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Experimental design of C4 olefins prepared by ethanol coupling

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Abstract

Ethanol coupling reaction is one of the important chemical experiment, the preparation of C4 olefin is of great significance in China's industrial production , and in the concrete experiment, catalyst and temperature is the important condition of experiment to change. With the continuous reduction of energy, how to improve the conditions of the experiment to increase the product has become a focus. By trying to configuration of different proportions of catalyst, temperature change variable to collect data for analysis, build a reasonable mathematical model of the study will help to improve the experimental effect. On problems, according to the data provided by the annex 1 catalyst in the combination of the characteristics of classifying different combinations, and use the build graphics to understand data characteristics such as python programming; Then under the combination of each catalyst, temperature and ethanol conversion rate and the return of C4 hydrocarbon selective model (see article 5.1.2), analyze the internal relationship between them. According to the data in Annex 2, the relationship between ethanol conversion rate and C4 olefins selectivity and experiment time was analyzed. It was found that ethanol conversion rate decreased with the increase of time and gradually tended to be stable. The selectivity of C4 olefins fluctuates over time, and the stability of experimental results is analyzed by means and variance statistics. In view of the question 2, under the condition of a problem, given the different combination of catalyst and temperature on the ethanol conversion and C4 olefin selectivity to have a certain influence, this article using two-factor variance analysis to analyze the experimental results, test results on the surface of catalyst and temperature have a significant impact on the result of the experiment. Then, by limiting six constraints, namely Co load, catalyst quality, ethanol concentration and Co/SiO2 and HAP charging ratio, the charging methods were classified one by one to refine the specific relationship between different constraints on the studied objects. For question 3, based on the problem of the conclusion of the first, second, the first use of attachment 1 data calculated all composition and temperature of C4 olefin yields, and then use merge sort, operation take the combination of C4 olefin yields higher as interval, effective output C4 olefin yields higher catalyst composition and temperature, when the limiting temperature, reduce the threshold temperature of the input layer, The program is run repeatedly, and the catalyst combination and temperature are output. For question 4, based on the previous three questions, in view of the different types of catalytic composition and temperature, the charging mode, the ratio of adjacent, different catalyst control variable designed five experiment, and explains the design of the related reasons.

Keywords

Ethanol conversion, C4 olefins, selective regression analysis, variance analysis, merge sort.

1. Restatement of the problem

Ethanol is dehydrogenated to form C4 olefins and other reactants by oxidative coupling in the presence of oxidation catalyst. Ethanol to prepare butene, butadiene and other reactions require catalyst combination, as well as high temperature heating. When the catalyst combination design is changed and the temperature is different, the regression model is established and the regression equation is obtained according to the change of ethanol conversion rate and the selectivity of C4 in the product. Then the variance analysis is used to construct the chart to obtain the catalyst combination with the maximum yield of C4 and the best temperature. It is requested to solve the following problems:

Problem 1: We first solved the correlation between temperature and ethanol transfer rate, C4 olefins selectivity, and the fluctuation of product selectivity as the ethanol conversion rate changes over time without considering Co load, catalyst mass, ethanol concentration, and Co/SiO2 / HAP charge ratio.

Problem 2: The influence of different catalyst combinations and temperature on the desired object was analyzed by variance analysis, and the conclusion was drawn by software simulation image.

Problem 3: In the experimental data of different catalyst combinations and temperatures, the yield of C4 olefin was obtained by calculating ethanol conversion rate and C4 olefin selectivity, and the maximum value was selected when the temperature range was less than 350 degrees.

Problem 4: Design experiments to verify the imperfections of the experiment.

2. Problem analysis

According to the requirements of the title, the following aspects of work have been done:

Part I: Establishment of regression model between temperature and ethanol conversion and C4 olefins selectivity:

Combined with the 21 sets of data in Annex 1, Python[6] and other programming software were used to cross-plot the fluctuations of ethanol conversion rate and C4R olefine selectivity of each group of images as the temperature changed, and establish a regression model. Then, SPSS software was used to substitute the values and obtain the specific regression correlation coefficients. According to the needs of subsequent analysis, the variables in the catalyst combination, namely, Co loading capacity, catalyst quality, ethanol concentration, Co/SiO2 and HAP charging ratio, and charging mode, were controlled by a single catalyst combination. The corresponding data from A1 to B7 were selected for analysis and the rule obtained.

Part two: analysis of variance of catalyst combination and temperature X

In question 2, the influence of different catalyst combinations and temperature on the target can be discussed. The results of 21 groups of chemical experiments can be classified according to the temperature through two-factor anOVA, and relevant tables can be established by grouping and applying data to test whether the combination and temperature have a "significant" effect on the target.

The third part: establish the maximum model to solve

Based on the results of the first part of the model, the yield calculation method was used to calculate the yield of C4 olefin below 350 degrees at all temperatures, and the maximum yield of C4 olefin was selected respectively, that is, the highest yield at this time. The process is shown in the mind map below.

3. Model hypothesis

(1) The external environment of the laboratory does not change during the default experiment.

(2) There will be no error due to manual operation during experimental operation.

(3) During the experiment, the catalyst will not be affected by temperature and lead to chemical properties change, without loss of its content.

(4) The default random error is 0 during the experiment.

(5) The experiment time is the same each time the data is collected.

4. Symbol description

Symbol	instructions	unit
x	temperature	limit
M	Catalyst combination	/
y	Ethanol conversion rate	%
z	Selectivity of C4 alkenes	%
a,b	Regression coefficient or undetermined coefficient of ethanol conversion rate regression equation	/
c,d	Regression coefficient or undetermined coefficient of C4 olefins selective regression equation	/
ε_i	Stochastic differential	/
$S_{回}$	Return to the sum of squares	/
$S_{剩}$	Residual sum of squares or residual sum of squares	/
R^2	Complex correlation coefficient squared	/
w	Yield of C4 olefins	%
P	Different catalyst combinations and temperatures	/
u	Factors in anOVA	/
α	The effect of level M	/
β	The effect of level N	

5. Model establishment and solution

5.1. Model establishment and solution of problem 1

5.1.1. Model establishment

During the preparation of C4 olefins and other products from ethanol, the catalyst combination was controlled unchanged to explore the relationship between ethanol conversion, C4 olefins selectivity and temperature.

Step 1: Through data testing, the ethanol conversion rate, C4 olefins selectivity and temperature were observed to be linearly correlated, and the data were sorted out as follows

ISSN: 2664-9640

Table 1: The relationship between ethanol conversion and temperature for each catalyst combination

temperature / combination	250	275	300	325	350	400	450
A1	2.07	5.85	14.97	19.68	36.80		
A2	4.60	17.20	38.92	56.38	67.88		
A3	9.7	19.2	29.3	37.6	48.9	83.7	86.4
A4	4.0	12.1	29.5	43.3	60.5	88.4	
A5	14.8	12.4	20.8	28.3	36.8	76.0	
A6	13.4	12.8	25.5		55.8	83.3	
A7	19.7	29.0	40.0		58.6	76.0	
A8	6.3	8.8	13.2		31.7	56.1	
A9	2.1	3.0	4.7		13.4	40.8	
A10	0.3	1.0	1.7		9.0	28.6	
A11	0.2	0.5	1.6		8.2	32.6	
A12	1.4	3.5	6.9		19.9	44.5	
A13	1.3	2.3	4.1		14.6	40.0	
A14	2.5	5.3	10.2		24.0	53.6	
B1	1.4	3.4	6.7		19.3	43.6	
B2	2.8	4.4	6.2		16.2	45.1	
B3	0.4	0.6	1.1	3.3	6.0	21.1	
B4	0.5	1.1	3.0	6.1	9.6	33.5	
B5	2.1	3.8	5.8	9.8	15.9	45.0	
B6	2.8	7.5	12.6	15.9	27.0	63.2	
B7	4.4	7.9	11.7	17.8	30.2	69.4	

Table 2: C4 olefins selectivity in relation to temperature for each catalyst combination

temperature / combination	250	275	300	325	350	400	450
A1	34.05	37.43	46.94	49.7	47.21		
A2	18.07	17.28	19.6	30.62	39.1		
A3	5.5	8.04	17.01	28.72	36.85	53.43	49.9
A4	9.62	8.62	10.72	18.89	27.25	41.02	
A5	1.96	6.65	10.12	13.86	18.75	38.23	
A6	3.3	7.1	7.18		10.65	37.33	
A7	5.75	6.56	8.84		18.64	33.25	
A8	5.63	8.52	13.82		25.89	41.42	
A9	5.4	9.68	16.1		31.04	42.04	

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A10	2.19	1.65	2.17		3.3	10.29
A11	0.1	1	1.82		4.35	7.93
A12	6.17	8.11	11.22		22.26	36.3
A13	5.19	7.62	12.74		23.46	27.91
A14	1.89	2.55	3.61		10.83	22.3
B1	6.32	8.25	12.28		25.97	41.08
B2	3.26	4.97	9.32		22.88	38.7
B3	2.85	5.35	7.61	7.74	13.81	21.21
B4	6.62	6.62	5.05	8.33	13.1	21.45
B5	4.3	5.06	7.92	11.69	15.34	25.83
B6	4.5	4.79	8.77	16.06	22.41	30.48
B7	4.08	6.62	12.86	18.45	25.05	38.17

It was found that, in addition to the influence of catalyst combination and charging mode, the relationship between temperature and the two was investigated separately, and it was easy to conclude that ethanol conversion and C4 olefins selectivity were positively correlated with temperature, so a linear regression model was established.

Step 2: There is a linear correlation, build a preliminary model, with temperature (x: degree) as the independent variable of the horizontal axis, ethanol conversion (y:%) and C4 olefins selectivity (z:%) as the longitudinal dependent variables, according to the principle of least square method.

$$\hat{y} = \hat{a} + \hat{b}x \tag{1}$$

Select undetermined coefficients a,b,c,d to establish regression equations respectively

Regression equation of ethanol conversion rate:

$$y = ax + b + \varepsilon_1 \tag{2}$$

Model equation of C4 olefins selectivity:

$$z = cx + d + \varepsilon_2 \tag{3}$$

Determine the coefficients of other equations:

$$S_1 = \sum_{i=1}^{n} \left(\hat{y}_i - \overline{y} \right)^2$$
$$S_2 = \sum_{i=1}^{n} \left(y_i - \hat{y}_i \right)^2 \tag{4}$$
$$R^2 = \frac{S_1}{S_2}$$

ISSN: 2664-9640

In the formula, a and b are regression coefficients, and ε is random parameter. SPSS software is used to calculate the regression coefficients, and the unitary linear programming model is obtained.

5.1.2. Solving the model

(I) regression model, a stochastic differential is 0, so does not affect a yuan regression coefficient of linear equation to plug in each group of data, when running into the SPSS, found that for a return to the correlation coefficient of the linear equation, a series of corresponding solutions can be obtained, and by comparing R2, found that its value is close to 1, 20 group has a significant impact. Therefore, the regression coefficients of the 21 sets of equations obtained were calculated in the following table:

Table 3: Coefficients of regression equation for ethanol conversion

combination	Constant term	temperature coefficient	The square of R	significant
A1	-3.242	0.154	0.787	0.045
A2	-41.546	0.222	0.836	0.03
A3	-59.195	0.261	0.913	0.001
A4	-52.411	0.227	0.917	0.003
A5	-57.813	0.230	0.940	0.001
A6	-50.748	0.203	0.784	0.046
A7	-44.262	0.187	0.937	0.007
A8	-57.257	0.242	0.983	0.001
A9	-59.095	0.254	0.995	0.000
A10	-12.357	0.052	0.742	0.061
A11	-10.695	0.043	0.989	0.005
A12	-74.796	0.286	0.928	0.008
A13	-67.333	0.253	0.877	0.019
A14	-86.644	0.336	0.929	0.008
B1	-73.190	0.028	0.925	0.009
B2	-70.859	0.272	0.863	0.022
B3	-36.184	0.131	0.792	0.018
B4	-56.900	0.208	0.809	0.015
B5	-72.400	0.272	0.833	0.011
B6	-99.883	0.383	0.883	0.005
B7	-109.343	0.420	0.876	0.006

Table 4: Coefficients of C4 olefins selective regression equation

A1	-3.242	0.154	0.787	0.045
A2	-41.546	0.222	0.836	0.030
A3	-59.195	0.261	0.913	0.001
A4	-52.411	0.227	0.917	0.003
A5	-57.813	0.230	0.940	0.001
A6	-50.748	0.203	0.784	0.046
A7	-44.262	0.187	0.937	0.007
A8	-57.257	0.242	0.983	0.001

A9	-59.095	0.254	0.995	0.000
A10	-12.357	0.052	0.742	0.061
A11	-13.307	0.052	0.978	0.001
A12	-47.727	0.205	0.967	0.003
A13	-35.889	0.163	0.977	0.002
A14	-35.116	0.138	0.920	0.010
B1	-56.728	0.240	0.972	0.002
B2	-61.073	0.244	0.970	0.002
B3	-28.294	0.120	0.943	0.001
B4	-22.208	0.102	0.801	0.016
B5	-34.599	0.146	0.956	0.001
B6	-45.757	0.190	0.965	0.000
B7	-56.451	0.234	0.989	0.000

As can be seen from the above table, ethanol conversion rate and temperature conform to the above linear equation. For each catalyst combination, temperature and C4 olefins selectivity show a positive correlation. Generally speaking, the operation results of $R^2 \rightarrow 1, Sig < 0.05$ the combined equation conform to the model.

In conclusion, all tests of the model are significant, and model (1) can be considered to be a better model.

(II) Ethanol coupling reaction in the preparation of C4 olefin reaction, acetaldehyde is the intermediate product of the reaction, then converted into C4 olefin and carbon number 4-12 fatty alcohol. As the reaction time lengthened, the ethanol conversion rate gradually decreased and reached a stable value of 29.9% at the 240th minute and later. 240 was divided into time nodes, during which the selectivity of various products varied inconsistent [3].

(1) Observe the change rule of ethanol conversion rate over time:

MATLAB[3] was used to make images, and it was found that it was in line with the model characteristics. However, at this time, the ethanol conversion rate gradually decreased with the extension of the experiment time and finally reached a balance, showing a negative correlation between the two.

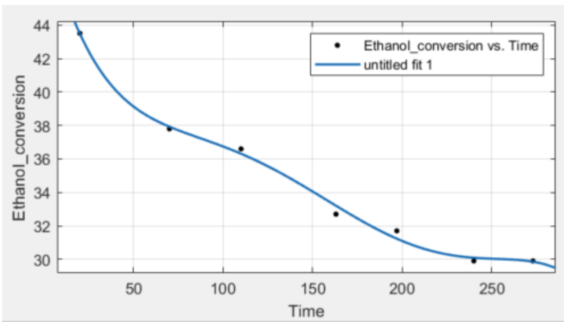


Figure 1: The relationship between ethanol conversion rate and time

(2) The relationship between product selectivity and time was observed

The selectivity of various products did not have collinearity. The selectivity of ethylene, acetaldehyde, and other products showed an increasing pattern except for occasional fluctuations. The selectivity of fatty alcohols with carbon number of 4-12 showed a decreasing pattern as a whole, but the selectivity of C4 olefins, methylbenzaldehyde, and methylbenzyl alcohol fluctuated around a fixed value in a certain range.

ISSN: 2664-9640

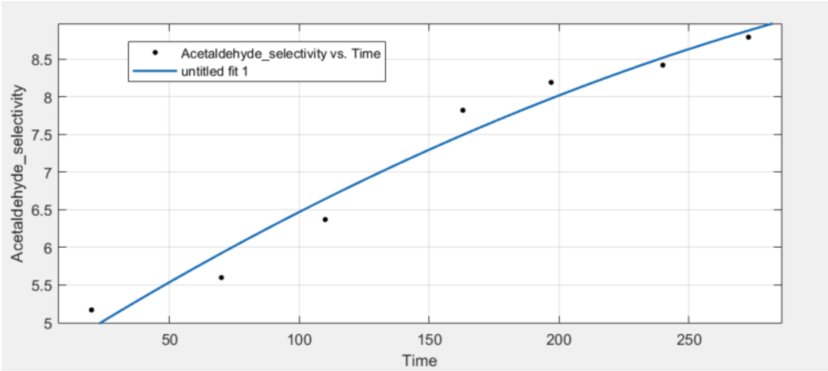
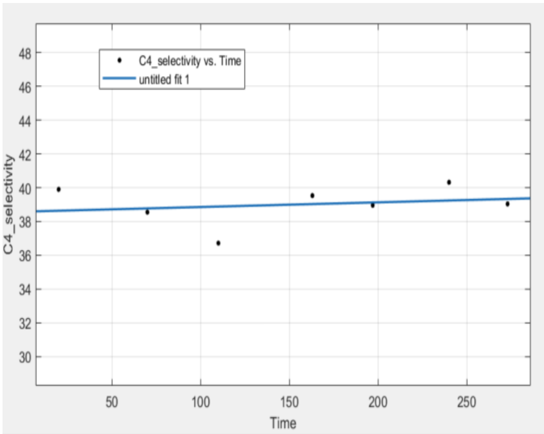


Figure 2: Acetaldehyde selectivity over time



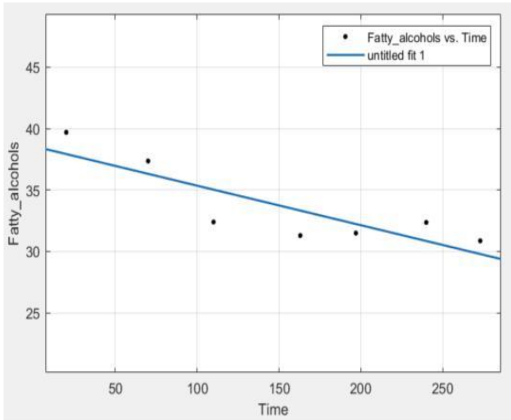


Figure 3: C4 olefins selectivity over time Figure 4: Selectivity of fatty alcohols over time

As the ethanol conversion rate stabilized, the stability test reached the expectation, but at this time, except acetaldehyde, the selectivity of other products all mutated, and the change trend was completely opposite to the node.

The variance equation is established here, and the following results can be obtained by substituting C4 olefin selectivity into the calculation. It is found that the variance is large and the fluctuation is large.

$$\sum_{j=1}^{7}\left(\sum_{i=1}^{7} z_i \div 7 - z_j\right)^2 \div 7 = 1.177 \tag{5}$$

5.2. Model establishment and solution of question 2

5.2.1. Modeling of Question 2

The values of Y and Z of different catalyst combinations have specific rules under the condition of temperature change. Now, based on the data, a two-factor anOVA model is established to compare the influence of ethanol conversion rate and C4 olefins selectivity under each combination.

Establishment of anOVA model [5] :

Anova is one of the commonly used statistical methods. It is used to reflect the average variation of a group of data based on the test statistical analysis of the average variance of the results, and to infer whether there is any difference between the mean by comparing the variation from different sources among each group. In this problem, the factor Mi is different catalyst combination, the factor Ni is the temperature value, and the 21 levels of M interact with the

ISSN: 2664-9640

level of N to test whether the sample means of the two factors have significant differences. Based on the comparison of factors and the significance probability, judge whether the two factors have a significant impact on the test index.

Remember

$$\mu \triangleq \frac{1}{rs}\sum_{i=1}^{r}\sum_{j=1}^{s}\mu_{ij} \tag{6}$$

$$\mu_{i\bullet} = \frac{1}{s}\sum_{j=1}^{s}\mu_{ij}\ ,\ i=1,2,\cdots,r \tag{7}$$

$$\mu_{\bullet j} = \frac{1}{r}\sum_{j=1}^{r}\mu_{ij}\ ,\ i=1,2,\cdots,s \tag{8}$$

And that's what we get the effect of level M

$$\alpha_i \triangleq \mu_{i\bullet} - \mu \tag{9}$$

the effect of level N

$$\beta_j \triangleq \mu_{\bullet j} - \mu \tag{10}$$

Therefore, the two-factor anOVA model is:

$x_{ijk} = \mu + \alpha_i + \beta_j + \varepsilon_{ijk}, i = 1, 2, \cdots, r; j = 1, 2, \cdots, s; k = 1, 2, \cdots, t; t > 1$

in the formula $\sum_{i=1}^{r}\alpha_i = 0, \sum_{j=1}^{s}\beta_j = 0$ and $\varepsilon_{ijk} \sim N\left(0, \sigma^2\right)$ Independent of each other.

The test of statistical hypothesis is as follows:

H_{01}: $\alpha_1 = \alpha_2 = \cdots \alpha_r = 0$

H_{02}: $\beta_1 = \beta_2 = \cdots \beta_s = 0$

If rejected H_{01},think factors A different levels have significant influence on the experimental results.

If rejected H_{02} ,Think factors B different levels have significant influence on the experimental results.

If H_{01}、 H_{02} Don't say no,Think factors A and factors B different levels have significant influence on the experimental results.

5.2.2. Model solution of Question 2

(I) Based on the theory of variance analysis and the operating results of SPSS, different sample means of the above two factors have an impact on the test results. For the two factors, the data

ISSN: 2664-9640

of each group can be compared in pairs, which is easier to explain the differences between groups. The following table shows the running results of SPSS:

Table 5: Test of intersubjective effect

Dependent variable: ethanol conversion rate

source	Mean square	significant
combination	836.702	0.000
temperature	6700.058	0.000

The significance sig is <.0.05, so the two factors have significant influence on ethanol conversion and C4 olefin selectivity.

Obviously, this model is significant to the test results, so the second mathematical model is obtained.

For the specific effects of different catalyst combinations and temperature on ethanol conversion rate and C4 olefins selectivity, we can divide them into two categories, six constraint conditions, control five constraint conditions, and compare the remaining one constraint condition to obtain specific effects.

(II) Constraints:

(1) Temperature

Based on question 1, the influence law of different temperatures on the data obtained under the same catalyst combination is obtained.

(2) Co load

S. Effects of different catalyst combinations and temperatures on ethanol conversion

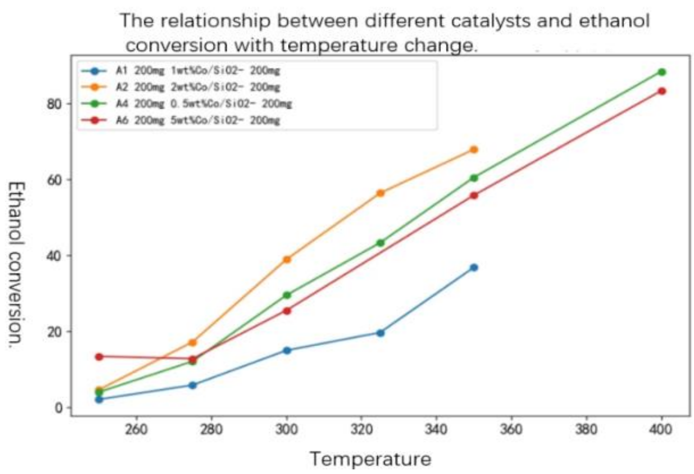


Figure 5

1. The total amount of input is 400mg

Using Python programming [6], it can be seen that under the same loading ratio, placing method, temperature and ethanol concentration, at the initial temperature of 250 ° C, the ethanol conversion rate has almost no significant influence at first as the Co loading increases, but when the added Co loading reaches 5wt%, the ethanol conversion rate increases significantly. When the temperature is greater than or equal to 280 ℃, the ethanol conversion rate fluctuates up and down at any temperature with the increase of Co loading.

2. The total amount of input is 100mg

ISSN: 2664-9640

Under the same conditions of temperature, feeding method, ethanol concentration and loading ratio, the ethanol conversion rate was negatively correlated with the increase of Co loading at any temperature.

T. Influence of temperature of different catalyst combination stages on C4 olefins selectivity

1. The total amount of input is 400mg

Under the same loading ratio, feeding method, temperature and ethanol concentration, it can be seen from the figure that C4 olefins selectivity is positively correlated with the increase of Co loading from 0.5wt% to 1wt%. When the Co load increased from 1wt% to 5wt%, the C4 olefins selectivity was negatively correlated with it, so we could infer that when the Co load was 1wt%, the C4 olefins selectivity almost reached its maximum value.

2. The total amount of input is 100mg

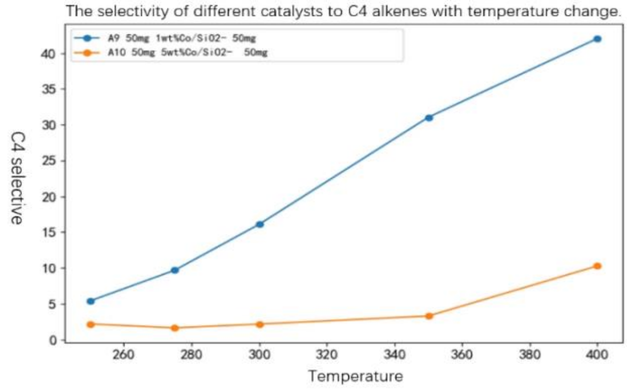


Figure 6

As shown in the figure, under the same conditions of the other four constraints, C4 olefins selectivity is negatively correlated with Co loading at any temperature as Co loading increases.

(3) Co /SiO2 and HAP charging ratio

S. Effects of different catalyst combinations and temperatures on ethanol conversion

Under the condition of the same sum of temperature, infusion method, ethanol concentration and infusion amount, as shown in FIG. 6, when Co /SiO2 mass increases and HAP mass decreases, it is positively correlated with ethanol conversion. In other words, the higher the mass ratio of Co /SiO2 to HAP, the higher the conversion rate of ethanol, and vice versa.

T. Effects of different catalyst combinations and temperature on C4 olefins selectivity

As shown in FIG. 7, when Co /SiO2 and HAP charging ratio are different and the constraint conditions are the same,

The mass ratio of Co /SiO2 and HAP was positively correlated with C4 olefins selectivity at temperatures between 280 and 350 degrees. When the ratio of Co /SiO2 to HAP is 1:1, the selectivity of C4 olefins is the highest when the ratio is lower than 280 degrees or higher than 350 degrees.

(4) input quality of catalyst

S. Effects of different catalyst combinations and temperatures on ethanol conversion

S.1 1wt% Co /SiO2, ethanol concentration 1.68 mL /min

As shown in the figure, under the conditions of the same temperature, feeding method, ethanol concentration and feeding ratio, it is obvious that the feeding total has the same trend with the ethanol conversion rate. The more the feeding total, the higher the ethanol conversion rate.

S.2 1wt% Co /SiO2, ethanol concentration 0.9 mL /min

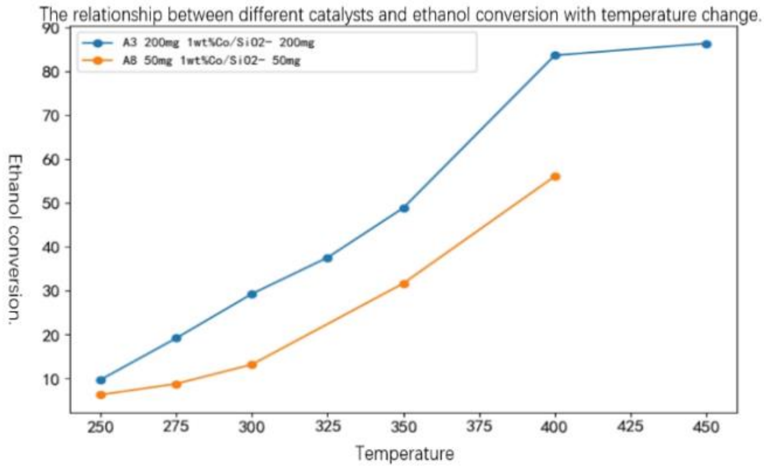


Figure 7

Similarly, the total feed was positively correlated with ethanol conversion rate.

T. Effects of different catalyst combinations and temperature on C4 olefins selectivity

T.1 1wt% Co /SiO2, ethanol concentration 1.68 mL /min

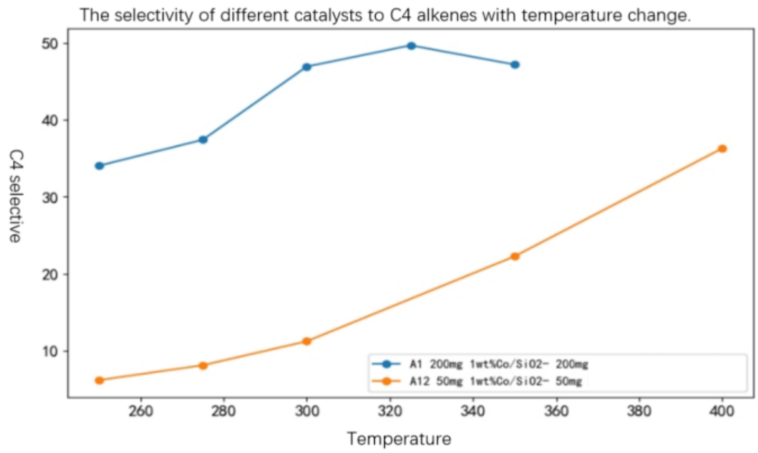


Figure 8

Under the same condition of the other four conditions, it can be seen from the figure that the total feeding quantity has the same selectivity trend with C4 olefin.

T.2 1wt% Co /SiO2, ethanol concentration 0.9 mL /min

Different from the figure, when ethanol concentration was 0.9 mL /min, there was almost no relationship between C4 olefin selectivity and the total amount of feeding before 275 ° C, but after 275 ° C, feeding was positively correlated with C4 olefin selectivity.

(5) Concentration of ethanol

S. Effects of different catalyst combinations and temperatures on ethanol conversion

S.1 50mg 1wt% Co /SiO2- 50mg HAP

When the catalyst filling ratio is 50mg:50mg: when the concentration of ethanol increases, the conversion rate of ethanol decreases continuously in longitudinal comparison at the same temperature.

S.2 200mg 1wt% Co /SiO2- 200mg HAP

When the catalyst charge ratio is 200mg:200mg: ethanol concentration is also negatively correlated with ethanol conversion. In conclusion, ethanol concentration is negatively correlated with ethanol conversion rate.

T. Effects of different catalyst combinations and temperature on C4 olefins selectivity

T.1 50mg 1wt% Co /SiO2- 50mg HAP

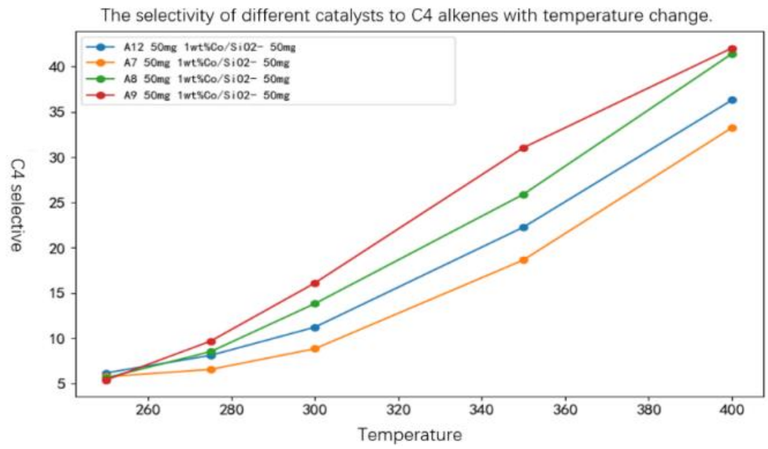


Figure 9

At the beginning, the fashion material ratio was 50mg:50mg, and the selectivity of C4 in each group was almost the same. As the concentration of ethanol in the catalyst combination increased from 0.3ml/min to 0.9ml/min and then to 2.1 mL /min, the selectivity of the experimental product C4 olefin increased sequentially. However, when the concentration was 1.68ml/min, The selectivity of C4 olefins was significantly lower than that of the combination with 0.9 mL /min concentration. So this is not a positive correlation.

T.2 200mg 1wt% Co /SiO2-200mg HAP

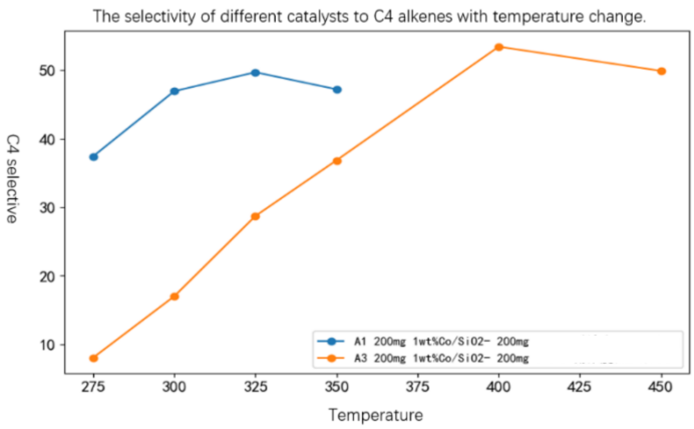


Figure 10

When the catalyst charge was increased to 200mg:200mg, the C4 olefins selectivity and concentration change trend were consistent at the same temperature.

In conclusion, with a large probability, ethanol concentration is positively correlated with C4 olefins selectivity, with occasional changes, which is not completely in line with the positive correlation.

(6) Delivery method

S. Effects of different catalyst combinations and temperatures on ethanol conversion

S.1 50mg 1wt% Co/sio2-50 mg hap-ethanol concentration 1.68ml/min

S.2 50mg 1wt% Co/Sio2-50mg HAP-ethanol concentration 2.1 mL /min

Image comparison shows that when the catalyst combination is the same and the charging method is changed, the ethanol conversion rate is almost unchanged. However, when the ethanol concentration is low (1.68 mL /min), the ethanol conversion rate of A assembling method I is higher.

However, when the concentration increased to 2.1 mL /min, the ethanol conversion rate of B assembly method II was higher.

T. Effects of different catalyst combinations and temperature on C4 olefins selectivity

T.1 50mg 1wt% Co/Sio2-50mg HAP-ethanol concentration 1.68 mL /min

According to the figure analysis, within 275 degrees, changing the feeding method has no effect on C4 olefin selectivity.

However, starting from 300 ℃, the selectivity gap between group B and Group A gradually increased under the catalyst combination.

T.2 50mg 1wt% Co/Sio2-50mg HAP-ethanol concentration 2.1 mL /min

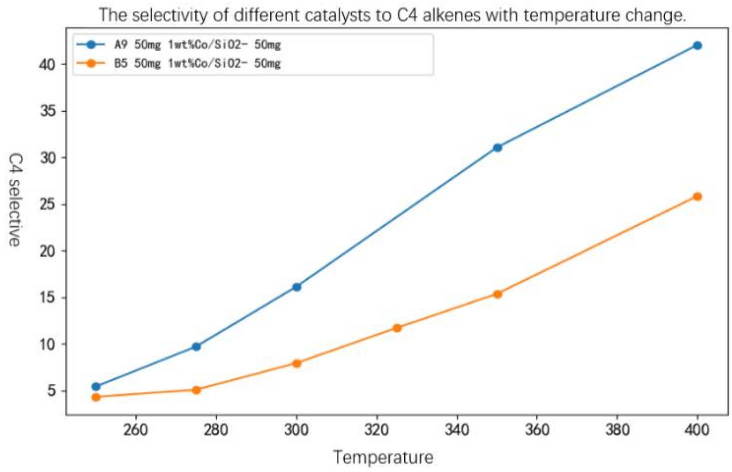


Figure 11

The selectivity of C4 olefins in group A was significantly higher than that in group B at the same temperature with the increase of ethanol concentration.

In conclusion, the feeding method has an opposite linear relationship with the ethanol conversion rate and C4 olefins selectivity of group A and Group B.

5.3. Model establishment and solution of question 3

The correlation interval estimation model was established and the yield of C4 olefin was estimated based on the relevant data. Analysis data model analysis, this paper will be through the establishment of matrix of C4 hydrocarbon yield of most of the calculations, under the known related data analysis of the prediction, analysis of temperature and Co load, mass of catalyst, the Co/SiO2 and HAP charging ratio, ethanol concentration and other factors influencing on the yield of C4 olefin, a mathematic model of the C4 hydrocarbon yield.

5.3.1. 5.3.1 Model establishment of question 3

Process the data in Annex 1.

Table 6: The influence of C4 olefins yield on catalyst combination and temperature

temperature / Catalyst combination	250	275	300	325	350	400	450
A1	0.704	2.190	7.026	9.782	17.374		
A2	0.832	2.971	7.629	17.264	26.541		
A3	0.532	1.547	4.975	10.793	18.033	44.728	43.118
A4	0.387	1.043	3.160	8.184	16.478	36.278	
A5	0.290	0.826	2.106	3.929	6.902	29.062	

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A6	0.442	0.907	1.829		5.938	31.114
A7	1.130	1.905	3.535		10.924	25.279
A8	0.353	0.746	1.821		8.212	23.243
A9	0.111	0.291	0.761		4.157	17.151
A10	0.007	0.017	0.037		0.298	2.942
A11	0.000	0.005	0.029		0.357	2.585
A12	0.089	0.282	0.776		4.432	16.166
A13	0.070	0.176	0.518		3.434	11.177
A14	0.047	0.136	0.366		2.603	11.956
B1	0.089	0.282	0.826		5.015	17.909
B2	0.090	0.219	0.580		3.704	17.467
B3	0.011	0.033	0.087	0.254	0.830	4.475
B4	0.036	0.074	0.152	0.504	1.263	7.184
B5	0.091	0.194	0.460	1.144	2.433	11.619
B6	0.125	0.360	1.107	2.547	6.058	19.277
B7	0.180	0.523	1.505	3.284	7.565	26.490

(I) Set up a matrix, take the temperature and catalyst combination as the horizontal and vertical Angle markers of the two-dimensional matrix, and make the element value of the matrix the yield value of C4 olefin corresponding to the catalyst combination and temperature.

$$\begin{bmatrix} a_{11} & \cdots & a_{1n} \\ \vdots & a_{ij} & \vdots \\ a_{m1} & \cdots & a_{mn} \end{bmatrix}$$

(1)Take the corresponding values of the matrix elements in turn, use the merge sort algorithm, will(a_{mn})rearrange

(2) The top 5% elements of the value are selected according to the interval estimation

$a_{kl}$for the lower limit,$a_{st}$for the upper limit

$$a_{kl} \le (a_{mn}) \le a_{st}$$

Among them $[a_{kl}, a_{st}]$ is the numerical interval

(3)extract $a_{st} = \max(a_{mn})$

5.3.2. 5.3.2 Model solution of Question 3

According to the above algorithm, the following values can be obtained by running the solution, which are all the data combinations of 5% in the sampling space of the desired catalyst combination and temperature for higher C4 olefin yield:

[(A3,400), (A3,450),(A4,400),(A6,400), (A5,400), (A2,350)]

Table 7: Catalyst combinations and temperatures with the highest possible C4 olefins yield obtained

Catalyst combination	temperature	Ethanol conversion rate %	C4 olefins selectivity %	C4 olefin yield %
A3	400	83.70	53.43	44.7281
A3	450	86.40	49.9	43.1184
A4	400	88.40	41.02	36.2778
A6	400	83.30	37.33	31.1137

A5	400	76.00	38.23	29.0624
A2	350	67.88	39.1	26.5408

5.4. Solution of Question 4

5.4.1. Experimental design

Ask for the third let we pray for C4 olefin yields as high as possible, adds five experiments we want to get the highest yield of C4 olefin, as you can see annex ii when temperature is 350 degrees, as the reaction progresses, when time reach 240 min, ethanol conversion rate to maintain stability, to get the highest yield of C4 olefin, would make C4 maximum selectivity, This will start with the control constraints of the second question.

5.4.2. Design Reasons

(1) When Co loading is different, other loading ratio, feeding method, temperature, total input and ethanol concentration are all the same, it can be seen that only at 0.5wt% to 1wt%, C4 olefins selectivity is positively correlated with it. Therefore, we can design the combination A15:200mg 1.5wt%Co/ sio2-200mg HAP-ethanol concentration 1.68mL /min. Through the experiment, we can get the results that when the temperature is greater than 350 degrees, the selectivity of C4 olefin is higher than that when the temperature is 1wt%Co/SiO2. It indicates that the selectivity of C4 olefin is not the highest at 1wt%Co/SiO2 under other conditions, that is, the yield of C4 olefin may be higher under other conditions.

(2) When the Co/SiO2 and HAP filling ratio are different, we increase the concentration of HAP-ethanol in experiment A16:90mg 1.5wt%Co/ Sio2-10mg 1.68mL /min, and obtain the experimental results. When the temperature is greater than 350 degrees, if the C4 olefin selective feeding ratio is 1: When 1 is large, it indicates that when the feeding ratio is 1:1, the feeding amount is increased, and the C4 olefin yield is higher.

(3) When the input quality of catalyst is different, increase the concentration of experiment A17:50mg 1wt%Co/SiO2-10mg HAp-ethanol 0.9 mL /min. When the temperature reaches 450 degrees, the selectivity of C4 olefin is not as high as that of A3 combination, which indicates that under the same other conditions, increase the feed amount. You end up with a higher yield of C4 alkenes.

(4) When the concentration of ethanol is different, the experiment A18:50mg 1wt%Co/ Sio2-10mg HAp-ethanol concentration is 3.0 mL /min. During the experiment, if the SELECTION of C4 olefin in A18 combination is higher than that in A9 combination, it indicates that when the concentration of ethanol increases by 3 times, the selection of C4 olefin also shows an upward trend. That is, the yield of C4 olefin will be on the rise.

When feeding methods were different, experiment A19:50mg 1wt%Co/ Sio2-10mg HAP-ethanol concentration was increased to 2.52ml/min. From the experimental data, it could be seen that feeding methods had little effect on C4 olefine selectivity when ethanol concentration was 1.68mL /min. However, when ethanol concentration was 2.1mL /min, The selectivity of C4 olefin in group A was significantly higher than that in group B. In the A19 experiment, the selectivity of C4 olefin in group A was also higher than that in group B, indicating that the higher the ethanol concentration was, the higher the selectivity of C4 olefin was and the higher the yield of C4 olefin was.

6. Evaluation and extension of the model

6.1. Advantages of the model

(1) The model is simple and easy to understand, easy to calculate and easy to promote

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In this paper, when other variables are controlled by linear programming model, the influence of temperature on ethanol conversion rate and C4 olefins selectivity can be solved by substituting data.

(2) It is convenient to analyze the independent effect between the two factors

In this paper, the two-factor anOVA model was used to deal with whether the catalyst combination and temperature had significant effects on the test results at different levels.

(3) In the case of complete randomness, this model can be used to quickly process the data without specific rules

6.2. Shortcomings of the model

(1) The model is too single, not very accurate, unitary linear regression model is difficult to model nonlinear data or polynomial regression with correlation between data features; It is difficult to express highly complex data well.

(2) It involves all the data, and the calculation is complicated, which requires a lot of experimental time;

(3) The numerical operation of matrix requires high software space complexity, and is more complicated for regular data processing.

6.3. Extension of the model

The regression model used in this paper is easy to find the relationship between the two quantities, while the anOVA model is easy to deal with the sample mean difference of different groups, which can be used to identify whether some factors have a significant impact on the results and the impact size. Regression model [7] is used to process sales according to business data, including price, number of consumers, number of reservations, etc.

Anova model can be used to test the significance of mean difference. Or isolate the relevant factors and estimate their contribution to the total variation; Or analyze the interaction between factors.

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