Research on Efficient Preparation of Ethanol and C4 Olefins Based on Polynomial Regression and Two-Way ANOVA

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Abstract. C4 olefins and ethanol are essential chemical raw materials, and efficiently preparing them is a valuable topic. In this paper, in order to explore the influence of different catalyst combinations and temperatures on ethanol conversion and C4 olefin selectivity, firstly, for each catalyst combination, by observing the scatter diagram of ethanol conversion, C4 olefin selectivity and temperature, a polynomial regression model of no more than three times was established. Then, 42 regression equations corresponding to 21 catalyst groups were obtained. Twenty-one kinds of catalyst combinations were grouped by controlling variables. After grouping, the relationship between a single factor and temperature was discussed. Non-interactive two-way ANOVA judged the significance of a single factor, and the control variables among different groups were compared to determine the strong significant factors of ethanol conversion rate and C4 olefin selectivity. For judging the significance of temperature, the input rate of ethanol is ignored based on grouping, and the same catalyst combination is regarded as a repeated test. By single factor analysis, it is finally found that the temperature has higher significance to ethanol conversion rate and 400℃, while the selectivity to C4 olefins is much lower.

Keywords: polynomial regression, control variable method, two-way ANOVA

1. Introduction

C4 olefin, as an important basic chemical raw material, can be used to make gasoline additives and other products. [1] It is widely used in chemical and pharmaceutical production. Ethanol is the raw material to produce C4 olefins. In the process of C4 olefins preparation, [2] the combination of catalysts (i.e., the combination of Co loading, Co/SiO2, and HAP loading ratio, ethanol concentration) and temperature will affect the selectivity and yield of C4 olefins. [3] Therefore, through the combination design of catalysts, the selectivity of by-products such as ethylene, acetaldehyde, and fatty alcohol with 4-12 carbon atoms can be reduced, and the yield of C4 olefins can be improved, which is of great significance and value for the production of C4 olefins. [5]

2. Temperature Factor Model Based on Polynomial Regression

A) the relationship between ethanol conversion rate and temperature

Import the data into MATLAB, use cftool fitting toolbox in MATLAB, [6] observe the scatter plot.

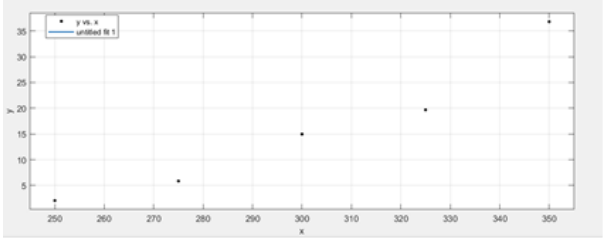


Figure 1 Catalyst group A1, scatter diagram of temperature and ethanol conversion rate

According to the scatter trend in Figure 1, choose quadratic polynomial fitting [7]

$$f(x) = 0.002545x^2 - 1.194x + 141.8(\ R^2: 0.9797) \quad (1)$$

The fitting result is shown in Figure 2.

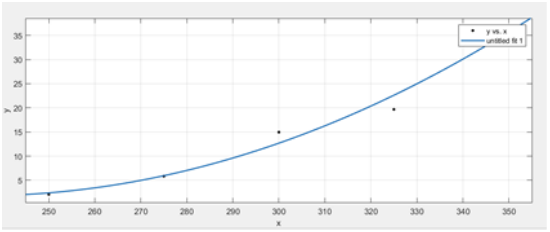


Figure 2 Catalyst group A1, fitting of temperature and ethanol conversion rate

B) Relationship between C4 olefin selectivity and temperature

Import the data into MATLAB, use the cftool fitting toolbox, and observe the scatter plot.

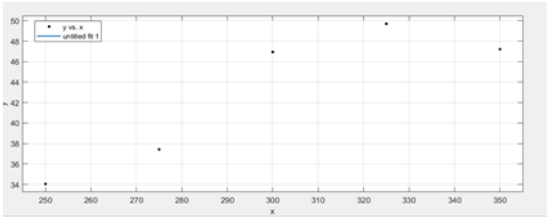


Figure 3 Scatter diagram of catalyst group A1, temperature and C4 olefin selectivity

Based on the scatter trend in Figure 3, choose quadratic polynomial fitting.

$$f(x) = -0.002113x^2 + 1.422x - 190.8(\ R^2: 0.916) \tag{2}$$

The fitting result is shown in Figure 4.

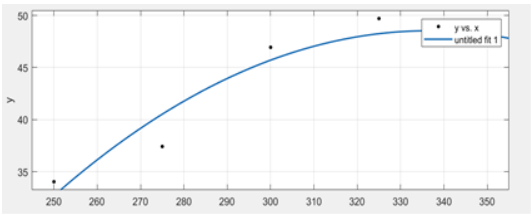


Figure 4 Catalyst group A1, temperature and C4 olefin selectivity fitting

3. Strong Significant Factors Model Based on Two-Way ANOVA

Because 21 kinds of catalyst combinations are different, the components of each catalyst combination are grouped by using the method of controlling variables [8] to reduce the influencing factors.

Table 1. Control variable grouping

variable	Grouping after controlling variables
Ethanol concentration	A1-A3, A2-A5, A7-A8-A9-A12, B1-B5, B2-B7
Co load	A9-A10, A1-A2-A4-A6
Loading mode	A9-B5, A12-B1
Gross mass	B1-B2-B3-B4-B6, A1-A12, A3-A8
Co/SiO2 and HAP charge ratio	A12-A13-A14

Because there is no repeated experiment in the two-factor group, the two-way ANOVA without interaction is chosen. [9]

Two-way ANOVA model without interaction: [10]

Suppose $\gamma_{ij} = 0$, then

$$\mu_{ij} = \mu + \alpha_j + \beta_i, i = 1,2, \dots, r, j = 1,2, \dots, s \tag{3}$$

At this point,

$$\begin{cases} X_{ij} = \mu + \alpha_j + \beta_i + \varepsilon_{ij}, \\ \sum_{j=1}^{s} \alpha_j = 0, \sum_{i=1}^{r} \beta_i = 0, \\ \varepsilon_{ij} \sim N(0, \sigma^2), i = 1,2, \dots, r, j = 1,2, \dots, s. \end{cases} \tag{4}$$

The hypothesis to be tested for this model is

$$H_{01}: \alpha_j = 0 (j = 1,2, \dots, s) \tag{5}$$

$$H_{02}: \beta_i = 0 (i = 1,2, \dots, r) \tag{6}$$

Test statistics are derived by a method similar to the one-way ANOVA model.
remember

$$\bar{X} = \frac{1}{rs} \sum_{i=1}^{r} \sum_{j=1}^{s} X_{ij} \tag{7}$$

$$\bar{X}_{i\cdot} = \frac{1}{s} \sum_{j=1}^{r} X_{ij} \tag{8}$$

$$\bar{X}_{\cdot j} = \frac{1}{r} \sum_{i=1}^{r} X_{ij} \tag{9}$$

$$S_T = \sum_{i=1}^{r} \sum_{j=1}^{s} \left(X_{ij} - \bar{X}\right)^2 \tag{10}$$

Where: S_T is the total variation of all experimental data, called the total sum of squares, which is decomposed:

$$\begin{aligned} S_T &= \sum_{i=1}^{r} \sum_{j=1}^{s} \left(X_{ij} - \bar{X}\right)^2 \\ &= \sum_{i=1}^{r} \sum_{j=1}^{s} \left(X_{ij} - \bar{X}_{i-} - \bar{X}_{\cdot j} + \bar{X}\right)^2 + s \sum_{i=1}^{r} (\bar{X}_i - \bar{X})^2 + r \sum_{j=1}^{s} \left(\bar{X}_{\cdot j} - \bar{X}\right)^2 \\ &= S_E + S_A + S_B \end{aligned} \tag{11}$$

It can be verified that the cross terms in the above sum of squares decomposition are all 0, where

$$S_E = \sum_{i=1}^{r} \sum_{j=1}^{s} \left(X_{ij} - \bar{X}_{i\cdot} - \bar{X}_{\cdot j} + \bar{X}\right)^2 \tag{12}$$

$$S_A = r \sum_{j=1}^{s} \left(\bar{X}_{\cdot j} - \bar{X}\right)^2 \tag{13}$$

$$S_B = s \sum_{i=1}^{r} (\bar{X}_i - \bar{X})^2 \tag{14}$$

where $\sum_{j=1}^{s} \left(\bar{X}_{\cdot j} - \bar{X}\right)^2$ reflects $\bar{X}_{\cdot 1}, \bar{X}_{\cdot 2}, \dots, \bar{X}_{\cdot s}$ degree of difference. The test statistic for the hypothesis shown in Eq.8 shall be taken as the ratio of S_A to S_E.

When H_{01} was established:

$$F_A = \frac{\frac{S_A}{s-1}}{\frac{S_E}{(r-1)(s-1)}} \sim F\big(r-1,(r-1)(s-1)\big) \tag{15}$$

When H_{02} was established:

$$F_B = \frac{\frac{S_B}{s-1}}{\frac{S_E}{(r-1)(s-1)}} \sim F\big(r-1,(r-1)(s-1)\big) \tag{16}$$

The inspection principle is

$F_A < F_\alpha\big(s-1,(r-1)(s-1)\big)$, accept H_{01}, otherwise, reject H_{01} (17)

$F_B < F_\alpha(r-1,(r-1)(s-1))$, accept H_{02}, otherwise, reject H_{02} (18)

Using MATLAB programming to solve, we can get the P-value and its significance as follows:

Table 2. Factors affect the significance

variable	group	Ethanol conversion rate		C4 olefin selectivity	
		P value	significance	P value	significance
Ethanol concentration	A1-A3	0.0014	Very significant	0.0031	Very significant
	A2-A5	0.1342	Not significant	0.0019	Very significant
	A7-A8-A9-A12	5.51E-07	Very significant	0.0056	Very significant
	B1-B5	0.6925	Not significant	0.0484	outstanding
	B2-B7	0.0805	Not significant	0.0872	Not significant
Co load	A9- A10	0.0729	Not significant	0.0377	outstanding
	A1-A2-A4-A6	0.0177	outstanding	0	Very significant
Loading mode	A9-B5	0.0807	Not significant	0.0377	outstanding
	A12-B1	0.3585	Not significant	0.1096	Not significant
gross mass	B1-B2-B3-B4-B6	0.0041	Very significant	0.0205	outstanding
	A1-A12	0.1498	Not significant	0.001	Very significant
	A3-A8	0.0203	outstanding	0.1298	Not significant
Co/SiO2 and HAP charge ratio	A12-A13-A14	0.0105	outstanding	0.0027	Very significant

Comparison of temperature significance by one-way ANOVA:

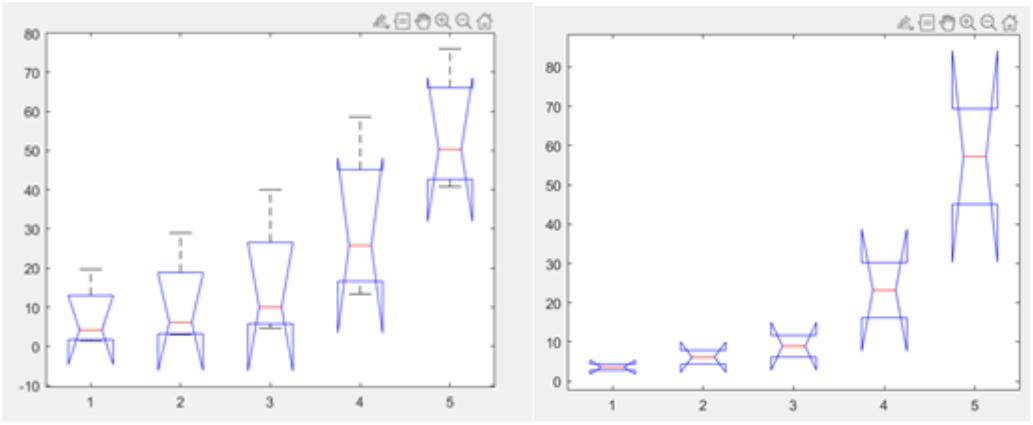


Figure 5 One-way ANOVA box diagram (different charging methods, ethanol conversion rate)

It can be seen from the figure that under different charging methods, P is 0.0031 and 0.0019, respectively, which shows that the ethanol conversion rate is significantly related to temperature, and the significant temperature is 400℃.

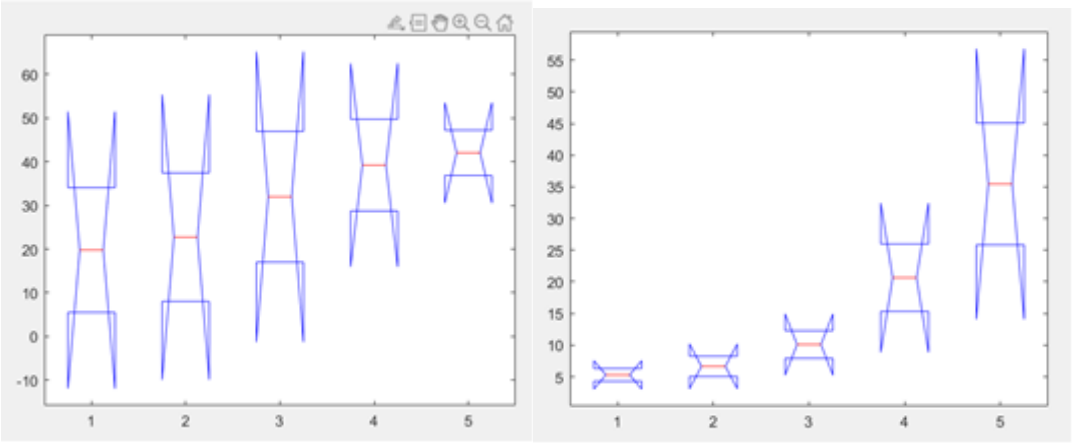


Figure 6 One-way ANOVA box diagram (different charging methods, C4 selectivity)

It can be seen from the figure that under different charging modes, P is 0.6708 and 0.0361, respectively, which shows that C4 selectivity has no significant correlation with temperature.

To sum up, the temperature has higher significance for ethanol conversion rate and lower significance for C4 olefin selectivity.

4. Conclusion

C4 olefins and ethanol are essential chemical raw materials, and efficiently preparing them is a subject with substantial industrial and economic value. To explore the influence of different catalyst combinations and temperatures on the ethanol conversion rate and C4 olefin selectivity, considering the classification of 21 groups of experiments, the number of strictly controlled variable groups is large, and the samples between experiments are independent. Therefore, the variance analysis method, which is not limited by the number of groups, is adopted, and the two-factor variance analysis of ethanol concentration, Co loading, loading method, total mass, Co/SiO2, and HAP loading ratio and temperature is carried out respectively. To ensure that the significance of each factor can be accurately expressed under the premise of controlling variables.

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