Research on C4 Olefins Prepared by Ethanol Coupling

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Abstract: In this paper, the effects of catalyst combination and temperature on the preparation of C4 olefins by ethanol coupling were studied. Firstly, using Spearman correlation coefficient, it is found that there is a strong correlation between temperature and ethanol conversion and temperature and C4 olefin selectivity under most catalyst combinations. With the increase of time, the ethanol conversion showed a downward trend, and the ethylene selectivity gradually tended to be flat. The number of the experimental catalyst combination was A1 calculated by European distance method. Finally, the regression model is established by OLS, and the multiple regression model is obtained by using the method of “OLS + robust standard error”. It was found that ethanol concentration had the greatest effect on ethanol conversion and temperature had the greatest effect on C4 olefin selectivity.

Keywords: Spearman correlation coefficient, multiple regression analysis

1. Introduction

Nowadays, ethanol has become a new raw material for the production of C4 olefins. In the production and preparation process, different combinations of catalysts (i.e. the combination of CO loading, Co/SiO2 and HAP loading ratio, ethanol concentration) and temperature will directly or indirectly affect the selectivity of C4 olefins and the yield of C4 olefins. Therefore, the combination of catalysts is designed to consider the influence of different temperature conditions on the target variables, therefore, it is of great significance and value to further explore the process conditions for the preparation of C4 olefins by ethanol catalytic coupling.

2. Determination of catalyst combination

2.1 Analyze the correlation between the three by using the linear relationship diagram

Considering that there are many catalyst combinations in this chemical experiment, and a large amount of data such as ethanol conversion of each reaction and selectivity of different reaction products need to be recorded at different temperatures, in order to avoid data recording errors and affect the subsequent discussion. We use Excel to calculate the sum of selectivity of reaction products of different catalyst combinations at different temperatures, and the result is 100%, that is, the data record is correct.

In order to explore the relationship among ethanol conversion, C4 olefin selectivity and temperature in each catalyst combination, we first judge whether there is a linear correlation between the two through the linear relationship diagram.

We found that the temperature and ethanol conversion of catalyst combination number A4, the ethanol conversion of number A14 were linearly related to the selectivity of C4 olefins, and the other two were nonlinear or non obvious linear.

We can intuitively see that the temperature of catalyst combination No. B6 is linearly related to the selectivity of C4 olefins, and the other two are nonlinear or non obvious linear.
2.2 Establishment of Spearman correlation coefficient model

From the previous analysis, it can be seen that only a small part of the two variables of catalyst combination have linear correlation, and most of them are nonlinear. Considering that the data are small samples, we use Spearman correlation coefficient to describe the correlation degree between the three.

First, we define X and y as two sets of variables, and then the Spearman correlation coefficient is:

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

(1)

Where \( d_i^2 \) is grade difference between \( X_i \) and \( Y_i \).

Since the data size \( n \leq 30 \) is a small sample, we judge the hypothesis test of Spearman correlation coefficient (original hypothesis \( H_0 : r_s = 0 \), alternative hypothesis \( H_1 : r_s \neq 0 \)) according to the critical value table of Spearman rank correlation. As shown in the following table:

**Table 1: Critical values related to Spearman grade.**

<table>
<thead>
<tr>
<th>n</th>
<th>Significance level of two tailed test</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.10</td>
</tr>
<tr>
<td>4</td>
<td>1.000</td>
</tr>
<tr>
<td>5</td>
<td>0.900</td>
</tr>
<tr>
<td>6</td>
<td>0.829</td>
</tr>
<tr>
<td>7</td>
<td>0.714</td>
</tr>
</tbody>
</table>

Where \( n \) is the number of recorded temperature values. When \( n = 7 \), the sample correlation coefficient \( R \geq 0.929 \) is called high correlation; When \( 0.829 \leq R \leq 0.886 \), it is called low correlation, and other times it is medium correlation.

We know that for catalyst group A2, there is a significant correlation between temperature and ethanol conversion, but the correlation between temperature and \( C_4 \) olefin selectivity is not high. For catalyst group A4, temperature has a significant correlation with ethanol conversion, while temperature has a strong correlation with \( C_4 \) olefin selectivity, ethanol conversion and \( C_4 \) olefin selectivity. For catalyst groups A14, B1 and B6, there are significant correlations between temperature and ethanol conversion, temperature and \( C_4 \) olefin selectivity, as well as ethanol conversion and \( C_4 \) olefin selectivity.

Comprehensive analysis, we get:

(1) For catalyst groups A1 and A2, the correlation between temperature and ethanol conversion is strong, and the correlation between temperature and \( C_4 \) olefin selectivity, ethanol conversion and \( C_4 \) olefin selectivity is small;

(2) For the catalyst groups A3, A7, A8, A9, A11, A12, A13 and A14, the correlation among temperature, ethanol conversion and \( C_4 \) olefin selectivity is strong;

(3) For catalyst group A4, the correlation between temperature and ethanol conversion is strong, and the correlation between temperature and \( C_4 \) olefin selectivity, ethanol conversion and \( C_4 \) olefin selectivity is medium;

(4) For the catalyst group, the correlation between \( A5 \) temperature and \( C_4 \) olefin selectivity is strong, and the correlation between temperature and ethanol conversion, ethanol conversion and \( C_4 \) olefin selectivity is medium;

(5) For the catalyst group, \( A6 \) temperature has a strong correlation with \( C_4 \) olefin selectivity, and the correlation between temperature and ethanol conversion, ethanol conversion and \( C_4 \) olefin selectivity is small;

(6) For the catalyst group, \( A10 \) temperature has a strong correlation with ethanol conversion, and there is no correlation between temperature and \( C_4 \) olefin selectivity, as well as ethanol conversion and \( C_4 \) olefin selectivity.

(7) For the catalyst groups B1, B2, B3, B5, B6 and B7, there is a strong correlation among temperature, ethanol conversion and \( C_4 \) olefin selectivity.
(8) For the catalyst group, B4 temperature has a strong correlation with ethanol conversion, but there is no correlation between temperature and C$_4$ olefin selectivity, as well as ethanol conversion and C$_4$ olefin selectivity.

2.3 Analyze test results

It can be seen intuitively that with the increase of time, the ethanol conversion and carbon number are 4-12, the selectivity of fatty alcohols generally shows a downward trend, the selectivity of acetaldehyde generally shows a slow upward trend, the selectivity of ethylene, methylbenzaldehyde and methylbenzyl alcohol gradually tends to be flat, and the selectivity of C4 olefins and the percentage of other products fluctuate greatly. Among them, the conversion of ethanol remains unchanged and the selectivity of C4 olefins changes little between 240 and 273min, so we can think that the chemical reaction reaches equilibrium at 273min.

It is known that when the catalyst combination is 350 degrees, the ethanol conversion is 29.9 and the C4 olefin selectivity is 39.04. In order to determine which catalyst combination the catalyst combination is, we judge the catalyst combination through the Euclidean distance. Let $a = 29.9$, $b = 39.04$, $a_i, b_i$ is the ethanol conversion and C4 olefin selectivity of combination I, respectively:

$$d_i = \sqrt{(a - a_i)^2 + (b - b_i)^2},$$

Finally, we calculate that when $i = A1$, the result is the smallest, that is, $d_{A1}$. The value of $A1$ is the smallest, so the catalyst combination is the catalyst combination numbered A1.

3. Influence analysis of catalyst

3.1 Data preprocessing

In order to study the effects of different catalyst combinations and temperatures on ethanol conversion and C$_4$ olefin selectivity, we divided the catalyst combinations into seven variables: two loading methods, CO loading, Co/SiO$_2$ mass, HAP mass, quartz sand mass, ethanol concentration and temperature. The ethanol conversion and C$_4$ olefin selectivity were used as dependent variables for regression analysis.

Since quartz sand is used for A11 and HAP is used for other catalysts, the influence of catalyst combination A11 at different temperatures has been analyzed earlier. Therefore, we clear this group of data.

Reorganize the data of all variables and make descriptive statistics with Stata. The following table is the statistical table of quantitative data and qualitative data.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Obs</th>
<th>Mean</th>
<th>Std. Dev.</th>
<th>Min</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co load</td>
<td>109</td>
<td>1.440367</td>
<td>1.183851</td>
<td>0.5</td>
<td>5</td>
</tr>
<tr>
<td>CoSiO$_2$</td>
<td>109</td>
<td>99.63303</td>
<td>70.97048</td>
<td>10</td>
<td>200</td>
</tr>
<tr>
<td>HAP</td>
<td>109</td>
<td>99.63303</td>
<td>70.97048</td>
<td>10</td>
<td>200</td>
</tr>
<tr>
<td>Ethanol concentration</td>
<td>109</td>
<td>1.473578</td>
<td>0.5277266</td>
<td>0.3</td>
<td>2.1</td>
</tr>
<tr>
<td>temperature</td>
<td>109</td>
<td>315.5963</td>
<td>52.24021</td>
<td>250</td>
<td>450</td>
</tr>
</tbody>
</table>

Variable description: Co load(Catalyzer1), CoSiO$_2$ mass(Catalyzer2), HAP mass(Catalyzer3), Ethanol concentration(Catalyzer4), temperature(Temperature), mode I($Way_1$), mode II ($Way_2$).

3.2 Explore the impact of various factors on ethanol conversion

In order to study the influence of each variable on ethanol conversion, this paper makes this variable as a dependent variable.

Due to the existence of qualitative data, we introduce two dummy variables $Way_1$ and $Way_2$ for this loading method. This paper constructs the following model:

$$\text{conversion} = \alpha^{(1)} + \sum \beta_i^{(1)} \times \text{Catalyzer}_i^{(1)} + \lambda_1^{(1)} \times \text{Temperature}^{(1)} + \lambda_2^{(1)} \times \text{Rate}^{(1)} + \varepsilon_i^{(1)}.$$
In this paper, Stata is used to estimate the coefficients through OLS (ordinary least squares estimation method), and the method of "OLS + robust standard error" is used to solve the heteroscedasticity problem. The multiple linear regression equation is as follows:

\[ Conversion = 0.11 \text{Catalyzer}3 - 8.66 \text{Catalyzer}4 + 0.347 \text{Temperature} - 82.63. \]  

According to multiple linear regression analysis, the variable that has the greatest impact on ethanol conversion is the ethanol concentration in the catalyst combination. When the mass of HAP increased by 0.11 mg, the conversion increased by 1% on average. When the temperature increases by 0.34°C, the conversion increases by 1% on average.

3.3 Explore the influence of various factors on C4 olefin selectivity

In order to study the effects of different factors on the selectivity of C4 olefins, we chose this variable as the dependent variable. This paper constructs the following model:

\[ Proportion = a_1^{(2)} + \sum \beta_n^{(2)} \times \text{Catalyzer}_n^{(2)} + \lambda_1^{(2)} \times \text{Temperature}^{(2)} + \lambda_2^{(2)} \times \text{Rate}^{(2)} + \epsilon_i^{(2)}. \]  

Repeat the above operation to calculate:

\[ Proportion = 7.18 \text{Way}_1 - 2.84 \text{Catalyzer}1 + 0.19 \text{Temperature} + 0.59 \text{Rate} - 42.99. \]  

According to the mathematical model, when other variables remain unchanged, the C4 olefin selectivity increases by an average of 1% for every 0.19°C increase in temperature. With other variables unchanged, the selectivity of C4 olefins increased by an average of 1% every time the co loading decreased by 1 unit. The selectivity of C4 olefins increased by 1% on average for each increase of 1 unit of CO / SiO2 and HAP. The C4 olefin selectivity of loading mode I is 7.18% higher than that of loading mode II.

3.4 Using two factor analysis of variance to explore the impact

The chemical experiment is an interactive experiment. In order to ensure the integrity and preciseness of the paper, we further analyze the data by analysis of variance on the basis of the previous paper. Through the observation of the data, we take the feed ratio of Co, SiO2 and HAP in the catalyst combination as an observation value and conduct comparative experimental analysis in combination with other observation values.

3.4.1 Analyze A

(1) The interaction between Co loading and temperature is discussed.

By analyzing the data, we found that the co loading of the catalyst combinations numbered A1, A2, A4 and A6 is different, while the other observed values are the same. According to the idea of control variables, using two-way ANOVA, we can see that the influence of CO loading on ethanol conversion is not significant, and the influence of temperature on ethanol conversion is very significant, but the interaction effect is not significant. Co loading and temperature have significant effects on C4 olefin selectivity, but the interaction effect is not significant.

Similarly, we conclude that the co loading of catalyst combinations numbered A9 and A10 is different, while the other observed values are the same. According to the idea of control variables, using two-way ANOVA, it can be seen that the influence of CO loading on ethanol conversion is not significant, and the influence of temperature on ethanol conversion is not very significant, but the interaction effect is not significant. The effect of CO loading and temperature on C4 olefin selectivity is very significant, but the interaction effect is not significant.

(2) The interaction between ethanol concentration and temperature is discussed.

For the catalyst combinations numbered A7, A8, A9 and A12, the ethanol concentration is different, but the other observed values are the same. According to the idea of control variables, using two-way ANOVA, it can be seen that the influence of ethanol concentration and temperature on ethanol conversion is very significant, and the interaction effect is also very significant. The effect of ethanol concentration and temperature on C4 olefin selectivity is also very significant, and the interaction effect is also very significant.
For the catalyst combinations numbered A1 and A3, the ethanol concentration is different, while the other observed values are the same. According to the idea of control variables, using two-way ANOVA, it can be seen that the influence of ethanol concentration and temperature on ethanol conversion is very significant, and the interaction effect is also very significant. The effect of ethanol concentration on C4 olefin selectivity is very significant, and the effect of temperature on C4 olefin selectivity and interaction effect are not significant.

For the catalyst combinations numbered A2 and A5, the ethanol concentration is different, while the other observed values are the same. According to the idea of control variables, using two-way ANOVA, it can be seen that the ethanol concentration and temperature have a significant impact on the ethanol conversion and C4 olefin selectivity.

(3) The interaction between charge ratio and temperature is discussed.

For the catalyst combinations numbered A12, A13 and A14, the loading ratio is different, while the other observed values are the same. According to the idea of control variables, using two-way ANOVA, it can be seen that the loading ratio and temperature have significant effects on ethanol conversion. The effects of loading ratio and temperature on C4 olefin selectivity are very significant, and the interaction effect is very significant.

(4) The interaction between catalyst quality and temperature is discussed.

For the catalyst combinations numbered A3 and A8, the catalyst quality is different, but the other observed values are the same. According to the idea of control variables, using two-way ANOVA, it can be seen that the catalyst quality has no significant effect on ethanol conversion and C4 olefin selectivity, and the temperature has a significant effect on ethanol conversion and C4 olefin selectivity, but the interaction effect is not significant.

3.4.2 Analyze B

(1) The interaction between catalyst quality and temperature is discussed.

For the catalyst combinations numbered B1, B2, B3, B4 and B6, the catalyst quality is different, but the other observed values are the same. According to the idea of control variables, using two-way ANOVA, it can be seen that the influence of catalyst quality on ethanol conversion and C4 olefin selectivity is not significant, and the influence of temperature on ethanol conversion and C4 olefin selectivity is very significant, but the interaction effect is not significant.

(2) The interaction between ethanol concentration and temperature is discussed.

For the catalyst combinations numbered B1 and B5, the catalyst quality is different, but the other observed values are the same. According to the idea of control variables, using two-way ANOVA, it can be seen that the catalyst quality has no significant effect on ethanol conversion and C4 olefin selectivity, and the temperature has a significant effect on ethanol conversion and C4 olefin selectivity, but the interaction effect is not significant.

For the catalyst combinations numbered B2 and B7, the catalyst quality is different, but the other observed values are the same. According to the idea of control variables, using two-way ANOVA, it can be seen that the catalyst quality has no significant effect on ethanol conversion and C4 olefin selectivity, and the temperature has a significant effect on ethanol conversion and C4 olefin selectivity, but the interaction effect is not significant.

4. Model Evaluation

4.1 Advantages of the model

1) Spearman correlation coefficient can be used to measure the correlation between nonlinear related variables.

2) Analysis of variance can not only find out the factors that have a significant impact on ethanol conversion and C4 olefin selectivity through data analysis, but also explore the significance of the interaction between various factors, so as to obtain the influence degree of various factors on the experimental results.
4.2 Disadvantages of the model

The data provided may not be comprehensive enough, and the results of this analysis may differ slightly from the actual situation.

References