

Preparation of C4 Olefins by Ethanol Coupling Based on Fuzzy Analytic Hierarchy Process

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Abstract: In this paper, the relationship between ethanol conversion and C4 olefin selectivity and temperature under different catalyst combinations was analyzed. Under the given catalyst combination conditions at 350 °C, the effects of reaction time on ethanol conversion and product selectivity were analyzed. According to the principle of grey correlation degree and the criterion of maximum and minimum closeness in fuzzy mathematics, the model of factors affecting ethanol conversion and C4 olefin selectivity is established. Through solving, the grey correlation degree and the maximum and minimum closeness of Co/SiO₂ and HAP loading ratio, Co loading, ethanol concentration and temperature on ethanol conversion and C4 olefin selectivity is obtained. Due to the low accuracy, finally, the weight coefficients of the four influencing factors are obtained through iteration, which are 0.2813, 0.2188, 0.1563 and 0.3438 respectively. Based on fuzzy analytic hierarchy process and quaternion function optimization, the catalyst combination as 200mg:200mg Co/SiO₂ and HAP loading ratio, 1wt% Co loading, 0.9ml/min ethanol concentration and the temperature as 400 °C can make the highest C4 olefin yield, up to 41.77%. When the temperature is lower than 350 °C, selecting the catalyst combination as 200mg:200mg Co/SiO₂ and HAP loading ratio, 2wt% Co loading, 1.68ml/min ethanol concentration and the temperature as 350 °C can make the C4 olefin yield the highest, up to 26.54%.

Keywords: C4 olefin, ethanol, grey correlation analysis, maximum minimum closeness, fuzzy analytic hierarchy process

1. The establishment and solution of the model

1.1. The effect of temperature

1.1.1. Data analysis

By analyzing the content of each substance at different temperatures of each catalyst combination, when the reaction temperature is greater than 350 °C, the main product is olefin, and when the reaction temperature is 400 °C, the selectivity of olefin reaches 53.4%, and the maximum yield of olefin is 44.73%. When the reaction temperature was higher than 400 °C, the conversion of ethanol continued to increase and the selectivity of ethylene increased, but the selectivity and yield of C4 olefins decreased.

1.1.2. Solution of model

According to each catalyst combination, the relationship between ethanol conversion and C4 olefin selectivity with temperature can be obtained. As can be seen from these figure, it is obvious that the relationship between them is not linear, so four functions are used to fit them, namely exponential function, power function, quadratic polynomial function and Fourier function. Using the function fitting toolbox and taking the best fitting degree as the standard, select the most appropriate function to fit it, and get the best fitting using Fourier function. The relationship between ethanol conversion and temperature and C4 olefin selectivity and temperature are as follows:

$$\begin{aligned}y_1 &= 56.62 - 38.68 \cos(0.6152x) + 32.08 \sin(0.6152x) \\y_2 &= 49.55 - 32.71 \cos(0.4272x) + 33.13 \sin(0.4272x)\end{aligned}\tag{1}$$

The test results of a given catalyst combination at 350 °C at different times of one experiment are analyzed. The effects of reaction time on ethanol conversion and product selectivity were analyzed. We

can conclude that with the increase of time, the ethanol conversion rate decreases continuously, and the selectivity of C4 olefins remains at about 40%. With the increase of reaction time, it can be found that the C4 olefin yield decreases continuously. Therefore, the activity of this given catalyst will decrease with the reaction, and there are many side reactions in this chemical reaction.

1.2. Fuzzy Analytic Hierarchy Process

The effects of different catalyst combinations and temperatures on ethanol conversion and C4 olefin selectivity were discussed. The influence of ethanol conversion and C4 olefin selectivity will be considered from two aspects: one is gray correlation; The second is the maximum and minimum closeness in fuzzy mathematics.

1.2.1. Calculation of grey correlation degree

By using the model of grey correlation degree by MATLAB software programming, we can obtain the influence of ethanol conversion and C4 olefin selectivity. The grey correlation degrees of the four factors of ethanol conversion and C4 olefin selectivity are $\gamma_1(X_i, Y), \gamma_2(X_i, Y)$, as shown in Table 1.

Table 1: Grey correlation degree of factors affecting ethanol conversion and C4 olefin selectivity

correlation degree \ factors	Co/SiO ₂ and HAP loading ratio (X ₁)	Co loading (X ₂)	Ethanol concentration (X ₃)	temperature (X ₄)
$\gamma_1(X_i, Y)$	0.6150	0.5916	0.6017	0.7134
$\gamma_2(X_i, Y)$	0.6603	0.6464	0.6393	0.7725

It can be concluded from the table:

$$\begin{aligned} \gamma_1(X_4, Y) > \gamma_1(X_1, Y) > \gamma_1(X_3, Y) > \gamma_1(X_2, Y) \\ \gamma_2(X_4, Y) > \gamma_2(X_1, Y) > \gamma_2(X_2, Y) > \gamma_2(X_3, Y) \end{aligned} \tag{2}$$

There are four factors affecting ethanol conversion: $X_4 \succ X_1 \succ X_3 \succ X_2$; For the four factors affecting C4 olefin selectivity: $X_4 \succ X_1 \succ X_2 \succ X_3$, which \succ represents the partial order relationship.

It can be seen that temperature has the greatest influence on ethanol conversion, relatively speaking, the influence of CO/SiO₂ and HAP loading ratio on ethanol conversion is slightly greater than that of Co loading and ethanol concentration, and the influence of Co loading on ethanol conversion is the least. The influence of these four factors on the selectivity of C4 olefins is roughly the same as that on the ethanol conversion. The influence of temperature is the largest, followed by the influence of loading ratio. The difference is that the ethanol concentration has the smallest influence on the selectivity of C4 olefins.

1.2.2. Calculation of maximum and minimum closeness

Firstly, their membership functions can be obtained by using the data. Therefore, the fuzzy subsets of each influencing factor and ethanol conversion can be obtained, and the influencing factors and fuzzy subset of C4 olefin selectivity. Then, the closeness of the four influencing factors to the maximum and minimum values of ethanol conversion and C4 olefin selectivity can be obtained are $N_{M1}(X_i, Y), N_{M2}(X_i, Y)$, as shown in Table 2.

Table 2: Closeness of influencing factors to the maximum and minimum values of ethanol conversion and C4 olefin selectivity

closeness \ factors	Co/SiO ₂ and HAP loading ratio (X ₁)	Co loading (X ₂)	Ethanol concentration (X ₃)	temperature (X ₄)
$N_{M1}(X_i, Y)$	0.3843	0.2194	0.3901	0.5903
$N_{M2}(X_i, Y)$	0.4467	0.3816	0.4424	0.5837

Among the four factors affecting ethanol conversion and C4 olefin selectivity, the effect of temperature on ethanol conversion and C4 olefin selectivity is the most affected; Effect of Co loading on ethanol conversion and C4 olefin selectivity was the least affected; Among the four factors affecting

ethanol conversion, the influence degree of ethanol concentration is slightly greater than that of loading ratio; Among the four factors of C4 olefin selectivity, the influence degree of ethanol concentration is slightly less than that of loading ratio.

1.3. Optimization

According to the basic steps of fuzzy analytic hierarchy process, the hierarchical structure diagram is determined first, and the decision-making problem is divided into three layers, the top layer is the target layer, is C4 olefin yield; The lowest layer is the decision-making layer, that is, a series of experiments; The middle layer is the criterion layer, including and Co/SiO₂ and HAP loading ratio C₁, Co loading C₂, ethanol concentration C₃ and temperature C₄, as shown in Figure 1.

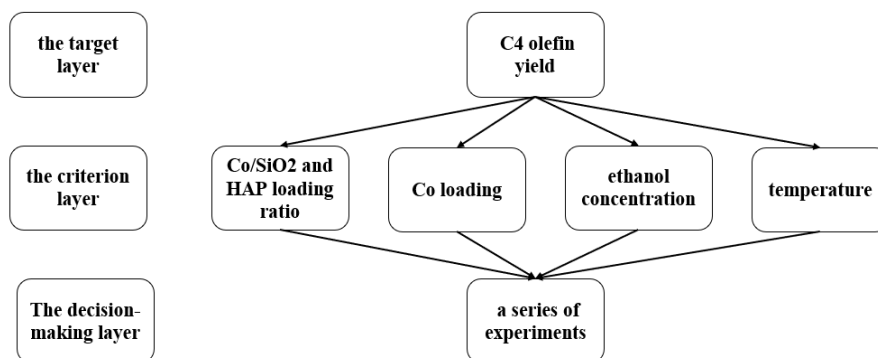


Figure 1: Hierarchy diagram affecting C4 olefin yield

According to the hierarchy, fuzzy three scale method and the importance of four factors affecting C4 olefin yield, the importance of olefin yield factors can be obtained O-C positive complementary judgment matrix, as shown in Table 3.

Table 3: Positive complementary judgment matrix

O	C ₁	C ₂	C ₃	C ₄
C ₁	0.5	1	1	0
C ₂	0	0.5	1	0
C ₃	0	0	0.5	0
C ₄	1	1	1	0.5

Then it is transformed into a fuzzy consistent matrix, and the weight vector is obtained by the sum row normalization method, so that the weight coefficients of the four influencing factors can be obtained:

$$W = (w_1, w_2, w_3, w_4) = (0.2813, 0.2188, 0.1563, 0.3438) \quad (3)$$

Among w_1, w_2, w_3, w_4 respectively Co/SiO₂ and HAP loading ratio, Weight coefficients of Co loading, ethanol concentration and temperature.

Quantitative weight through the correlation of various factors v'_{ip} and the weight coefficient of each influencing factor w_i , the model of fuzzy analytic hierarchy process affecting C4 olefin yield can be established:

$$Z_p = \sum_{i=1}^4 w_i v'_{ip} \quad (4)$$

Under the same experimental conditions, the C4 olefin yield can be as high as 41.77% by selecting the catalyst combination as 200mg:200mg Co/SiO₂ and HAP loading ratio, 1wt% Co loading, 0.9ml/min ethanol concentration and the temperature as and 400 °C through quaternion function optimization. When the temperature is lower than 350 °C, selecting the catalyst combination as 200mg:200mg Co/SiO₂ and HAP loading ratio, 2wt% Co loading, 1.68ml/min ethanol concentration and the temperature as and 350 °C can make the C4 olefin yield the highest, up to 26.54%.

2. Conclusion

In this paper, exponential function, power function, quadratic polynomial function and Fourier function are used to obtain the best fitting function according to the best fitting standard to explore the relationship between ethanol conversion and olefin selectivity and temperature. At the same time, the optimal catalyst combination and optimal temperature are determined by using the grey correlation analysis and the maximum and minimum closeness degree in fuzzy mathematics, and the fuzzy analytic hierarchy process.

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