprocessing

In the known catalyst data, first of all, statistical analysis of the impact of charging method on the optimization target A9 and B5, A12 and B1 are the same catalyst, the charging method used is different [3]. The two groups of experimental data were compared by Excel, and the t-test of two-sample equal variance of ethanol conversion rate y1 and C4 olefin conversion rate y2 was used to obtain the data as shown in table 1 and table 2.

Table 1. T-test of A9, B5 and y1, y2

	A9.y1	B5.y1	A9.y2	B5.y2
On average,	12.79497	13.73273	20.852	11.69
P (T < = T) single tail	0.462898		0.116905	
t one-tailed critical	1.833113		1.833113	
P (T < = T) double tail	0.925796		0.233809	
t two-tailed critical	2.262157		2.262157	

Table 2. T-tests for A12, B1 and y1, y2

	A12.y1	B1.y1	A12.y2	B1.y2
On average,	12.79497	13.73273	12.79497	13.73273
P (T < = T) single tail	0.462898		0.462898	
t one-tailed critical	1.833113		1.833113	
P (T < = T) double tail	0.925796		0.925796	
t two-tailed critical	2.262157		2.262157	

All two-tailed P values >0.05 showed that the loading method had no effect on the conversion rate of ethanol and C4 olefin by two-sample t-test with equal variance. Therefore, catalyst A and catalyst B can be analyzed together.

3. Data fitting and solving

The data of 21 catalysts A and B were visualized, respectively by means of graphs and graphs, which were intuitive for each catalyst combination, the relationship between ethanol conversion and C4 olefin selectivity and temperature was shown in Figure 1 and Figure 2[4].

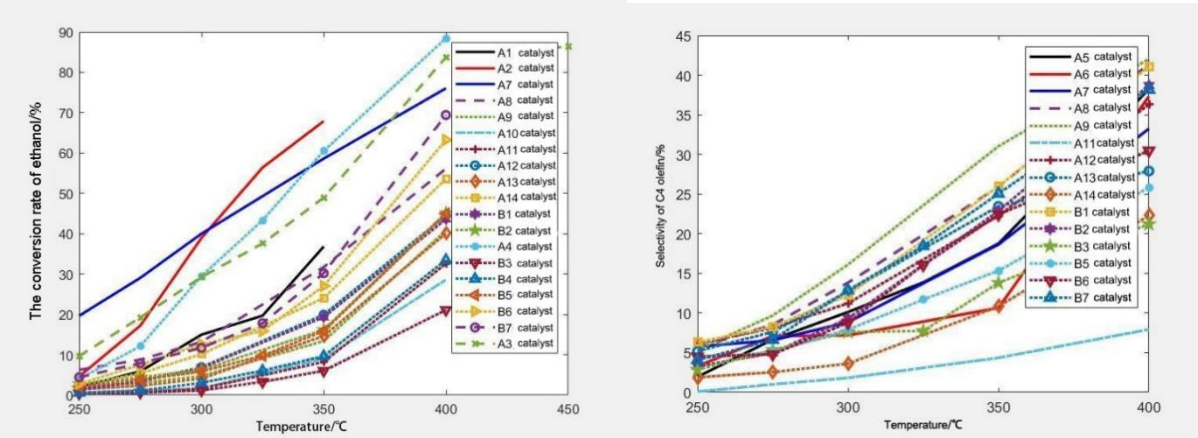


Figure 1. Catalyst with ethanol conversion rate increasing with temperature **Figure 2.** Catalyst with C4 selectivity increasing

The ethanol conversion rate and C4 selectivity of most catalyst combinations increased with the increase of temperature, and the increasing speed was different with different k values [5]. In the study of the relationship between the selectivity of C4 olefin and temperature, most of them are still in direct proportion, but the inverse ratio is increased. For catalyst A1, the temperature rises from 325 ° C to 350 ° C, and the slope is -0.0996.A2 increases 275 degrees from 250 degrees with a slope of -0.0316;A3 temperature increases 450 degrees from 400 degrees, the slope is -0.0706;A4 temperature 250 degrees to appreciate 275 degrees, the slope is -0.04;A10 appreciates 275 degrees from 250 degrees, the slope is -0.0216;B4 appreciates 275 degrees from 250 degrees with a slope of 0, and 300 degrees from 275 degrees with a slope of -0.0628.(The graph and slope k value of each catalyst are shown in the Appendix and supporting materials.) The following analysis of ethanol conversion with temperature slope table of different catalysts, and the basic fitting of the curve was tested by MATLAB.5. The slope tables of A6 and ethanol conversion and temperature are shown in Table 3[6].

Table 3. Slope table of A5, A6 and ethanol conversion rate and temperature

catalyst	Slope table for ethanol conversion and temperature				
A5	0.09453	0.335383	0.301612	0.338508	0.784165
A6	0.02434	0.507929	0.605516	0.551852	

Different from other catalysts, when the temperature is increased from 250 ° C to 275 ° C, the ethanol conversion rate is negatively correlated with the temperature, and the slope is -0.094526902 and -0.024336238, respectively. After 275 degrees, the selectivity is directly proportional to the temperature [7]. The cubic equation of ethanol conversion from catalyst A6 is y1=-7.581z3+ 9.531z2 +37.45z+32.71, r2=0.998, which shows that the fitting is good. The trend of A5 was similar to that of A6, so the cubic equation was also used to fit A5, and y=5.399e-6 z3-0.00206z2 +0.01578z+54.84, r2=0.9945, indicating that the degree of fit was good. Therefore, the relationship between catalyst and ethanol conversion obtained by such comparison method is valid. The relationship between the fitting results and temperature is shown in figure 3 and figure4.

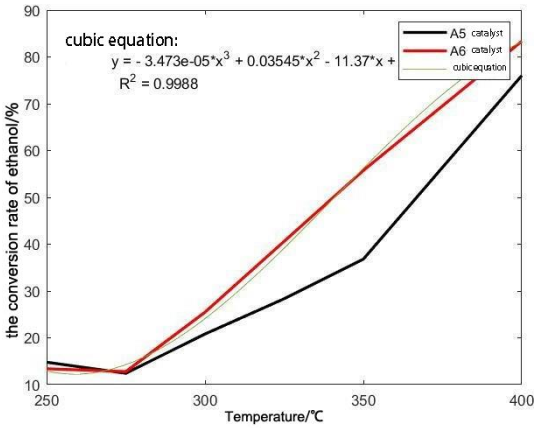


Figure 3. Fitting of A6 ethanol conversion and temperature

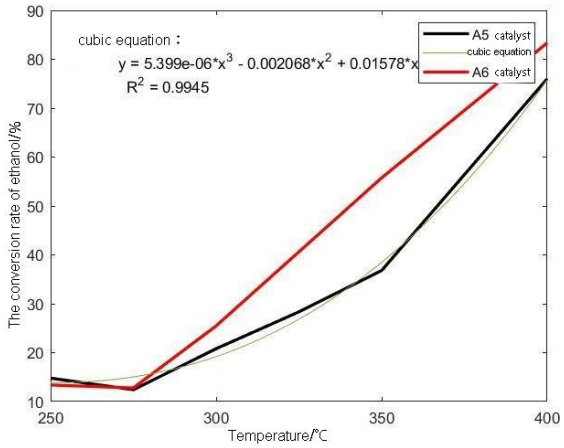


Figure 4. Relationship of A5 ethanol conversion and temperature

The overall trend of C4 selectivity of catalysts A1 and A3 is similar. We put them together for comparison. According to the value of slope k, we can see that the C4 olefin selectivity of catalysts A1 and A3 increases with the temperature at 325 and 400 degrees, respectively, and the k value is positive. After this temperature, the selectivity of C4 decreases, and the k value is negative, which is -0.0996 and -0.0706, respectively [8]. The relationship between C4 selectivity and temperature of the four catalysts is shown in Table 4.

Table 4. C4 selectivity of four catalysts as a function of temperature

catalyst	Slope table for C4 alkene selectivity and temperature					
A1	0.1352	0.3804	0.1104	0.0996		
A3	0.1016	0.3588	0.4684	0.3252	0.3316	0.0706
A2	0.0316	0.0928	0.4408	0.3392		
A4	0.04	0.084	0.3268	0.3344	0.2754	
A10	0.0216	0.0208	0.0226	0.1398		

B4	0	0.0628	0.1312	0.1908	0.167

According to the slope table and the fitting plot, as shown in Figs. 5 and 6, the C4 olefin selectivity of the four catalysts A2, A4, A10, and B4 showed similar trends with temperature, so these four catalysts were compared [9]. The C4 olefin selectivity of A2, A4 and A10 catalysts decreased first and then increased with temperature before 300 ° C. The selectivity of B4 decreased first and then increased with temperature before 350 ℃.

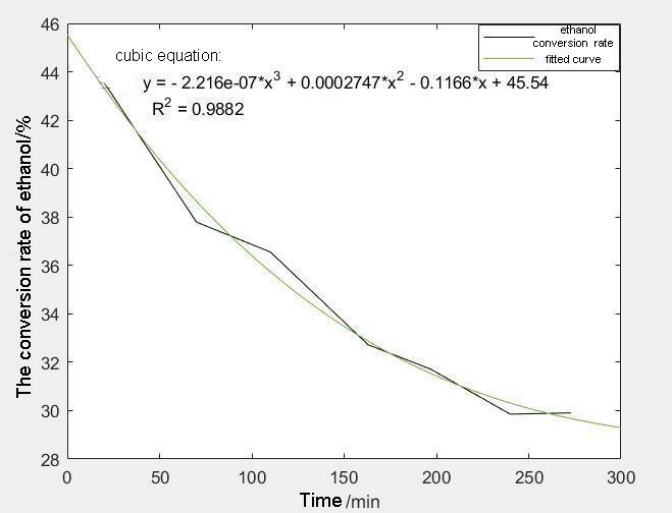


Figure 5. Conversion rate of ethanol of a substance at 350o as a function of time

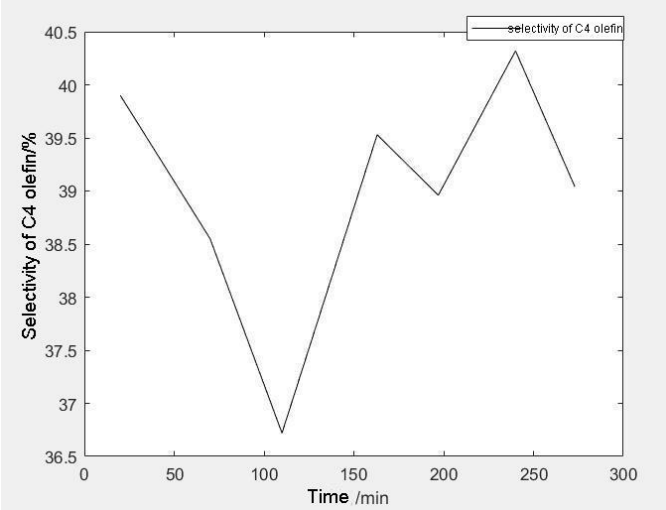


Figure 6. C4 selectivity of a substance at 350o versus time

We draw the ethanol according to the data in 350 - degree under a catalyst for the conversion rate of images of the change over time, as shown in figure 5 and figure 6, can intuitive see ethanol conversion rate increased with time gradually decline, at the same time has carried on the quantitative analysis of the image in the paragraphs are applied to solve the slope, it is concluded that the slope in paragraphs all negative, MATLAB curve fitting was used to draw the conclusion that under this condition, the conversion rate of ethanol with reaction time polynomial equation: y1=-2.216x10-7x3+0.00027x2-0.1166x+45.46.However, the selectivity of C4 olefin is the minimum at 110 min, which changes irregularly with the increase of time. The literature on chemical industry data is reviewed. [10] Conversion rate of ethanol of a substance at 350o as a function of time is shown as figure5.C4 selectivity of a substance at 350o versus time is shown as figure6.

According to the quantification results and images, the ethanol conversion and olefin selectivity of most catalyst combinations increased with the increase of temperature. When the temperature of A5 and A6 increased from 250 ° C to 275 ° C, the ethanol conversion increased inversely with the temperature after 275 ° C. The selectivity of catalysts A1 and A3 to olefin increases at 325 and 400

degrees, respectively, and the selectivity of olefin decreases after this temperature. The selectivity of catalysts A2, A4 and A10 decreased first and then increased with temperature before 300 ° C.B4 decreased first and then increased with temperature before 350 ° C. In Annex II, the conversion rate of ethanol of a given substance at 350 degrees is polynomial equation with time: y=-1.92x10-7x3+0.0002x2-0.1144x+45.46; The selectivity of olefin is minimum at 110 min. The reason may be that the material in the given catalyst reacts with the reactant, leading to the decrease of the proportion of C4 olefin first. As the reaction goes on, the proportion increases, but the reaction is still produced at the same time, so the selectivity is not stable.

4. Multiple linear sample regression model

By analyzing the composition of the catalyst combination, we isolated four main factors: Co/SiO2, Co loading, ethanol added per minute, and HAP. One catalyst contained quartz sand, but none of the other catalysts did, so we did not consider quartz sand as a factor. In addition to the catalyst, temperature is also a factor. According to the explanation in the research background, the Co/SiO2 and HAP loading ratio refers to the mass ratio of Co/SiO2 and HAP. This factor is related to Co/SiO2, so HAP is not considered, and the results of this factor and the Co/SiO2 factor are similar. Therefore, the four factors of temperature, Co/SiO2, Co loading, and ethanol added per minute were selected. Multiple linear sample regression model was used. This model is based on the 21 catalysts with different compositions given in Annex I. We use known data as samples, a total of 114 data, the amount of data is small, and considering that the chemical experiment is a scientific experiment, the random term is not accurate, and the residual error is reasonable, so the multivariate linear sample regression model is used for analysis.

4.1. Solution of multiple linear sample regression model

Spss software was used to conduct multiple linear regression model, and the regression equation of ethanol conversion rate was obtained as follows:

$$y1= -80.701 + 0.333X1 +0.108X2 +0.237X3-9.002X4. \quad (1)$$

The regression equation of C4 selectivity is:

$$y2= -48.839 + 0.09X1-3.1X2 +0.181X3+2.529X4. \quad (2)$$

Table 5. Multiple regression equations of ethanol conversion and four factors

	B	The standard error	Beta	VIF	R^2	DW value
constant	80.701	7.336			0.788	0.912
The temperature	0.333	0.019	0.764	1.002		
Co/SiO2	0.108	0.016	0.332	1.182		
Co load	0.237	0.901	0.224	1.155		
Ethanol added per minute	9.002	2.092	0.012	1.098		

Table 6. Multiple regression equations of C4 olefin selectivity and four factors

	B	The standard error	Beta	VIF	R^2	DW value
constant	48.839	5.162			0.701	0.582
The temperature	0.09	0.011	0.466	1.182		
Co/SiO2	3.1	0.64	0.266	1.098		
Co load	0.181	0.014	0.701	1.002		
Ethanol added per minute	2.529	1.472	0.097	1.155		

As shown in Table 5 and Table 6, the r2 obtained from the analysis is 0.788 and 0.701 respectively, which is not close to 1.VIF is the variance inflation coefficient, and the closer the VIF value is to 1, the lighter the multicollinearity is. The results showed that VIF was near 1, and the multicollinearity was light, so this model could be adopted.

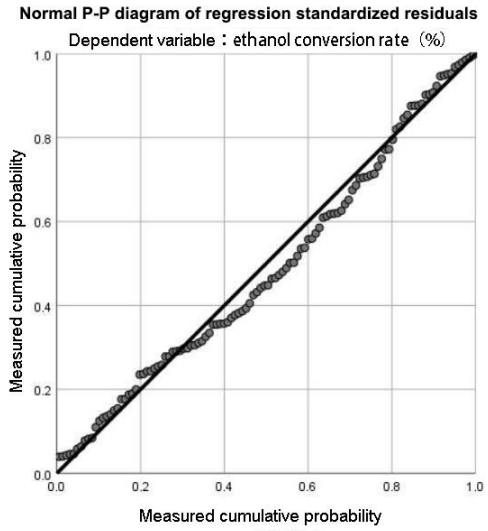


Figure 7. P-P plot of normalized residuals of ethanol conversion

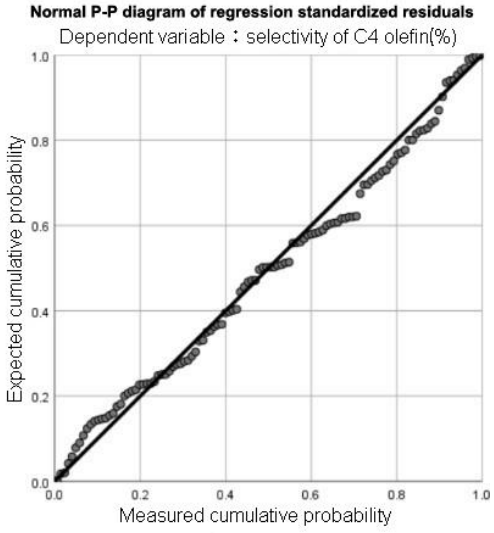


Figure 8. P-P plots of the standardized residuals of C4 olefin selectivity

According to the normalized residuals of ethanol conversion regression shown in Figures 7 and 8 and the P-P plot normality test, the P-P plot normality test shows the relationship between the cumulative frequency distribution of the sample and the cumulative probability distribution of the theoretical normal distribution. The points are very close to the line and most of the points are on the line, indicating that the data has a strong normality, so the data has a good normality. The obtained DW value is 0.9, which is slightly different from the better value of 2.

According to the software of C4 olefin selective regression standardized residual plot and P-P plot normality test, the points are very close to the line, and most of the points are on the line, indicating that the data has a strong normality, so the data has a good normality. The obtained Durbin-Watson value is 0.5, which is slightly different from the better value of 2.

Therefore, for problem two, the effects of different catalyst combinations and temperatures on ethanol conversion and C4 olefin selectivity can be obtained by using the regression equation: y1= -80.701 + 0.333X1 +0.108X2 +0.237 x3-9.002 X4, y2= -48.839 + 0.09 x1-3.1 X2 +0.181X3+2.529X4. After software test, multivariate

Linear sample regression is more suitable, and the equation obtained is feasible.For the differences in DW values, we analyzed the possible reasons for autocorrelation among factors and insufficient sample size.

4.2. Correlation analysis

Table 7. Correlation matrix of four factors on ethanol conversion rate and C4 olefin conversion rate

	The temperature	Co /SiO2 and HAP loading ratio	Co load	Ethanol added per minute The amount of
Ethanol conversion rate (%)	0.3946	0.7478	0.9103	0.911
C4 olefin selection (%)	0.4038	0.747	0.9325	0.9337

Table 7 shows the result of a of MATLAB code running, namely the value of correlation degree. The value of a was compared: the value of a added in each fraction of ethanol was the largest among the four factors, that is, this factor had the largest correlation degree and the greatest influence on the conversion rate of ethanol and the selectivity of C4 olefin.

We analyzed the original data and compared the results of the control variable method: the data of A1 and A3 were selected. At the same temperature of the two catalysts,

In the previous multiple linear sample regression model, we can also find that the coefficient of X4 has a large absolute value, which is consistent with the results of the correlation matrix. It is concluded that the factor of ethanol added per minute in different catalyst combinations has a large impact on ethanol conversion rate and C4 olefin selectivity.

5. Conclusion

In this paper, the influencing factors of ethanol conversion, C4 olefin selectivity and C4 olefin yield in the experiment of ethanol coupling preparation were analyzed, and then quantified modeling was carried out, and the combination design of catalyst was carried out, so as to make the above three variables reach the optimal value. Using the experimental data, professional and statistical analysis methods were used to analyze the correlation and regression of the possible influencing factors.On the basis of the experimental data given in the research background, the optimal catalyst combination and temperature for the above targets in the process of preparing C4 olefin were obtained.

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