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Research on the optimum conditions for preparing C4 alkenes by ethanol coupling

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Abstract: In this paper,the experimental problem of preparing C4 olefin by ethanol coupling was solved by curve fitting and control variables,and the influence of classification variables on the experimental results was studied by using two-factor analysis of variance model. Finally, the data conclusions were summarized and analyzed. The relatively complete relationship between each catalyst combination and temperature and C4 olefin yield was obtained, and the influence of each variable on the experiment was analyzed. For some variables, the curve fitting method was used to find the best experimental data points and explore the best combination of catalyst and temperature under the same experimental conditions.

1. Background

The reaction[1] of ethanol to C4 olefins needs to undergo dehydrogenation, dehydration and condensation, and the reaction mechanism is different with different accelerators. At present, the reaction of ethanol to butadiene is more studied. There are two main reaction mechanisms: Prince Mechanism and hydroxylaldehyde condensation mechanism. According to Prince Mechanism, acetaldehyde and ethylene are respectively generated by reactant ethanol under the catalytic action of alkaline and acidic sites, and then the nucleophilic addition reaction is generated into butadiene. The mechanism of hydroxyl aldehyde condensation proposed that carboanion nucleophilic addition of carbonyl carbon, alkaline site catalyzed ethanol dehydrogenation and alcohol-aldehyde coupling, surface acidic site inhibited ethanol dehydration and ensured crotonol dehydration into 1,3-butadiene[2].

2. Data preparation and model preparation

Curve fitting was used to analyze and solve the problem.MMA software was used for curve fitting and function solving to observe its suitability. The curve fitting results and fitting function are shown below[3].

Ethanol conversion rate function can be obtained:

$$y = 38.854 + \frac{108.645}{x} - 0.0372029x \tag{1}$$

C4 olefin selectivity function:

$$y = \frac{188404.+37821.5x-26.5523x^2}{2920.33+1044.38x-1.x^2} \quad (2)$$

C4 olefin yield function:

$$y = 14.0707 + \frac{70.0918}{x} - 0.00987821x \quad (3)$$

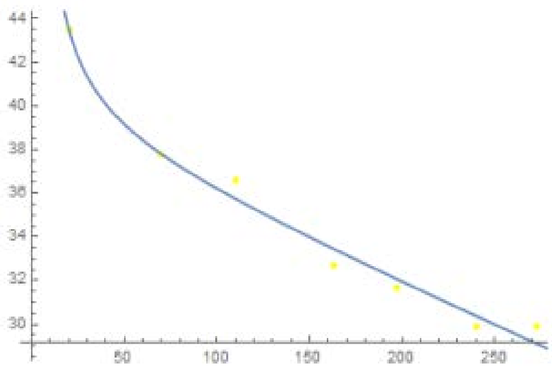

Figure 1: Ethanol conversion rate fitting curve

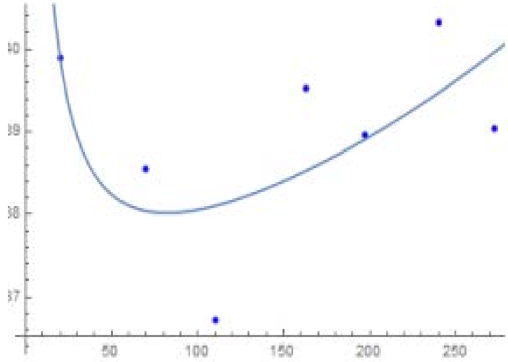

Figure 2: C4 olefins selective fitting curve

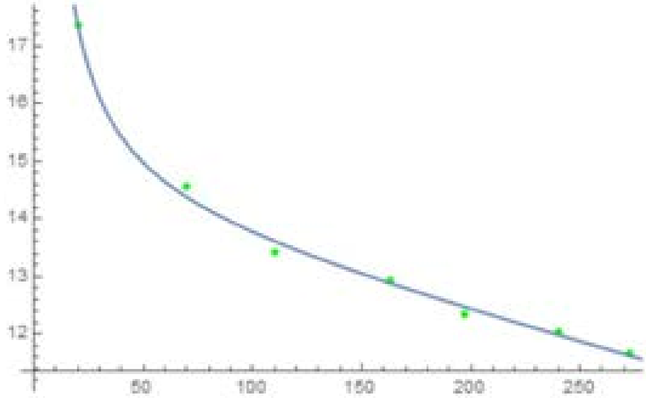

Figure 3: C4 olefin yield fitting curve

In the above fitting curve, the fitting degree of ethanol conversion is 0.985, and the fitting degree of C4 olefin yield is 0.996. The closer the fitting degree is to 1, the better the fitting degree is. It can be seen that the above curve fitting effect is high. According to Fig.1 and fig.3, ethanol conversion rate and C4 olefin yield decrease with the increase of time.It can be seen from Fig.2 that the C4 olefins selectivity decreases first and then increases with time, but the degree is very small.In summary, the optimal reaction time was 20min for a given catalyst combination at 350℃.

Categorical variables refer to variables that differ only in kind but not in size.In the experiment, the method of charging and the choice of HAP and quartz sand were classified variables. For categorical variables, two-factor analysis of variance can be used to test whether these categorical variables have significant experimental effects[4]. The factors are corresponding classification variables and temperature.

The catalyst support and temperature were taken as the two changing factors in the two-factor test, and they were set as A and B, with two and five different levels respectively, denoted as A1, A2 and B1, B2, B3, B4, B5. Only the main effect of factors A and B is analyzed by combining the interaction with the experimental error as the error.

Assume $X_{ij} \sim \mathrm{N}(\mu_{ij}, \sigma^2)$, where $X_{ij}(\mathrm{i} = 1,2; \mathrm{j} = 1,2, \cdots, 5)$ is independent of each other and μ_{ij}, σ^2 is an unknown parameter,the model is obtained:

$$\begin{cases} X_{ij} = \mu_{ij} + \varepsilon_{ij} \\ \varepsilon_{ij} \sim (0, \sigma^2) \end{cases} \tag{4}$$

The sum of squares can be obtained by the formula:

$$SS_A = \sum_{i=1}^{k} n_i \left(\overline{X_\iota} - \overline{\overline{X}}\right)^2 \tag{5}$$

$$SS_B = \sum_{i=1}^{n_i} k \left(\overline{X_\iota} - \overline{\overline{X}}\right)^2 \tag{6}$$

$$SS_T = \sum_{i=1}^{k} \sum_{j=1}^{n_i} \left(\overline{X_{\iota J}} - \overline{\overline{X}}\right)^2 \tag{7}$$

The mean square sum is obtained:

$$MS_A = \frac{SS_A}{df_A} \tag{8}$$

$$MS_B = \frac{SS_B}{df_B} \tag{9}$$

$$MS_E = \frac{SS_E}{df_E} \tag{10}$$

Establish F value:

$$F_A = \frac{MS_A}{MS_E} \tag{11}$$

$$F_B = \frac{MS_B}{MS_E} \tag{12}$$

The critical value of F value is obtained:

$$F_\alpha\big((\alpha - 1), (a - 1)(b - 1)\big) \tag{13}$$

$$F_\alpha\big((b - 1), (a - 1)(b - 1)\big) \tag{14}$$

Finally, it is concluded that the F value is not very large for catalyst carrier because the data error is too large. Therefore, the hypothesis cannot be rejected, that is, whether there is an influence factor is uncertain. For the loading method, regardless of the control group, the yield can be considered significantly insignificant.

3. Model conclusions

(1) With the selection of multiple experimental data of temperature, the yield of C4 olefin was low before 350℃, and other products were generated. When the temperature exceeded 350℃, the yield of C4 olefin increased rapidly, and the yield was the highest when the temperature was 400℃, so 400℃ was selected.

(2) Selection of charging method:Although it was concluded from the anOVA model that different charging methods A and B had no effect on the experiment, the comparison of experimental data showed that the effect of charging method A on the yield of C4 olefin increased under certain reaction conditions, so the charging method A was selected.

(3) Selection of catalyst carrier: Other reaction conditions are the same, HAP in the use of less than quartz sand, the experimental results of each group of data are far better than quartz sand, it can be seen that HAP is very suitable as catalyst carrier, and in this experiment with Co/SiO2 synergistic

effect is strong, so the selection of catalyst carrier HAP.

(4) Selection of Co/SiO2 and HAP charging ratio: Through comparison and analysis of charging ratio under different reaction conditions, when Co/SiO2 and HAP charging ratio is 1:1, the catalytic performance of ethanol conversion to C4 olefin is the best, so the selection of Co/SiO2 and HAP charging ratio is 1:1.

4. Evaluations of Model

4.1 Advantages

(1) The model reflects and describes the problem to a certain extent, and further simplifies the problem so that it is easy to understand and operate.

(2) By using covariance analysis method, the influence of covariable on dependent variable is separated from independent variable, which can further improve experimental accuracy and statistical test sensitivity.

4.2 Disadvantages

(1) In order to simplify the calculation and make the obtained results more ideal, some verified minor influencing factors are ignored in the model.

(2) The conclusions obtained from the treatment of experimental influencing factors are not accurate enough.

References

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