

# Research on the Optimum Preparation of C4 Olefin by Ethanol Coupling

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**Abstract:** In this paper, the effects of catalyst combination and calcination temperature on the preparation of C4 olefin by alcohol coupling were quantitatively studied to find the suitable conditions of catalyst combination and temperature for the preparation of C4 olefin. Firstly, the relationship between variables was quantified by a grey comprehensive correlation degree. It was found that the correlation degree between ethanol conversion and C4 olefins selectivity was the closest on the whole. Then the influence of each factor on ethanol conversion was analyzed by ridge regression. Finally, a nonlinear model of C4 olefin yield was constructed from the perspective of ethanol and optimized by a particle swarm optimization algorithm. It was found that when the temperature was set below 350 degrees, the ethanol concentration of 2mL/min, 200mgHAP, 200mg 0.5wt%Co/SiO<sub>2</sub> and a bagging mode, C4 olefin yield was the highest, and the appropriate temperature was 300 degrees.

**Keywords:** C4 Olefin, Grey Comprehensive Correlation Degree, Ridge Regression.

## 1. Background

With the rapid development of the economy, the demand for C4 olefins in medicine and chemical products is increasing. At present, the production of low carbon olefin in industrial production depends on petroleum resources. Conventional C4 olefins production methods require a lot of fossil fuels [1]. As the pollution of the environment becomes more and more serious, the development of new clean energy becomes more and more urgent. Therefore, the process of producing low carbon olefins such as ethylene from coal, natural gas and new clean energy as raw materials has attracted wide attention in recent years.

## 2. Grey relational analysis

Grey relational analysis analyzes and determines the influence degree of various factors in the system or the contribution measure of factors to the main behavior of the system through the grey relational degree. The basic idea of grey relational analysis is to distinguish the correlation degree of multiple factors in the system according to the comparison of geometric similarity degree of statistical sequence curves. The closer the geometric shapes of sequence curves are, the greater the degree of correlation between them [2].

Suppose have two sets of data:  $X_0=(x_0(1),x_0(2),\dots,x_0(n))$ ,  $X_i=(x_i(1),x_i(2),\dots,x_i(n))$ . The two sets of data are presented as two broken lines on two-dimensional coordinates. Grey absolute correlation degree  $\varepsilon_{0i}$ , grey relative correlation degree  $\gamma_{0i}$ , grey comprehensive correlation degree  $\rho_{0i}$  formula is as follows:

$$\varepsilon_{0i} = \frac{1 + |s_0| + |s_i|}{1 + |s_0| + |s_i| + |s_i - s_0|} \quad (1)$$

$$s_i = \int_1^n (X_i - x_i(1)) dt \quad (2)$$

$$\gamma_{0i} = \frac{1 + |s_0'| + |s_i'|}{1 + |s_0'| + |s_i'| + |s_i' - s_0'|} \quad (3)$$

$$\rho_{0i} = \theta \varepsilon_{0i} + (1 - \theta) \gamma_{0i} \quad \theta = 0.5 \quad (4)$$

The temperature was denoted as T, ethanol conversion was denoted as E, and C4 olefins selectivity was denoted as C. The grey comprehensive correlation degree between the three variables in each catalyst combination was calculated in turn, where A6-B2 lacked temperature 325. The final results were shown in the following table by interpolation method:

*Table 1: Grey comprehensive correlation degree under each catalyst combination*

	$\rho_{TE}$	$\rho_{TC}$	$\rho_{EC}$		$\rho_{TE}$	$\rho_{TC}$	$\rho_{EC}$
A1	0.58	0.75	0.7	A12	0.56	0.59	0.75
A2	0.67	0.71	0.56	A13	0.55	0.58	0.79
A3	0.63	0.59	0.88	A14	0.57	0.55	0.72
A4	0.64	0.62	0.54	B1	0.56	0.59	0.81
A5	0.64	0.56	0.73	B2	0.56	0.57	0.95
A6	0.64	0.57	0.77	B3	0.52	0.56	0.71
A7	0.66	0.59	0.82	B4	0.53	0.68	0.61
A8	0.59	0.59	0.94	B5	0.56	0.58	0.76
A9	0.55	0.59	0.82	B6	0.58	0.58	0.74
A10	0.53	0.66	0.55	B7	0.59	0.58	0.9
A11	0.53	0.51	0.84				

Row A1,  $\rho_{TC} > \rho_{EC} > \rho_{TE}$  in this table shows that temperature is more correlated with C4 olefins selectivity. Similarly, by sorting the three grey comprehensive correlation degrees of each catalyst combination from A1 to B7, it was found that ethanol conversion was most closely correlated with C4 olefins selectivity on the whole, because most catalyst combinations had the largest value of  $\rho_{EC}$ . Secondly, by comparing the degree of correlation between temperature and these two indexes, it is found that the degree of correlation between temperature and C4 olefins selectivity is greater in general, because most of them are  $\rho_{TC} > \rho_{TE}$ .

### 3. Model establishment and solution

#### 3.1. Influence analysis of C4 olefin selectivity

Ridge regression analysis is used to solve the collinearity of independent variables in linear regression analysis. By introducing the k identity matrix, the regression coefficient can be estimated. The introduction of an identity matrix will result in information loss, but at the same time can obtain a reasonable estimate of the regression model [3]. The multiple linear regression model involving N independent variables can be expressed as:

$$y_i = \beta_1 x_{i1} + \beta_2 x_{i2} + \dots + \beta_k x_{ik} + \varepsilon_i \quad (i = 1, 2, \dots, n) \quad (5)$$

$$\begin{aligned} \hat{\beta} &= \arg\text{Min} \left[ \sum_{i=1}^n (y_i - x_i' \hat{\beta})^2 + \lambda \sum_{i=1}^k \hat{\beta}_i^2 \right] \\ &= \arg\text{Min} \left[ (y - x\hat{\beta})'(y - x\hat{\beta}) + \lambda \hat{\beta}' \hat{\beta} \right] \end{aligned} \quad (6)$$

$$\hat{\beta} = (x'x + \lambda I)^{-1} x'y \quad (\lambda > 0) \quad (7)$$

M, Cofz, Co/SiO<sub>2</sub>, HAP, SYS, T, CH were used as a independent variables, while ethanol conversion was used as dependent variable for Ridge regression analysis. When the K value ranges from 0 to 1, the selection principle of the K value is the minimum K value when the standardized regression coefficient of each independent variable tends to be stable. When the K value is 0.99, the standardized regression coefficient of the independent variable tends to be stable, so the K value is 0.99. Then input K value, get ridge regression model estimate. Finally, the following conclusions are drawn:

(1) Co/SiO<sub>2</sub>, HAP, T had a significant positive effect on ethanol conversion, while ch per minute had a significant negative effect on ethanol conversion.

(2) Co/SiO<sub>2</sub>, HAP, T have a significant positive effect on C4 selectivity, while Cofz has a significant negative effect on C4 selectivity. When Co loading is 1wt%-5wt%, C4 olefins selectivity has a maximum value, while with the increase of Co loading, C4 olefins selectivity gradually decreases, so there is a negative effect. M, CH and SYS did not affect C4 selectivity.

### 3.2. Model establishment

As can be seen from the confirmation of K value with ridge trace map, when the K value is 0.99, the standardized regression coefficient of the independent variable tends to be stable, so it is recommended to set the optimal K value to 0.99.

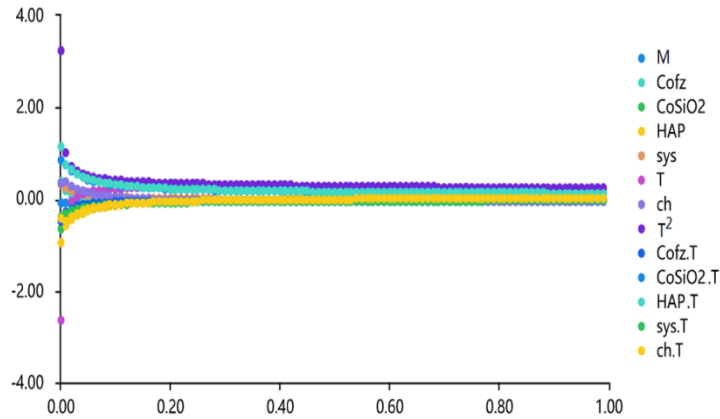


Figure 1: Ridge trace diagram of olefin yield effect

Then input K value to obtain ridge regression model estimation. Finally, according to the regression results, it is found that the catalyst combination and temperature have nonlinear effects on the C4 olefin yield. In the existing experimental temperature range, the effect of temperature T presents a U-shaped shape, and the effect is increased in a certain temperature range, while it is weakened in a certain temperature range. Temperature T has a positive regulating effect on Co/SiO<sub>2</sub> and HAP, that is, enhances the catalytic effect of these two elements.

In this part, the particle swarm optimization algorithm is introduced to solve the nonlinear equation. The nonlinear equation of C4 olefin yield action is as follows:

$$\begin{aligned}
 C4SL = & 20.101 - 3.041 * ch - 1.282 * ch^2 + 0.019 * HAP.ch + 0.015 \\
 & * Co/SiO2.ch - \\
 & 0.365 * Cofz.ch - 0.919 * M - 0.495 * Cofz + 0.030 * Co/SiO2 + 0.034 * HAP \quad (8)
 \end{aligned}$$

### 3.3. Model solving and conclusions

Particle swarm optimization (PSO) is a kind of evolutionary computing technology, whose basic idea is to find the optimal solution through cooperation and information sharing among individuals in a group [4]. By designing a kind of particle to simulate the catalyst composition of the experiment, each particle separate search optimal solution in search space, the individual extreme value as a whole to find the optimal particle swarm of the current global optimal solution, all the particles in the particle swarm according to their to find the current individual extreme value and the current global optimal solution of the whole particle swarm sharing to adjust their own position and speed. At each iteration, the particle updates itself by tracking two "extremes". After finding these two optimal values, the particle updates its position and velocity by using the following formula:

$$v_i^d = \omega v_i^{d-1} + c_1 r_1 (pbest_i^d - x_i^d) + c_2 r_2 (gbest^d - x_i^d) \quad (9)$$

$$x_i^{d+1} = x_i^d + v_i^d \quad (10)$$

The speed of the bird at step d = the speed of the bird at the previous step inertia + self cognition part+ social cognition part.

The bird's position at step d + step 1 = position at step D + speed at step D times the time of movement.

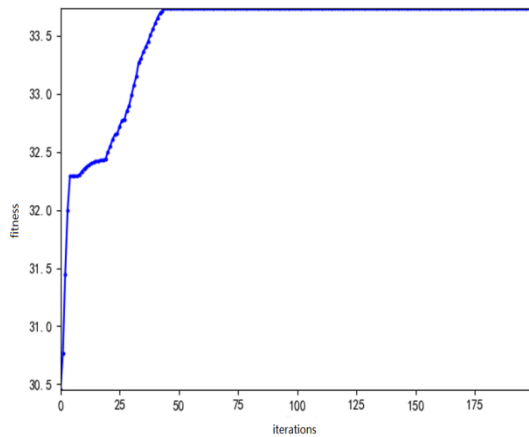


Figure 2: Yield optimization without limitation

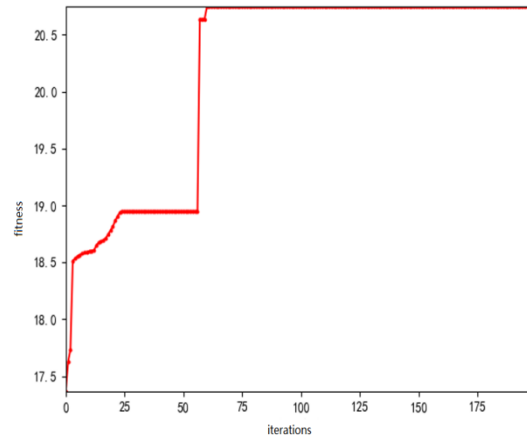


Figure 3: Yield optimization below 350 degrees

Firstly, the nonlinear programming of C4 olefin yield was optimized without setting temperature limits, as shown in the figure. At this time, the optimization parameter is: [1. 39366474 200 200 0.5 1], which represents successively: Ethanol concentration, HAP mass, Co/SiO<sub>2</sub> mass, Co loading capacity and catalyst bagging method indicated that when ethanol concentration was 1.39 mL/min, 200mg HAP, 200mg 0.5wt% Co/SiO<sub>2</sub> and A bagging method, c4 olefin yield was the highest. In the absence of temperature limitation, the activity of the same catalyst is highest at 400 °C, so the optimum temperature is 400 °C.

Next, the temperature was set below 350 degrees to optimize the nonlinear programming of C4 olefin yield, as shown in the figure. At this time, the optimization parameters are: [2 200 200 0.5 1], which represent successively: Ethanol concentration, HAP mass, Co/SiO<sub>2</sub> mass, Co loading capacity and catalyst bagging method indicated that when ethanol concentration was 2 mL/min, 200mg HAP, 200mg 0.5wt% Co/SiO<sub>2</sub> and A bagging method, c4 olefin yield was the highest. When the temperature is lower than 350 °, the catalyst activity is positively correlated with the increase of temperature, so the optimum temperature is 300 °.

#### 4. Evaluations of Model

(1) The grey comprehensive correlation degree is used to calculate the relationship between variables in each catalyst combination, which can quantify the relationship and fully consider the data characteristics. The disadvantage is that a6-B2 lacks temperature 325 in addition to the few data. The interpolation method is used to arrange the data into a 1-time-interval sequence of equal length before calculation.

(2) The nonlinear effect is confirmed and the nonlinear equation is established, which is more in line with reality. Particle swarm optimization (PSO) is used to optimize the nonlinear programming of the equation function.

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