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Study on the process of preparing C4 olefin from ethanol based on optimal method

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Abstract: *Olefins are mainly derived from petroleum and are important raw materials in the petrochemical industry. In this paper, the combination of catalysts for the preparation of C4 olefins by catalytic coupling of ethanol was analyzed. First of all, under each combination of catalysts, the relationship between the conversion of ethanol at different temperatures, the selectivity of alkenes and temperature was studied. Because the change of temperature is equal, but the change of ethanol conversion is not equal to that of olefin selectivity, so the relationship between them and temperature must be non-linear. Because the value of temperature is large, the conversion of ethanol and C4 olefin is relatively small, so calculating the logarithm of temperature can eliminate the influence of heteroscedasticity on the one hand, and it is easy to find a suitable fitting function on the other hand. Then the equation is established, the goodness of fit is 0.99, and the model is established. Then, with the change of time, there is an obvious first-order function relationship between ethanol conversion, acetaldehyde selectivity, ethylene selectivity and time, ethanol conversion is negatively correlated with time, acetaldehyde selectivity and ethylene selectivity are positively correlated with time. In addition, we use correlation analysis, factor analysis and other statistical methods to analyze different reaction products to find the correlation between them.*

Keywords: *Fitting function, Correlation analysis, Ethanol to olefin*

1. Introduction

C4 olefins are mainly prepared by ethanol industry and are prepared by dehydration. They are widely used in a wide range of fields, such as medical and health care, food processing and so on. Chemical kinetics has an in-depth study on the reaction conditions in the preparation process, in which the combination of catalysts and temperature have a significant effect on the selectivity and yield of C4 olefins. In engineering, the establishment of a mathematical model and the design of the combination of catalysts can effectively improve production efficiency, save energy and protect the environment. Therefore, it is of great practical value and significance to explore the best process conditions for the preparation of C4 olefins from ethanol.

2. Model of the effect of temperature on the preparation of C4 Olefins

2.1. Model construction

In chemistry, the reversible reaction reaching equilibrium means that the forward reaction rate is equal to the reverse reaction rate, while when the reversible reaction reaches equilibrium depends on the temperature and a series of catalysts, which is mainly due to the thermal effect in the chemical reaction. From a microscopic point of view, chemical reactions are mainly manifested in the bonding and breaking of chemical substances, bond absorption, bond breaking and exothermic release. In this experiment, ethanol produces C4 olefins and a series of by-products by endothermic dehydration, which is a typical endothermic reaction, so it is necessary to consider the effect of temperature on the reaction [1].

A reversible reaction can be written as follows:

$$aA+bB=cC+dD \tag{1}$$

As for the influence of temperature in chemical reaction, Arrhenius formula was used to establish a mathematical model to describe the relationship between temperature, activation energy and reaction rate, as shown below.

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$$\frac{d\ln k}{dT}=\frac{E_\alpha}{RT^2} \tag{2}$$

$$E_\alpha = RT^2\frac{d\ln k}{dT}=-R\frac{d\ln k}{d\frac{1}{T}} \tag{3}$$

Ea represents the activation energy constant, independent of temperature. T stands for absolute temperature, 273.15K.

2.2. Model solution

The forward reaction rate is expressed as

$$r_1 = k_1 c_1 \tag{4}$$

The inverse reaction rate is expressed as:

$$r_2 = k_2 c_2 \tag{5}$$

c1 represents the concentration of the reactant and c2 represents the concentration of the product. Note that the net reaction rate of this chemical reaction is re=r1-r2. It is necessary to study the relationship between the conversion of ethanol and the selectivity of C4 olefins and temperature T, the change of the value of K1 and K2 at different temperatures. The concentration of the product in the test is c_{20}=0.

The ratio of ethanol consumption per unit time is studied, that is, the consumption rate of ethanol. According to the relation between velocity and time in physics, a differential equation of velocity with respect to time can be established

$$\left(-r_e\right)=-\frac{dc_1}{dt}=k_1c_1-k_2c_p=k_1c_1-k_2\left(c_{10}-c_1\right) \tag{6}$$

According to the analysis of the properties of the microelement, the reactant concentration here is not constant. Therefore, this K2 is meaningful and the general solution can be obtained through the basic knowledge of differential equations. K1 and K2 here are defined as a function related to the ambient temperature T. According to this information, it can be basically concluded that the reaction rate at equilibrium is related to temperature, and when we simplify K1Graine K2 as a function of T, according to the data observation, we can find that the conversion of ethanol and the selectivity of C4 olefins are positively correlated with temperature. Therefore, a series of experimental data can be analyzed, and then the relationship between them can be obtained more accurately by fitting. But because we don't know what the explicit function expression between K1 and T is, we try several different methods to fit it.

In order to ensure the accuracy of the fitting results, three fitting methods were tried. The first was direct fitting to investigate whether there was a linear relationship between them. However, the results were different from what we expected, and the correlation coefficient R^2 in the results was too large to be used as fitting results.

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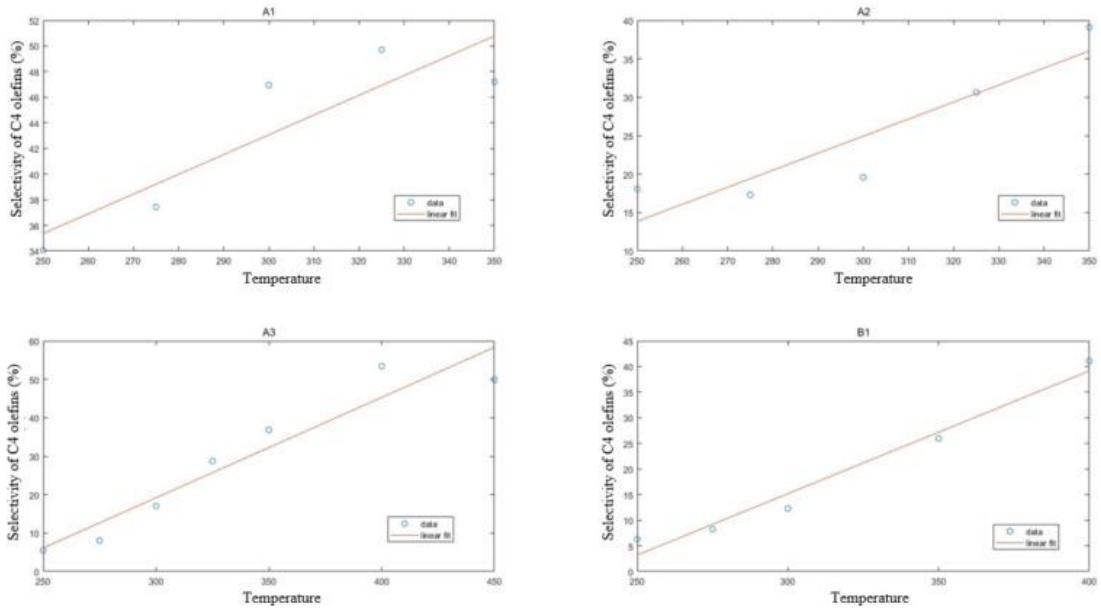

Figure 1: Results of the first fitting

Through the fitting of the quadratic function by interpolation, the results are as follows: it can be seen that the value of goodness of fit 2 in the result is 0.9 very close to 1. After further study, it is found that the reason why the fitting result is not ideal may be that there is an order of magnitude difference between the temperature and the percentage. Therefore, we continue to optimize the fitting scheme, taking the logarithm of temperature, ethanol conversion and the selectivity of C4 olefins, thus reducing the absolute value of the data, convenient calculation and weakening the heteroscedasticity of the data. Then fit it for the second time and the third time, and finally find that the fitting effect is good.

3. Selective analysis

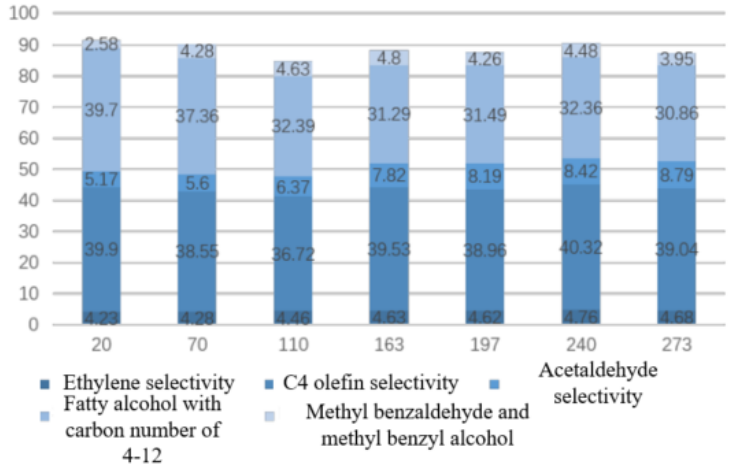

Figure 2: The ratio of each product

The test data of a certain catalyst combination given at 350 degrees are analyzed. in order to improve the reliability and rationality of the above analysis, the function of the selectivity of each product with time and the conversion of ethanol are obtained by secondary fitting[2]. The covariance and correlation coefficient are calculated and quantitatively analyzed based on SPSS software.

$$\rho_{X,Y} = \frac{\operatorname{cov}(X,Y)}{\sigma_X \sigma_Y} = \frac{E\left[(X-\mu_X)(Y-\mu_Y)\right]}{\sigma_X \sigma_Y} \tag{7}$$

r > 0 is positive correlation, r < 0 is negative correlation 2. |r| = 0 means there is no linear relationship. 3. |r| = 1 means completely linear

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The correlation coefficients between ethanol conversion and ethylene selectivity, acetaldehyde selectivity and carbon number of 4-12 fatty alcohols were observed. There were two asterisks on the right side of these data, indicating that there was a significant correlation at the 0.01 significant level. Ethylene selectivity is also significantly related to ethanol conversion, acetaldehyde selectivity and carbon number of 4-12 fatty alcohols. X4 olefins are only significantly related to other olefins. The selectivity of acetaldehyde was significantly correlated with ethanol conversion, ethylene selectivity and carbon number of 4-12 fatty alcohols. The carbon number of 4-12 fatty alcohols was significantly correlated with ethanol conversion, ethylene selectivity and acetaldehyde selectivity.

4. Factor analysis model

By establishing a linear mapping from high dimensional space to low dimensional space, the mapping still retains some structure of sample points in high dimensional space, and the idea of dimensionality reduction is used to transform multiple indexes into a few comprehensive indexes. These few unmeasured comprehensive indicators are considered to be common factors. Factor analysis will group the original variables according to the magnitude of correlation, so that the correlation of intra-group variables is high and that of inter-group variables is low [3].

General model of factor analysis:

$$X = \begin{bmatrix} x_{11} & x_{12} & \cdots & x_{1p} \\ x_{21} & x_{22} & \cdots & x_{2p} \\ \vdots & \vdots & & \vdots \\ x_{n1} & x_{n2} & \cdots & x_{np} \end{bmatrix} \tag{8}$$

The covariance moment sigma of X can be decomposed as follows:

$$\begin{aligned} &COV(\boldsymbol{X},\boldsymbol{X}) = \mathbf{COV}(\boldsymbol{AF}+\varepsilon,\boldsymbol{AF}+\varepsilon) = E(\boldsymbol{AF}+\varepsilon)(\boldsymbol{AF}+\varepsilon)^{\mathrm{T}} \\ &=AE(\boldsymbol{FF}^{\mathrm{T}})A^{\mathrm{T}} + AE(\boldsymbol{F}\varepsilon^{\mathrm{T}}) + E(\varepsilon\boldsymbol{F}^{\mathrm{T}})A^{\mathrm{T}} + E(\varepsilon\varepsilon^{\mathrm{T}}) \\ &=AA^{\mathrm{T}} + D \end{aligned} \tag{9}$$

Table 1: Common variance

	Initial	Extraction
Ethanol conversion.	1.000	.968
Ethylene selectivity	1.000	.978
C4 olefin selectivity	1.000	.977
Acetaldehyde selectivity.	1.000	.966
The carbon number is 4-12 fatty alcohols	1.000	.979
Methyl benzaldehyde and methyl benzyl alcohol	1.000	.698
Other	1.000	.934

The last column of the table shows the common degree of variables after the extraction of a common factor, with the exception of methyl benzaldehyde and methylbenzyl alcohol, the values of other products are more than 0.9, indicating that the degree of common factor extracted by each variable is relatively high. Less information is lost. By observing the composition matrix above, it can be seen that the first four variables in the composition 1 are 4-12 fatty alcohols, ethanol conversion, ethylene selectivity and acetaldehyde selectivity are all more than 0.9, and the load is very large, which can be divided into one category. Among the 2 components, C4 olefin selectivity and other loading are very large, which can be divided into one category. As can be seen from the above table, SPSS has extracted two common factors (whose characteristic value is greater than 1, the default option of the system), and the cumulative contribution rate of variance has reached 92.851%. Combined with the gravel map, it can also be seen that it is more appropriate to extract two common factors, because to the third common factor, the eigenvalues have tended to be stable.

Through the factor analysis of the four indexes, it was found that there was a great correlation between methyl benzaldehyde and methylbenzyl alcohol, ethylene selectivity and acetaldehyde selectivity, and they were all positively correlated with time, while the olefin selectivity of xylene 4 was less correlated with the first three. The correlation with time is also small, all fluctuating around 39%. The conversion of ethanol was negatively correlated with time.

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5. Conclusion

As we all know, the study of the best process conditions for the preparation of olefins in ethanol industry is beneficial to improve the efficiency of industrial preparation, save resources and protect the environment. In this paper, the catalyst combination and temperature conditions for the preparation of C4 olefins by catalytic coupling of ethanol were analyzed, the relationship between reaction effect and reaction conditions was found, and an optimization model was established based on simulated annealing algorithm to find the best reaction conditions. First of all, under each catalyst combination, the relationship between ethanol conversion, C4 olefin selectivity and temperature at different temperature was studied, and the corresponding fitting function was obtained. Finally, it is found that there may be a quadratic function relationship between temperature and ethanol conversion and C4 olefin selectivity. Then it was found that the temperature and catalyst combination were the same, and there was an obvious first-order function relationship between ethanol conversion, acetaldehyde selectivity, ethylene selectivity and time, and there was a negative correlation between ethanol conversion and time. Acetaldehyde selectivity and ethylene selectivity are positively correlated with time.

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