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The Effects of Different Conditions on the Preparation of C4 Olefins by Ethanol Coupling

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Abstract

In this paper,a model of catalyst combination, temperature, time and yield of C4 olefins was established for the process of preparing C4 olefins in ethanol production.The Spearman correlation coefficient was further used to obtain the correlation between temperature, catalyst combination, ethanol conversion rate,and C4 olefin selectivity. Using the multiple linear regression model and using the F hypothesis test to test the joint significance of the regression coefficients, we obtained the variation law of the yield of C4 olefins under different conditions.Finally, the effect of different conditions on the yield of C4 olefins prepared by ethanol coupling was obtained.

Keywords

Optimization model; Spearman correlation coefficient; Multiple linear regression.

1. Introduction

1.1. Research Background

C4 olefins are widely used in chemical products and pharmaceutical production. There are many raw materials for the preparation of C4 olefins. The traditional raw materials are fossils. Due to the lack of fossil resources and the traditional preparation methods will have a negative impact on the environment. Therefore, the preparation of C4 olefins from ethanol has the advantages of green environmental protection and wide sources. However, ethanol as the reactant for the production of C4 will be affected by many factors, such as temperature, time, catalyst combination and so on, which will affect the conversion rate of ethanol and the selectivity of C4 olefins, thus affecting the efficiency of the preparation of C4 olefins. In order to find the optimal preparation conditions to improve the yield of C4 olefins, we need to research the influencing factors of ethanol coupling preparation of C4 olefins and compare the effects of different conditions on the preparation of C4 olefins.

In this paper, based on a series of experimental data of different catalysts at different temperatures in a chemical laboratory, the effects of time, temperature and catalyst combination on ethanol conversion and C4 olefin selectivity were studied.

1.2. Model Assumptions

1. Ignore the non-standard quantity and proportion of materials due to operation, and there are no other impurities in the catalyst.

2. It is assumed that in the reaction process, the pressure of the reaction environment does not change and has no effect on the forward and reverse direction of the reaction.

3. Ignore the influence of the equipment used in the chemical reaction on the reaction, it is assumed that the solution (or gas) in the container is in full contact with the catalyst, and the mixing, heating, pressure and density are uniform.

4. When measuring key data such as ethanol conversion and ethylene selectivity, the environment is stable and closed, and the collected and measured data are true, accurate and reliable.

5. It is assumed that the concentration of reactants in the reaction process will not be affected by the products.

1.3. Symbol Description

Table 1. Meaning and unit description of symbols

Symbol	Significance	Unit
y1	Ethanol conversion	%
y2	C4 olefin selectivity	%
x1	temperature	℃
x2	Co load	wt%
x3	Co/SiO2	mg
x4	HAP	mg
x5	Ethanol addition rate	ml/min
A1	Catalyst support (HAP or quartz sand)	

2. Model Establishment

This paper analyzes the influence of different conditions on the preparation of C4 olefins by ethanol coupling. Firstly, we use Spearman correlation coefficient [1,2]to analyze the effect of different time on ethanol conversion at a given temperature and catalyst. Then, the effects of temperature on ethanol conversion and C4 olefin selectivity under different catalyst combinations are discussed. Multiple linear regression model[3,4,5] was used to explore the effects of different catalyst combinations and temperature on ethanol conversion and C4 olefin selectivity.

2.1. Spearman Correlation Coefficient Analysis

By plotting the given data, it can be seen that when the temperature and catalyst combination are constant at 350 ℃, the time is negatively correlated with the ethanol conversion. Within 400 ℃, with the increase of temperature, under the catalysis of the same kind of catalyst combination, the conversion of ethanol shows a broken line upward trend and the selectivity of C4 olefins also shows an upward trend. In order to verify this conclusion again, we draw the Spearman correlation coefficient to calculate the correlation between the conversion of ethanol, the selectivity of C4 olefins and temperature.

Spearman correlation coefficient is defined as Pearson correlation coefficient between grades. Assuming that X and Y are two groups of data, the calculation formula of Spearman (grade) correlation coefficient is:

$$r_s = 1 - \frac{6\sum_{i=1}^{n} d_i^2}{n(n^2-1)} \tag{1}$$

where d_i is grade difference between $X_i$and Y_i. Using equation 1-1, the Spearman correlation coefficient between ethanol conversion and temperature, and the selectivity of C4 olefins and temperature can be calculated.

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2.2. Multiple Linear Regression Model

We divided the experiment into two groups, A and B. The difference between the two groups lies in the different loading methods of raw materials. In order to study the correlation between different catalyst combinations and temperatures, ethanol conversion and C4 olefin selectivity, and achieve the purpose of predicting dependent variables through independent variables, the univariate linear regression model is first introduced. Assuming that x is an independent variable and y is a dependent variable, the following linear relationship is satisfied:

$$y_i = \beta_0 + \beta_1 x_i + \mu_i \tag{2}$$

β_0 and β_1 is the regression coefficient, μ_i is the disturbance term that cannot be observed and meets certain conditions, so that the predicted value is

$$\hat{y}_i = \hat{\beta}_0 + \hat{\beta}_1 x_i \tag{3}$$

$$\hat{\beta}_0, \hat{\beta}_1 = \underset{\beta_0,\beta_1}{\arg min} \left(\sum_{i=1}^{n} (y_i - \hat{y}_i)^2\right) = \underset{\beta_0,\beta_1}{\arg min} \left(\sum_{i=1}^{n} \left(y_i - \hat{\beta}_0 - \hat{\beta}_1 x_i\right)^2\right) \tag{4}$$

leting $\hat{\mu}_i = y_i - \hat{\beta}_0 - \hat{\beta}_1 x_i$, we have

$$\hat{\beta}_0, \hat{\beta}_1 = \underset{\beta_0,\beta_1}{\arg min} \left(\sum_{i=1}^{n} (\hat{\mu}_i)^2\right). \tag{5}$$

Since our research involved two independent variables and two dependent variables, we optimize model 1-5 into multiple linear regression model.

Set$x_1, x_2 \cdots, x_p$and the observed value is $x_{i1}, x_{i2} \cdots, x_{ip}$and observed value y corresponding to dependent variable y_i satisfy the relation:

$$y_i = \beta_0 + \sum_j \beta_j x_{ij} + \varepsilon_i,\ i = 1,2,\cdots,n; j = 1,2,\cdots,p \tag{6}$$

The observed value y_i corresponding to the dependent variable y can be obtained from equation 1-6.

Firstly, calculate the data, calculate the average value, maximum value and other relevant quantities, and then calculate the value of statistic F

$$F = S_1^2/S_2^2 \sim F(n_1 - 1, n_2 - 1) \tag{7}$$

The F distribution was used to test the joint significance of the regression coefficient (i.e$\beta_1 = \beta_2 = \cdots = \beta_k = 0$). After calculating the significance level, look up the F distribution table to obtain the acceptance domain, so as to obtain the probability p falling within the confidence interval, and then conduct t-test on the statistics. If the p value is less than 0.05, it means that under the 95% confidence level, the correlation of the regression coefficient is significant.

Based on the univariate linear regression model and f hypothesis test, the multivariate linear regression model is derived. Assuming that there is a multiple linear regression model between the dependent variable and the independent variable, take y1 of the experimental group with the concentration of 200mg 1wt% Co / SiO2 - 200mg HAP ethanol of 1.68ml/min as an example

$$y1 = \beta_0 + \beta_1 x1 + \beta_2 x2 + \beta_3 x3 + \beta_4 x4 + \beta_5 x5 + \beta_6 A1 \quad (8)$$

Solve with Stata software, find F, the probability p corresponding to F, and judge whether the model regression is ideal. In the table, "**" indicates significant correlation at level 0.01 and "*" indicates significant correlation at level 0.05. Considering that y1 may be related to the ratio of x3 and x4, introducing Co / SiO2 and HAP charge ratio d1 instead of x3 and x4, y1 can be expressed as

$$y1 = \beta_0 + \beta_1 x1 + \beta_2 x2 + \beta_3 d1 + \beta_5 x5 + \beta_6 A1 \quad (9)$$

3. Results and Discussion

3.1. Analysis Conclusion of Spearman Correlation Coefficient

Through the analysis of Spearman correlation coefficient, it can be concluded that when the temperature is constant at 350℃, under the same catalyst combination, the ethanol conversion decreases with the increase of time, as shown in Figure 1. The selectivity of ethylene and acetaldehyde increases and the selectivity of fatty alcohol decreases. The conversion rate of ethylene and acetaldehyde is positively correlated and negatively correlated with the conversion rate of fatty alcohol with carbon number of 4-12, as shown in Figure 2. It shows that with the increase of reaction time, the ethylene and acetaldehyde produced by the reaction inhibit the formation of fatty alcohols with carbon number of 4-12, which has little effect on the formation of other substances. From the Spearman correlation coefficient in Table 2, it can be concluded that there is a significant correlation between ethanol conversion and temperature, and the selectivity of C4 olefins and temperature. Within 400 ℃, with the increase of temperature, under the catalysis of the same kind of catalyst combination, the conversion of ethanol shows a broken line upward trend, and the selectivity of C4 olefins also shows an upward trend.

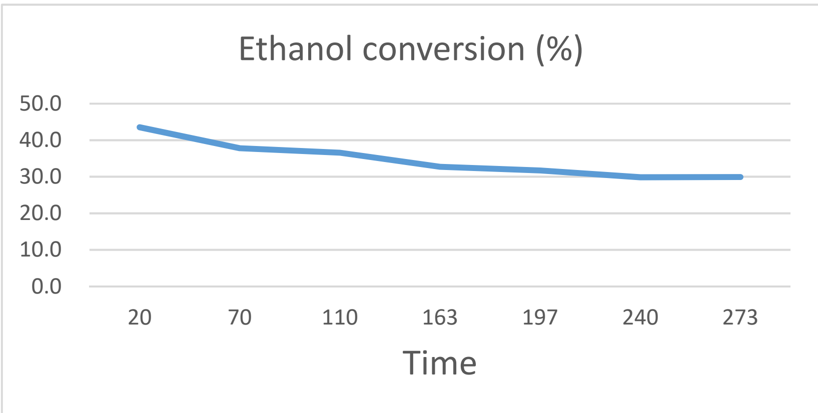

Figure 1. Relationship between ethanol conversion rate and time

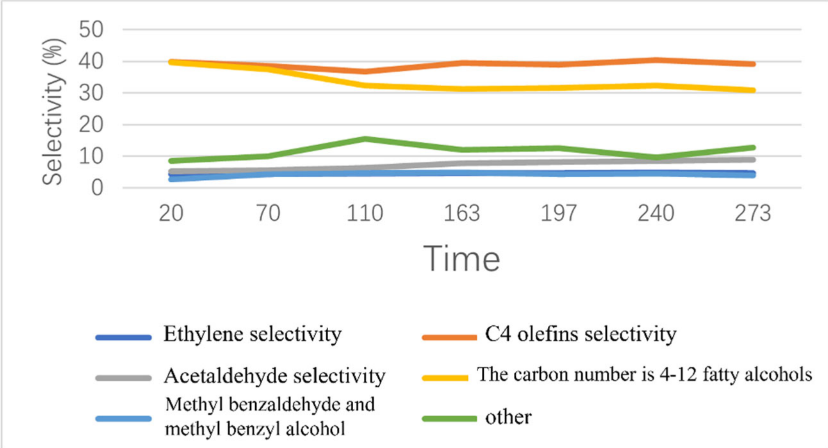

Figure 2. Relationship between selectivity of other products and time

Table 2. Spearman coefficient of ethanol conversion and temperature, C4 olefin selectivity and temperature

Spearman														
	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	A11	A12	A13	A14
N	5	5	7	6	6	5	5	5	5	5	5	5	5	5
Temperature and ethanol conversion (%)	1.000**	1.000**	1.000**	1.000**	0.943**	0.900*	1.000**	1.000**	1.000**	1.000**	1.000**	1.000**	1.000**	1.000**
Temperature and C4 olefin selectivity (%)	0.900*	0.900*	0.964**	0.943**	1.000**	1.000**	1.000**	1.000**	1.000**	0.700	1.000**	1.000**	1.000**	1.000**
**At the level of 0.01 (two tailed), the correlation is significant* At the level of 0.05 (two tailed), the correlation is significant.														

3.2. Conclusion of Multiple Linear Regression Model and Hypothesis Test

Using multiple linear regression model and hypothesis test, the following conclusions can be drawn:

(1) Under feeding mode A, according to table 3, for ethanol conversion y1, the relevant variables are temperature x1, ethanol addition rate x5 and catalyst support type A1. The loading ratio d1 of CO / SiO2 and HAP has a greater influence than the amount x3 of CO / SiO2 and the amount x4 of HAP. Among them, temperature x1 has the greatest influence on ethanol conversion y1. When other conditions remain unchanged, each rise of 1°C can increase ethanol conversion by 0.36%. The ethanol conversion rate decreased by 8.75% with the increase of ethanol addition rate of 1ml / min; Using HAP as catalyst carrier can increase the ethanol conversion by 15.00% compared with quartz sand. For C4 olefin conversion y2, the relevant variables are temperature x1, CO loading x2, amount of CO / SiO2 x3, ethanol addition rate x5 and catalyst support type A1. Under other conditions, the amount of CO / SiO2 x3 has a greater impact than Co / SiO2 and HAP loading ratio d1. Among them, the amount of CO / SiO2 added x3 has the greatest impact on the selectivity y2 of C4 olefins. Every increase of 1°C can increase the ethanol conversion by 0.18%, every increase of 1wt% of CO load will reduce the C4 olefin conversion by 3.63%, every increase of 1mg of CO / SiO2 will increase the C4 olefin conversion by 0.14%, and every increase of 1ml / min of ethanol addition speed will reduce the C4 olefin conversion by 4.12%, Using HAP as catalyst carrier can increase the conversion of C4 olefins by 11.26% compared with quartz sand.

Table 3. Correlation between y1 and dependent variables in group A

y1	Regression coefficient β	P>t	Standard regression coefficient
x1	0.3592767	0**	0.780256
x2	-0.2164429	0.829	-0.0122759
x3	-0.0515943	0.626	-0.1588169
x4	0.1438272	0.177	0.431905
x5	-8.747602	0.001**	-0.2062155
A1	14.97608	0.032**	0.1542515
β0	-99.99396	0	.
F = 46.25, probability corresponding to F, P = 0.0000			

(2) Under feeding mode B, according to table 4, for ethanol conversion y1, the relevant variables are temperature x1, Co / SiO2 and HAP loading x3. Among them, the temperature x1 has a great influence on the ethanol conversion y1. Under other conditions unchanged, the ethanol conversion can be increased by 0.28% for every rise of 1°C, and 0.07% for every increase of 1mg Co / SiO2 and HAP loading. For C4 olefin conversion y2, the relevant variables are temperature x1, Co / SiO2 and HAP charge x3; The temperature x1 has a great influence on the selectivity y2 of C4 olefins. When other conditions remain unchanged, the conversion rate of C4 olefins can be increased by 0.89% for every 1°C increase; For every 1mg of CO / SiO2 and HAP, the C4 olefin conversion rate increases by 0.07%.

Table 4. Correlation between y1 and dependent variables in group B

y1	Regression coefficient β	P>t	Standard regression coefficient
x1	0.2812172	0**	0.8304101
x3	0.1515682	0.003**	0.287962
x5	-2.336282	0.605	-0.0463039
β0	-79.17895	0	.
F = 44.03, probability corresponding to F, P = 0.0000			

4. Conclusion

After studying the effects of different conditions on the preparation of C4 olefins by ethanol coupling, the conversion of ethanol and the selectivity of C4 olefins increased in a broken line with the increase of temperature. When the temperature is constant at 350℃, the longer the time, the lower the conversion rate of ethanol, the selectivity of ethylene and acetaldehyde increases, and the selectivity of fatty alcohol decreases. The conversion rate of ethylene and acetaldehyde is positively correlated, and negatively correlated with the conversion rate of fatty alcohol with carbon number of 4-12. It shows that with the increase of reaction time, the ethylene and acetaldehyde produced by the reaction inhibit the formation of fatty alcohols with carbon number of 4-12, and have little effect on the formation of other substances. Temperature, ethanol addition rate and the type of catalyst all have an impact on ethanol conversion, among which temperature has the greatest impact on ethanol conversion. For C4 olefins, the influencing factors are temperature, CO loading, amount of CO / SiO2, rate of ethanol addition and type of catalyst, among which the amount of CO / SiO2 has the greatest influence on the selectivity of C4 olefins.

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