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Research on the Preparation of C4 Olefins by Ethanol Coupling Based on Regression Analysis and Optimized Model

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Abstract:

As a green raw material to prepare C4 olefins, ethanol molecules have wide sources, clean and low in consumption with considerable economic and environmental benefits. For the sake of improving the yield of C4 olefins by changing catalyst combinations in ethanol coupling, several sets of controlled experiments under different catalyst and temperature conditions were designed in this paper to search the effect of different catalyst combinations and temperatures on the conversion rate of ethanol and the selection of C4 olefins. And based on regression analysis, we established the yield of C4 olefins about independent variables including the catalyst carrier, Co loading, total Co/SiO2, Co/SiO2 and HAP loading ratio, ethanol concentration and temperature, in accordance with experimental data. Then we optimized the model to further explore ways to increase C4 olefin production. In this study, selecting the appropriate catalyst combination is helpful to realize the stable and efficient production of C4 olefins.

***Keywords**: Ethanol coupling, Multiple regression, C4 Olefin yield model, Data fitting.*

I. INTRODUCTION

As an important chemical raw material, C4 olefins are widely used in the production of chemical products and pharmaceutical intermediates [1]. Due to the shortage of fossil resources and serious pollution in the development process, the traditional method of using fossil energy as raw material to produce C4 olefins is no longer advisable.

Ethanol has a extensive range of molecular sources, is clean and low-consumption, and has more considerable application prospects and economic benefits as a green raw material for the preparation of C4 olefins, and has received extensive attention at home and abroad [2]. After exploration, it was found that in the process of ethanol catalytic coupling to prepare C4 olefins, the temperature and catalyst combinations will comprehensively affect the selectivity and yield of C4 olefins [3].

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TABLE I. Catalyst Combination

<table>
<tr><th>catalyst type</th><th>Co loading</th><th>carrier</th><th>the loading ratio of Co/SiO_2 and HAP</th><th>The rate of addition of ethanol</th><th>catalyst type</th><th>Co loading</th><th>carrier</th><th>the loading ratio of Co/SiO_2 and HAP</th><th>The rate of addition of ethanol</th></tr>
<tr><td>A1</td><td>1 wt%</td><td rowspan="10">HAP</td><td rowspan="6">200mg : 200mg</td><td rowspan="2">1.68 ml/min</td><td>A12</td><td rowspan="10">1 wt%</td><td rowspan="10">HAP</td><td>50mg : 50mg</td><td rowspan="7">1.68 ml/min</td></tr>
<tr><td>A2</td><td>2 wt%</td><td>A13</td><td>67mg : 33mg</td></tr>
<tr><td>A3</td><td>1 wt%</td><td>0.9 ml/min</td><td>A14</td><td>33mg : 67mg</td></tr>
<tr><td>A4</td><td>0.5wt%</td><td>1.68 ml/min</td><td>B1</td><td>50mg : 50mg</td></tr>
<tr><td>A5</td><td>2 wt%</td><td>0.3 ml/min</td><td>B2</td><td>100mg : 100mg</td></tr>
<tr><td>A6</td><td>5 wt%</td><td>1.68 ml/min</td><td>B3</td><td>10mg : 10mg</td></tr>
<tr><td>A7</td><td>1 wt%</td><td rowspan="4">50mg : 50mg</td><td>0.3 ml/min</td><td>B4</td><td>25mg : 25mg</td></tr>
<tr><td>A8</td><td>1 wt%</td><td>0.9 ml/min</td><td>B5</td><td>50mg : 50mg</td><td>2.1 ml/min</td></tr>
<tr><td>A9</td><td>1 wt%</td><td rowspan="2">2.1 ml/min</td><td>B6</td><td>75mg : 75mg</td><td>1.68 ml/min</td></tr>
<tr><td>A10</td><td>5 wt%</td><td>B7</td><td>100mg : 100mg</td><td>0.9 ml/min</td></tr>
<tr><td>A11</td><td>1 wt%</td><td>Quartz sand</td><td>50mg :90mg</td><td>1.68 ml/min</td><td></td><td></td><td></td><td></td><td></td></tr>
</table>

In the course of preparing C4 olefins by ethanol coupling, the combination of catalyst combination (Co loading, Co/SiO_2 and HAP charge ratio, ethanol concentration) and emperature will have an effect not only on the selectivity of C4 olefins but also the yield of C4 olefin.

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Hence by rationally designing the catalyst combination, it is possible to explore the process conditions that are beneficial to the catalytic coupling of ethanol to prepare C4 olefins, which is of great importance and practicality.

In this paper, we prepare C4 olefins in the process of ethanol catalytic coupling, by changing the catalyst combination type and temperature, combined with the mathematical model, the experimental results were analyzed, and the catalyst combination conditions were optimized to obtain higher the yield of C4 olefin. The combination conditions of the catalysts are A1~A14, B1~B721, of which A and B are two different charging methods.

II. CORRELATIONS AND DATA FITTING

2.1 Correlation Analysis

The correlation coefficient is a statistical indicator designed by the statistician Pearson, and it is the quantity of the degree of correlation between the research variables, which is represented by the letter ρ in this paper. Regression analysis uses correlation coefficients to study the relationship between dependent and independent variables, and is usually used to find causal relationships between predictors.

$$\mathrm{p}_{x,y} = \frac{\mathrm{cov}(x,y)}{\sigma_x \sigma_y} = \frac{E\left[(x-x_i)(y-y_i)\right]}{\sigma_x \sigma_y} \quad (1)$$

Correlation coefficients were calculated for several sets of data of temperature and the rate of ethanol conversion, temperature and the selectivity of C4 olefins beneath 21 catalyst combinations, and a total of 19 sets of correlation coefficients were higher than 0.9, indicating a strong correlation.

In the catalyst experiments A1~A14 using the charging method I, as the temperature increased within a certain range, the rate of ethanol conversion and the selectivity of C4 olefins in disparate catalyst combinations almost showed an unabated trend, indicating that the higher the temperature, the better temperature can catalyze the ethanol coupling performance.

However, the selectivity of C4 olefins rises with the rise of temperature before 325°C and 400°C in the A1 and A3 catalyst combinations respectively, and has shown a downward trend at 350°C and 450°C, which may be higher. Temperature increases the selectivity of reaction by-products. It shows that the C4 olefin selectivity reaches the maximum before 350°C under A1 catalysis condition, while the C4 olefin selectivity reaches the maximum before 450°C under A2 catalysis condition. In the catalyst experiments B1 to B7 of charging mode II, the rate of ethanol conversion and the selectivity of C4 olefins both increased with the temperature rise when the temperature ranged from 250°C to 400°C.

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2.2 Establishment of Multiple Regressions

Taking the temperature as the abscissa, and taking the ethanol conversion and C4 olefin selectivity as the ordinate under each catalyst combination, the scatter diagrams are drawn as shown in Fig 1 and Fig 2. Similar trends in ethanol conversion and overall selectivity to C4 olefins with temperature were found for each catalyst combination.

Select the overall data to perform polynomial fitting, establish a regression model, and determine the specific functional relationship.

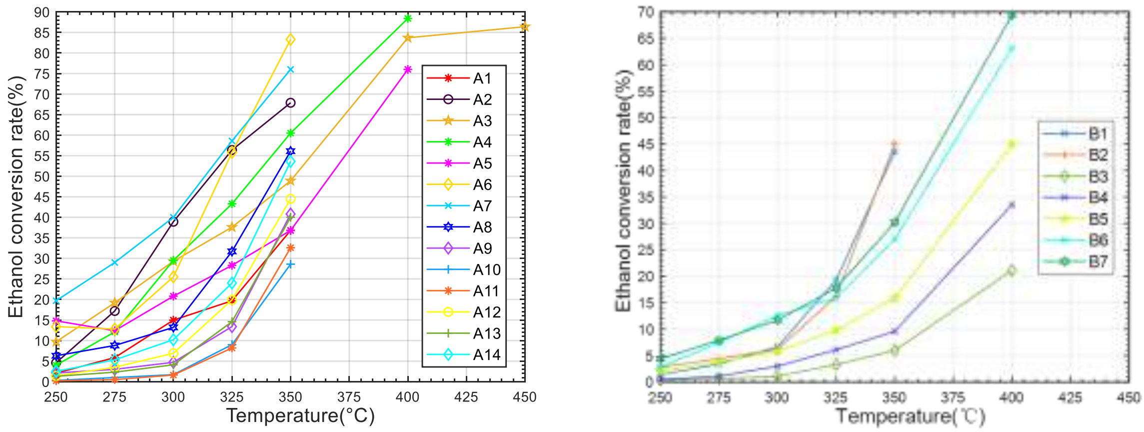

Fig 1: the relation between the rate of ethanol conversion and temperature

From Fig 1, it can be observed that the rate of ethanol conversion rises at 250-400 °C, that is, as the temperature increases, both the rate of ethanol conversion and the selectivity of C4 olefins early slow down and then increase. 300°C showed a turning point in the change, and after 400°C, the A3 group showed a slower ethanol conversion rate, similar to the S-curve of population growth.

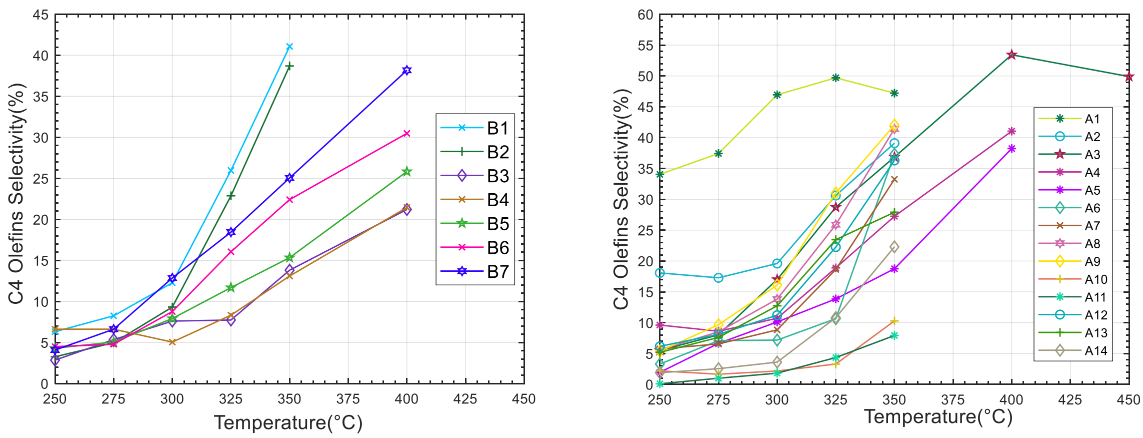

Fig 2: the relation between the selectivity of C4 olefins and temperature

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Similar to Fig 1, as the temperature increases, the selectivity of C4 olefins rises initially and later decreases, among which the A1 group is more sensitive to temperature, reaching a maximum at 325°C and then starting to decrease.

In addition, it can be seen that although the charging methods of groups A and B are ifferent, the conversion rate of ethanol and the selectivity of C4 olefins have similar changing trends.

III. ESTABLISHMENT OF THE OPTIMAL C4 OLEFINS YIELD MODEL

3.1 The Relationship between Each Factor and the Yield of C4 Olefins

For the sake of searching the relationship between the change of each component of the catalyst combinations and the yield of C4 olefins, the catalyst combination is classified under the principle of controlling the uniqueness of the catalyst variable, as shown in the following table.

TABLE II. Catalyst groups affecting the yield of C4 olefins

GROUP	CATALYST COMBINATION	CLASSIFICATION CRITERIA
y1	A1~A14, B1~B7	temperature
y2	A7 A8 A9 A12	rate of ethanol addition
y3	B1 B2 B3 B4 B6	Co/SiO2 & HAP charging ratio
y4	A1 A2 A4 A6	Co Loading

The yield of C4 olefins, which is the conversion rate of ethanol multiplied by the selectivity of C4 olefins, was calculated. Then the functional relationship between each influencing factor and the C4 olefin yield was analyzed separately in Fig 3~Fig6.

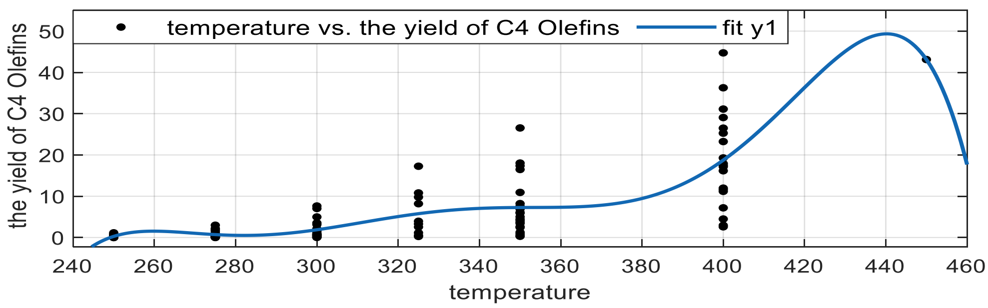

Fig 3: fitting graph about temperature vs. C4 Olefins

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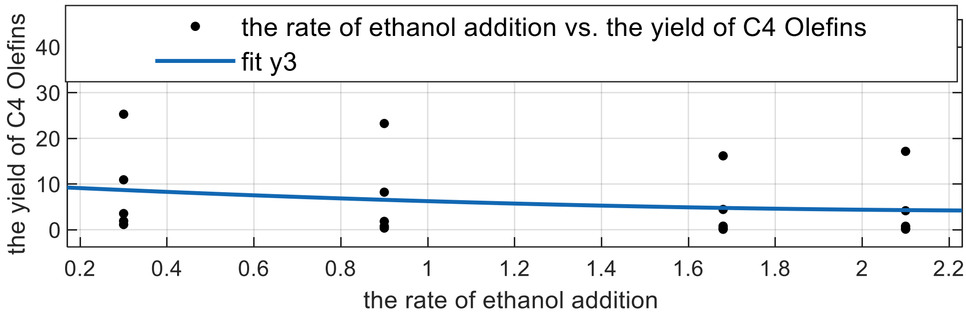

Fig 4: fitting graph about the rate of ethanol addition vs. C4 Olefins

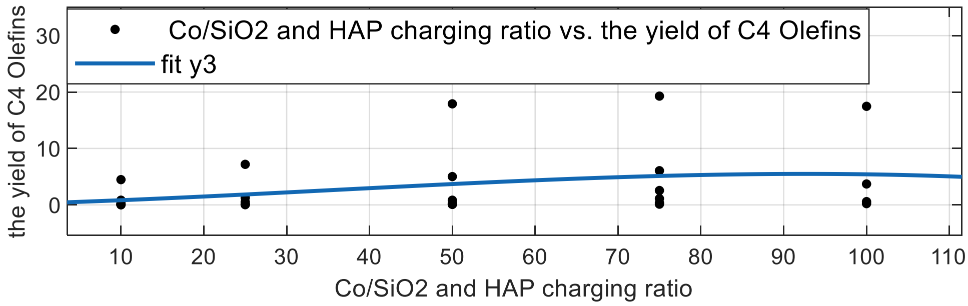

Fig 5: fitting graph about Co/SiO2 and HAP charging ratio vs. C4 Olefins

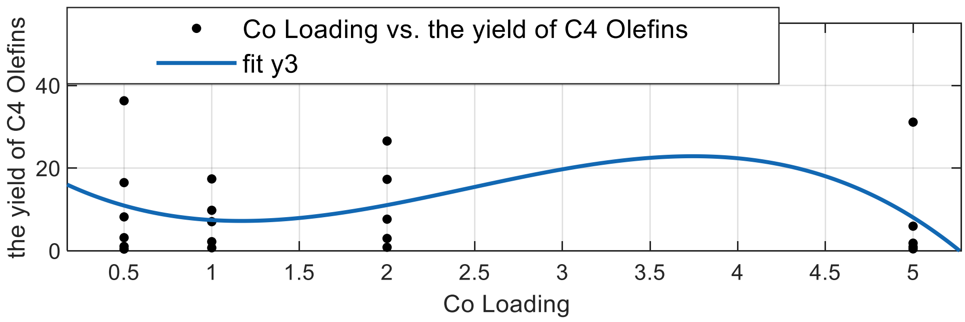

Fig 6: fitting graph about Co Loading vs. C4 Olefins

3.2 Optimal C4 Olefin Yield Model

3.2.1 The functional relationship between each factor and the yield of C4 olefins

Using the data screened by the above questions, a regression was performed to obtain a fitting graph and function of the effect of temperature on the yield of C4 olefins.

$$y_1 = 0.00001213x_1^2 - 0.006338x_1 + 0.8279 \qquad (2)$$

The effect of ethanol addition rate on the yield of C4 olefin is a function of the following,

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$$y_2 = -0.0072x_2^4 - 0.0236x_2 + 0.1148 \tag{3}$$

The effect of Co/SiO2 and HAP loading on the yield of C4 olefin is a function of the following,

$$y_3 = \frac{0.0009x_3(x_3 + x_5)}{10x_5} + 0.0171 \tag{4}$$

The effect of Co loading on the yield of C4 olefin is a function of the following,

$$y_4 = -0.0298x_4^2 + 0.1441x_4 + 0.0851 \tag{5}$$

3.2.2 Establishment of weights

Then, according to the data selected in the above questions, the correlation coefficients of temperature, ethanol addition rate, Co/SiO2 and HAP loading, Co loading and C4 olefin yield were calculated as 0.90136369, - 0.98187, 0.138009, - 0.63918. Then normalize the four correlation coefficients to get -2.58648,2.817502, -1.06516, and 1.83414 are the weights of the four influencing factors.

3.2.3 Derivation of the C4 olefin yield model

The expression of C4 olefin yield z is obtained by synthesizing the four influencing factors and their weights as follows:

$$\max z = -2.58648y_1 + 2.817502y_2 - 1.06516y_3 + 1.83414y_4 \tag{6}$$

Finally, we get $x1$, $x2$, $x3$, $x4$, $x5$ as decision variables, and the maximum C4 olefin yield as the objective function.

The equation of the temperature, rate of the ethanol addition, Co/SiO2 and HAP loading, and the numerical value of Co loading are the constraints of the model.

$$\begin{aligned} max\ z &= 0.0000313740024x_1^2 - 0.0202860144x_2^2 - 0.0000958644x_3^2 \\ &- 0.054657372x_4^2 + 0.01639311024x_1 - 0.0664930472x_2 \\ &+ 0.264299574x_4 - 0.0000958644x_5 - 1.6800264844 \end{aligned} \tag{7}$$

$$\text{s.t.} \qquad 250 < x_1 < 450 \tag{8}$$

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$$x_3 + x_5 - 10n = 0 \tag{9}$$

$$0.5x_5 < x_3 < 2x_5 \tag{10}$$

$$x_3 > 5 \tag{11}$$

$$x_5 > 5 \tag{12}$$

$$0.9 < x_4 < 2.1 \tag{13}$$

$$0.3 < x_2 < 2.1 \tag{14}$$

$$x_1, x_2, x_3, x_4, x_5 > 0 \tag{15}$$

n: an integer (16)

When the temperature is below 350 degrees, then change the above constraint 250 < x1 < 450 to 250 < x2 < 350.

Input the above function expressions and constraints into lingo for programming and solution. It is found that when the temperature is 259.9453 degrees, the ethanol addition rate is 0.3ml/min, the Co/SiO2 and HAP loading ratio is 0.256292, and the Co loading is 2.1wt%, the C4 olefin yields highest rate.

At the same time, we found that no matter how the experimental conditions were changed, the experimental temperature when the C4 olefin yield was the highest was lower than 350 degrees, so it was judged that when the temperature was less than 350 degrees, the experimental conditions when the C4 olefin yield was the highest were the same as above.

3.3 Sensitivity Analysis

Through the sensitivity analysis of the C4 olefin yield to the ethanol addition rate concentration, and by changing the parameters before the experimental variables, it is found that the ethanol addition rate concentration has a low sensitivity to the C4 olefin yield.

It can be seen from Fig 7 that the rate of ethanol addition is inversely related to the yield of C4 olefins, that is, to increase the yield of C4 olefins, the rate of ethanol addition should be reduced as much as possible. And the ethanol addition rate has a great influence on the absorption rate of C4 olefins, and the small change in the addition rate of ethanol can also cause a large change in the yield of C4 olefins.

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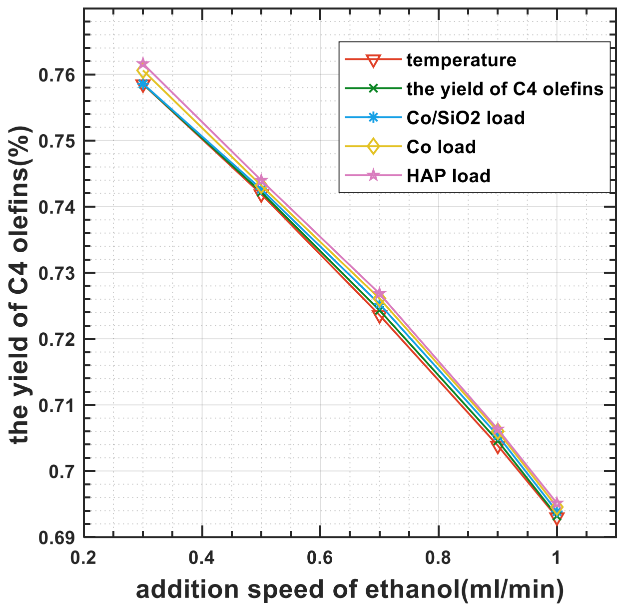

Fig 7: Sensitivity analysis

III. CONCLUSION

The effects of catalyst combination and temperature on ethanol conversion and C4 olefin selectivity are explored in this paper. Under the premise of controlling variables, we select the experimental group and the control group, establish a regression model to solve the specific functional relationship, and then establish regression models. The optimal catalyst composition parameters and temperature conditions for the C4 olefins yield were determined by comprehensive optimization functions.

The ethanol conversion, C4 olefins selectivity, C4 olefins yield as a function of catalyst composition and temperature, and the optimal catalyst composition parameters for C4 olefins yield established in this study can be widely used in the chemical production of C4 olefins by catalytic coupling with ethanol.

DECLARATION

The author declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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