Research On the Reaction Process of Ethanol Coupling to C4 Olefins Based on Multi-Objective Programming Model

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Abstract: In this paper, a statistical regression model is established to analyze and study the relationship between temperature, catalyst combination and catalytic performance, and a multi-objective programming model is established to obtain the optimal process conditions. Firstly, after filtering and completing the data, it is found that there is a nonlinear correlation with the change of temperature. Then one-way ANOVA was used to calculate that the effect of temperature on ethanol conversion and C4 olefin selectivity was significantly positively correlated. Then, using the method of controlling variables, taking different catalyst combinations and temperature as independent variables, ethanol conversion and C4 olefin selectivity as dependent variables, and further splitting different catalyst combinations into three independent variables. The data were analyzed by two-way variance model to obtain the specific significance. Finally, taking the maximum C4 olefin yield as the goal, it is decomposed into two objective functions: the maximum ethanol conversion and the maximum C4 olefin selectivity, and a multi-objective programming model for the optimal C4 olefin yield is established. Compared with other traditional solving methods, evolutionary algorithm does not need the reference of weight dimension or ideal value, which is more suitable for the situation of this problem. The fast non dominated sorting genetic algorithm based on elite strategy (NSGA-II) is used to solve the problem

1. Introduction

Ethanol is a clean energy with a wide range of sources, so it is of great economic and environmental significance to use ethanol as raw materials to produce high value-added downstream products. For example, ethanol can be used to prepare C4 olefins by coupling reaction, which is a chemical raw material widely used in pharmaceutical production. In this process, the combination and temperature of three kinds of catalysts, which are composed of Co loading [1], Co/SiO2 and HAP loading ratio and ethanol concentration, will also have an effect on the selectivity of C4 olefins and the yield of C4 olefins. In this paper, by analyzing the experimental results of different catalyst combinations, the technological conditions for the preparation of C4 olefins by catalytic coupling of ethanol were explored.

2. Construction of a model for the effect of temperature on ethanol conversion and C4 olefin selectivity

2.1 Model preparation

In this paper, the experimental data of related reactions are collected. First, the experimental data are filtered, leaving only the key data lines: temperature, ethanol conversion, C4 olefin selectivity.

The observation data found that the temperature settings of the 21 groups of experiments collected were not completely consistent. In order to smooth the curve, supplement the data of ethanol conversion and C4 olefin selectivity under the conditions of partial temperature and catalyst combination. Then the spline interpolation method is used to estimate the approximate value of ethanol conversion and C4 olefin selectivity at the unknown point (325 degrees A6~A14, B1~B2) through the value of ethanol conversion and C4 olefin selectivity at a limited number of points. For the missing data of 400 degree A1 and A2 groups, we use the time series prediction method to calculate. After preliminary data processing, it is found that the conversion of ethanol and the selectivity of C4 olefins are related to temperature.

When the processed data are drawn into a broken line graph, it is obvious that ethanol conversion rate and C4 olefins selectivity are correlated with temperature.

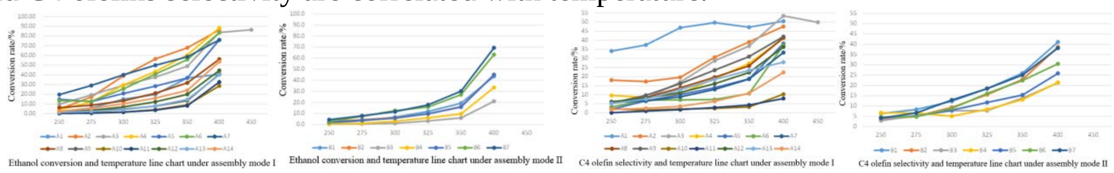


Fig. 1 Processed data

2.2 Model building

This paper uses single factor analysis of variance, which can be used to analyze whether there is a significant difference in the mean value of multiple groups of samples under the influence of a single control variable. In the variable view of SPSS, the variables "ethanol conversion", "selectivity of C4 olefins" and "temperature type" are established to represent the specific values of ethanol conversion and the specific values of C4 olefin selectivity and temperature under each catalyst combination, respectively. In the "temperature type" variable, use "1, 2, 3, 4, 5, 6" to represent "temperature 250, 275, 300, 325, 350, 400 degrees" to enter the relevant data into each variable.

The results show that different temperature types have a significant effect on the specific value of ethanol conversion under each catalyst combination. In addition, the trend test results in linear form are also given in this table. the part of intergroup variation that can be explained (compared) by temperature type is 31023.925, and 4797.953 is explained (deviation) by other factors. and the part of intergroup variation that can be explained by temperature type is very significant. Then, based on the multiple comparison results, it can be seen from the average difference that the temperature type has a significant effect on ethanol conversion under each catalyst combination, that is, 400 degrees has the most significant effect on ethanol conversion. Here, take 250°C 275°C 300°C as an example [4].

Tab. 1 Single factor analysis of variance

(I) Temperature type(°C)	(J) Temperature type	Average difference (I-J)	Standard error	Significance	95% Confidence interval	
					Lower limit	Upper limit
250	275	-3.08952	4.53991	0.497	-12.0782	5.8992
	300	-9.12952*	4.53991	0.047	-18.1182	-0.1408
	325	-15.51381*	4.53991	0.001	-24.5025	-6.5251
	350	-24.45286*	4.53991	0	-33.4416	-15.4642
	400	-50.22095*	4.53991	0	-59.2097	-41.2323
275·	250	3.08952	4.53991	0.497	-5.8992	12.0782
	300	-6.04	4.53991	0.186	-15.0287	2.9487
	325	-12.42429*	4.53991	0.007	-21.413	-3.4356
	350	-21.36333*	4.53991	0	-30.352	-12.3746
	400	-47.13143*	4.53991	0	-56.1201	-38.1427
300	250	9.12952*	4.53991	0.047	0.1408	18.1182
	275	6.04	4.53991	0.186	-2.9487	15.0287
	325	-6.38429	4.53991	0.162	-15.373	2.6044
	350	-15.32333*	4.53991	0.001	-24.312	-6.3346
	400	-41.09143*	4.53991	0	-50.0801	-32.1027

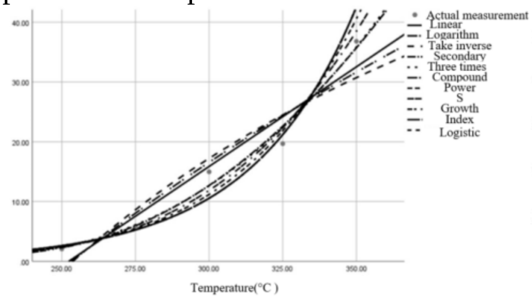
Similarly, we also obtained the results of one-way ANOVA for the selectivity of C4 olefins. Different temperature types have a significant effect on the specific value of C4 olefin selectivity under each catalyst combination. The significant effect of temperature type on the selectivity of C4 olefins under each catalyst combination showed an increasing trend, which was consistent with the results of ethanol conversion analysis.

2.3 The relationship between temperature and ethanol conversion and C4 olefins selectivity

In order to further obtain a more specific relationship, we choose the appropriate curve type to fit the observed data through curve fitting, analyze the relationship between the two variables with the fitted curve equation, and compare the fitting degree of the curve equation to the observed value, namely the goodness of fit R^2 to determine the optimal fitting relationship, the calculation formula is as follows.

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

Then, after testing and calculating the R^2 of 11 models, such as linear model, logarithmic model, polynomial regression model, exponential model and logistic model, it is found that the R^2 of cubic polynomial regression model is the largest, indicating that there is a cubic polynomial regression relationship between temperature and ethanol conversion and C4 olefin selectivity.



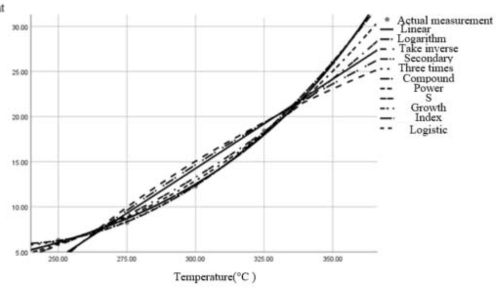


Fig. 2 Ethanol conversion curve fitting   Fig. 3 C4 olefin selectivity curve fitting

3. Effect of time on ethanol conversion and product selectivity

The conversion of ethanol will decrease with the increase of time, and the selectivity of C4 olefins is very stable and generally does not change with time. The selectivity of fatty alcohols with carbon number 4-12 was the highest at 20 minutes, and fluctuated and decreased with the increase of time. C4 olefins can be produced into ethylene by cracking reaction under certain conditions. In this test data, the catalyst conditions do not accord with the cracking reaction, so the selectivity of C4 olefins and ethylene fluctuates slightly, while ethanol can catalyze dehydrogenation to acetaldehyde, so the selectivity of acetaldehyde increases with the increase of time.

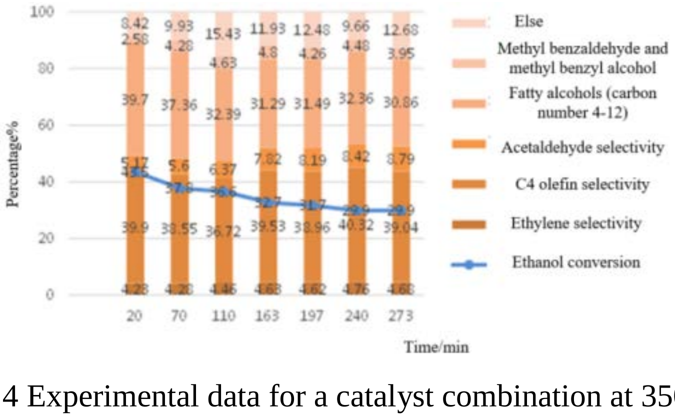


Fig. 4 Experimental data for a catalyst combination at 350 °C

4. Model of the effect of different reaction conditions on ethanol conversion and C4 olefin selectivity

Based on the basic idea of control variables, the data were divided into group An and group B according to the different loading modes. Secondly, we chose different catalyst combinations and temperature as independent variables, ethanol conversion and C4 olefin selectivity as dependent variables, and further divided different catalyst combinations into three independent variables: Co loading, Co/SiO2 and HAP loading ratio and ethanol concentration.

4.1 Effects of various variables on ethanol conversion and C _ 4 olefin selectivity under loading mode I

(a) Co load

We select A1, A2, A4 and A6 groups, and control the Co/SiO2 to HAP charging ratio of 200mg:200mg, ethanol concentration was controlled at 1.68mL /min, and Co loading was changed at 250°C, 275°C, 300°C, 325°C, 350°C and 400°C. Let μ be the total mean, α I be the effect of level Ai on the index, βj be the effect of level Bj on the index, γij be the interaction effect of level Ai and Bj on the index, the model table is:

$$\begin{cases} x_{ijk} = \mu + \alpha_i + \beta_j + \gamma_{ij} + \varepsilon_{ijk} \\ \sum_{i=1}^{r} \alpha_i = 0, \sum_{j=1}^{s} \beta_j = 0, \sum_{i=1}^{r} \gamma_{ij} = \sum_{j=1}^{s} \gamma_{ij} = 0 \\ \varepsilon_{ijk} \sim N\left(0, \sigma^2\right), i = 1, \cdots, r, j = 1, \cdots, s, k = 1, \cdots, t \end{cases} \tag{2}$$

With the increase of Co load, there is a positive correlation with ethanol conversion and a negative correlation with C4 olefin selectivity. The change of temperature has a positive correlation with ethanol conversion and C4 olefin selectivity. However, Co load is not significant to the dependent variable, while temperature is significant to the dependent variable.

(b) Co/SiO2 and HAP loading ratio

According to the data, it can be found that Co/SiO2 and HAP filling ratio are 1:1 in group A, but the quality input is different. Therefore, we divided them into the high-quality Co/SiO2 / HAP charge ratio group and the low-quality Co/SiO2 / HAP charge ratio group, and carried out more detailed analysis in these two cases. As a result, when the mass of Co/SiO2 and HAP [2] increased, the ethanol conversion and the selectivity of C4 olefins increased significantly. And the positive correlation between the selectivity of high-quality Co/SiO2 and HAP charge ratio to C4 olefins is significant.

(c) The ethanol concentration

We divided A2 and A5 groups into high quality Co/SiO2 and HAP charge ratio groups to study the influence of ethanol concentration on the dependent variable, and divided A7, A8 and A9 groups into low quality Co/SiO2 and HAP charge ratio groups to study the influence of ethanol concentration on the dependent variable. The experimental results of A2 and A5 groups showed that under the significant influence of high-quality Co/SiO2 and HAP loading ratio [3], low ethanol concentration could promote ethanol conversion and inhibit the production of C4 olefins. Temperature had a positive correlation with ethanol conversion and C4 olefin selectivity, which were 0.808 and 0.806, respectively. The experimental results of A7, A8 and A9 groups showed that under the significant influence of low Co/SiO2 and HAP loading ratio, high ethanol concentration could inhibit the conversion of ethanol and promote the production of C4 olefins. The temperature has a positive correlation with ethanol conversion and C4 olefin selectivity, which is 0.701 and 0.923 respectively. It has a positive correlation with ethanol conversion and a significant positive correlation with C4 olefin selectivity.

4.2 Effects of various variables on ethanol conversion and C _ 4 olefin selectivity under loading mode II

Co loading was set at 1%, so we did not take it as a variable and only studied the effects of temperature, Co/SiO2 and HAP loading ratio, ethanol concentration on ethanol conversion and C4 olefins selectivity

Co/SiO2 and HAP loading ratio

Groups B1, B2, B3, B4 and B6 were selected to change the charge ratio of Co/SiO2 and HAP when the concentration of ethanol was 1.68ml/min and the temperature was 250,275,300,325,350,400 degrees respectively.

It can be concluded that the charge ratio of Co/SiO2 and HAP is positively correlated with ethanol conversion and C4 olefin selectivity. With the increase of the ratio of-15Co/SiO2 to HAP at 1:1, the ethanol conversion and C4 olefin selectivity will be promoted, and the increase of temperature will promote the ethanol conversion and C4 olefin selectivity.

The ethanol concentration

Select B1 and B5, control the Co/SiO2 and HAP charging ratio of 50mg: 50mg, also control the concentration of ethanol under six temperature conditions, and conduct two-factor analysis of variance for the extracted data.

With the increase of ethanol concentration, it has a weak inhibitory effect on ethanol conversion and C4 olefin, and the increase of temperature can promote ethanol conversion and C4 olefin selectivity.

5. The establishment of multi-objective programming model

5.1 The establishment of the model

From the results of the previous analysis, we can get the following results:

$$Y1 = 0.0022 + 0.0003x_3^3 - 0.0287x_2^2x_1 + 2.9209x_2^2x_3 - 0.1984x_3^2x_2 - 0.0018x_1x_2 + 0.5022x_2X_3.$$

$$Y2 = 0.0004 + 0.0004x_3^3 - 0.0249x_2^2x_1 + 3.9824x_2^2x_3 - 0.1028x_3^2x_2 - 0.0011x_1x_2 + 0.1586x_2X_3$$

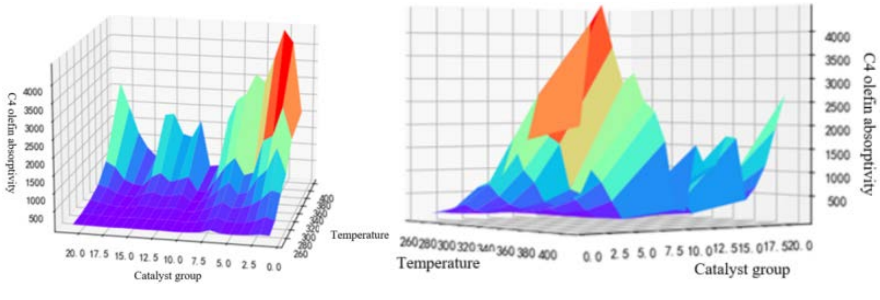


Fig.5 Three-dimensional relationship diagram and extreme data of catalyst combination, temperature, and C4 olefin yield

By observing the three-dimensional map, we find that there is a negative correlation between ethanol conversion and C4 olefin selectivity to a certain extent, so our objective function should be to maximize ethanol conversion and C4 olefin selectivity, from which the following mathematical models are established [5][6].

$$\begin{cases} \max\ f_1 = f(T_i,\ CoD_i,\ ChD_i,\ MD_i) \\ \max\ f_2 = f(T_i,(\sigma_i * CoD_i),(\omega_i * ChD_i),\ MD_i) \end{cases}$$

$$s.t.\begin{cases} T = T(t_1,t_2,t_3,t_4,t_5,t_6) \\ CoD = CoD(Cod_1,Cod_2,Cod_3,Cod_4) \\ ChD = ChD(Chd_1,Chd_2,Chd_3,Chd_4) \\ MD = MD(Md_1,Md_2) \end{cases} \quad (3)$$

Tab.2 Model symbols and meanings

Symbols		Represent meaning
t1		250
t2		275°C
t3		300°C
t4		325°C
t5		350°C
t6		400°C
other variables A1, A2, A4, A6 are the same, but the Co load is different.	Co1	1wt%Co/SiO2
	Co2	2wt%Co/SiO2
	Co3	0.5wt%Co/SiO2
	Co4	5wt%Co/SiO2
The other variables of A1 and A2 are the same, but the quality of loading ratio is different.	M1(high)	200mg 1wt%Co/SiO2-200mgHAP
	M2(low)	50mg 1wt%Co/SiO2-50mgHAP
The other variables of A2 A5 are the same, but the ethanol concentration is different (under the condition of high mass ratio).	Ch1	Ethanol concentration 1.68ml/min
	Ch2	Ethanol concentration 0.3ml/min
The other variables (A7, A8, A9) are the same, but the ethanol concentration is different (low mass ratio).）	Ch3	Ethanol concentration 0.3ml/min
	Ch4	Ethanol concentration 0.9ml/min
	Ch5	Ethanol concentration 2.1ml/min
x_5		HAP quality
MD /.x_4		Charge ratio of Co/SiO2 to HAP
ChD / x_3		Ethanol concentration
CoD / x_2		Co load
x_1		Temperature
Cod_1		0.5wt%Co/SiO2
Cod_2		1wt%Co/SiO2
Cod_3		1.5wt%Co/SiO2
Cod_4		2wt%Co/SiO2
Chd_1		0.3ml/min
Chd_2		0.9ml/min
Chd_3		1.68ml/min
Chd_4		2.1ml/min

Because in the previous chapter, it is concluded that the effect of loading mode Ⅰ is obviously better than that of charging mode Ⅱ, and the effect of high-quality loading ratio is obviously better than that of low quality, so the model can be further optimized.

$$\begin{cases} \max f_1 = f(T_i, CoD_i, ChD_i) \\ \max f_2 = f(T_i, (\sigma_i * CoD_i), (\omega_i * ChD_i)) \end{cases}$$
$$s.t. \begin{cases} 0 < CoD_i \le 0.1 \\ 0 < ChD_i < 2.5 \\ 0 < T_i < 450 \end{cases} \quad (4)$$

After controlling the variables, the effects of Co loading and ethanol concentration on ethanol conversion were graded. In this paper, the corresponding influence factor coefficient is set as follows:

$$\begin{aligned} & Cod_1 = 1.7, \ Cod_2 = 1.2, \ Cod_3 = 0.7, \ Cod_4 = 0.4 \\ & Chd_1 = 2, \ Chd_2 = 1.5, \ Chd_3 = 1, \ Chd_4 = 0.5 \end{aligned} \quad (5)$$

5.2 Solution of the model

In this paper, the fast non-dominated sorting genetic algorithm (NSGA-II) based on elite strategy is used to solve the problem. In Matlab, it can be solved by the function *gamultiobj* based on the fast non-dominated sorting elitist strategy genetic algorithm. The Pareto optimal solution obtained is:

Under the condition that there is no temperature limit, the yield of C4 olefin can be as high as possible when using the catalyst combination with Co/SiO2 / HAP loading ratio of 1:1, input mass of [194.08mg-205.19mg], Co loading of [0.54wt%-0.69wt%], ethanol concentration of [0.74ml/min-0.8ml/min] and temperature of [395.64 ℃-403.27 ℃]. This is consistent with the extreme data we have observed in the three-dimensional diagram, which shows that there is no problem in the solution process.

6. Conclusion

In this paper, based on the single factor analysis of variance, the ethanol conversion and C4 olefin selectivity produced by the combination of catalysts were taken as the experimental index and temperature as the factor. it was calculated that there was a significant positive correlation between the effect of temperature on ethanol conversion and C4 olefin selectivity. Then, based on the method of control variables, the data are divided into two charging modes I and II, respectively. The results showed that under I loading mode, Co loading was positively correlated with ethanol conversion and negatively correlated with C4 olefin selectivity; the quality of Co/SiO2 and HAP input was significantly positively correlated with ethanol conversion and C4 olefin selectivity; ethanol concentration was negatively correlated with ethanol conversion and positively correlated with C4 olefin selectivity. Under Ⅱ loading mode, the charge ratio of Co/SiO2 and HAP was positively correlated with ethanol conversion and C4 olefin selectivity, while ethanol concentration was negatively correlated with ethanol conversion and C4 olefin selectivity. Finally, the multi-objective programming method is adopted to maximize the yield of C4 olefins. Therefore, the fast non-dominated sorting genetic algorithm (NSGA-II) based on elite strategy is used to solve the problem. The optimal range of the solution is that the loading ratio of Co/SiO2 to HAP is 1:1, the mass is [194.08mg-205.19mg], the Co load is [0.54wt%-0.69wt%], the ethanol concentration is [0.74ml/min-0.8ml/min] and the temperature is [395.64 degrees-403.27 degrees].

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