

Study on the Preparation of C4 Olefins by Catalytic Coupling of Ethanol

Yang Chen^{1,*}, Zheng Wang¹, Jiye Tan¹, Siyuan Zhang¹, Zihao Liu²

¹ College of Artificial Intelligence, Nanjing Agricultural University, Nanjing, Jiangsu, China, 210031

² College of Engineering, Nanjing Agricultural University, Nanjing, Jiangsu, China, 210031

* Corresponding Author Email: chenyang220302@163.com

Abstract. In this paper, we investigated the relationship between ethanol conversion, C4 olefin selectivity, and temperature by establishing a series of mathematical models. Specifically, the relationship between temperature and ethanol conversion and selectivity to C4 olefins is discussed by solving linear regression equations. In addition, the support vector machine regression (SVR) model was used to describe the effect of independent variables on the ethanol conversion rate and C4 olefin selectivity. Finally, we investigated the effect of temperature change on catalyst activity.

Keywords: coefficient color scale matrix; support vector machine regression (SVR); permutation and combination; temperature gradient.

1. Introduction

Olefins are ubiquitous in our daily life. They have various uses and often synthesize some polymer materials with special requirements. They are abundant in polyolefins, synthetic rubber, plant essential oils, and many spices. As a unique existence, C4 olefins are widely used in chemical products and pharmaceutical products and have important practical and commercial value, which makes it particularly important to explore the preparation of C4 olefins. Industrially, ethanol to prepare C4 olefins is a traditional technique. In the preparation process, the use of different catalysts means different reaction mechanisms.

This paper discusses the preparation of metal oxides as catalysts. Many factors affect a reaction in a chemical experiment. The combination of catalyst combination (Co loading, Co/SiO₂, HAP charge ratio, ethanol concentration) and temperature will have an effect on C4 olefin selectivity and C4 olefin yield. Therefore, it is of great significance to explore the process conditions for the preparation of C4 olefins by catalytic coupling of ethanol through the design of catalyst combinations.

Firstly, the relationship between ethanol conversion, C4 olefin selectivity, and temperature was studied. For the quantitative evaluation of the relationship, the first thought is to use the correlation coefficient model to analyze each piece of data, and it is necessary to judge the approximate correlation through the image. Meanwhile, the data should also be judged whether it obeys the normal distribution. Therefore, we consider using interpolation to supplement sample points. After interpolation, it observes whether the images generated by the data may be linearly correlated and perform correlation analysis on all data.

Secondly, it shows that different catalyst combinations and temperatures affect ethanol conversion and C4 olefin selectivity [3]. The catalyst combinations were disassembled into Co loading, loading ratio, HAP mass, ethanol addition rate, and temperature. Therefore, we consider building a mathematical model to describe this effect concretely. Because of the advantages of the support vector machine regression (SVR) model, we adopted the SVR model to describe the effect of each variable on ethanol conversion and C4 olefin selectivity.

Finally, through the analysis of the given data, it is known that the two parts that make up the yield of C4 olefins are not maximized under the same conditions, which means that an optimal model needs to be established to solve the problem. Therefore, taking the yield of ethanol as the objective function and other related variables (for example Co loading, loading ratio, temperature, etc.) as independent variables to solve a peak value of the yield. Using the idea of iteration, constantly changing the values

of the remaining independent variables to search for a set of suitable conditions for the C4 olefin yield to reach the peak value to determine the optimal catalyst combination and temperature.

2. The Establishment and Solution of Model

2.1. Data Analysis

EXCEL was used to plot the data into temperature and ethanol conversion, temperature, and C4 olefins selectivity line graph, which is shown in Fig. 1.

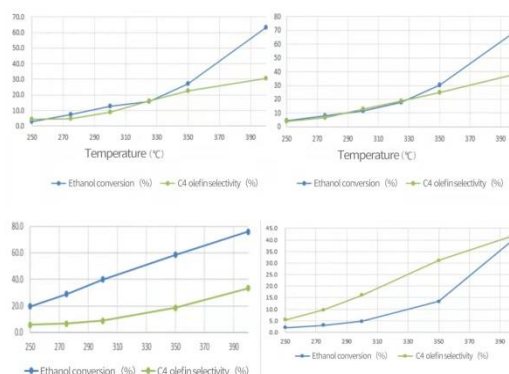


Figure 1. Ethanol conversion and C4 olefins selectivity of the four catalyst combinations concerning temperature.

In order to maintain the continuity and smoothness of the experimental data, cubic spline interpolation is used for each group of data, and the original 5-7 sample points are expanded to 15, while ensuring the same experimental temperature gradient in the same group.

To verify the correlation between temperature and the two, it is generally required to test whether the data conforms to a normal distribution when calculating the correlation coefficient. The Shapiro-Wilk test is usually used for the normal distribution test with a sample size of less than 30 [1]. We need to use this method to test for normal distribution. The test steps are as follows:

Step1. Make a hypothesis

Null hypothesis: The conversion rate of ethanol or the selectivity of C4 olefins obeys a normal distribution, and the statistic is:

$$W = \frac{\sum a_i y_i^2}{\sum (y_i - \bar{y})^2} \quad (1)$$

Where y_i is the sorted sample data of i , $\bar{y}$ is the sample average, and a_i is an undetermined constant.

Alternative hypothesis: ethanol conversion or C4 olefin selectivity does not obey a normal distribution.

Step2. Take the significant level α as 0.05.

Step3. Calculate the statistic W and its corresponding value p .

2.2. Correlation and Regression Analysis of Temperature-Ethanol Conversion Rate

In the data that meets the conditions, the correlation analysis between temperature and ethanol conversion rate is carried out, the person correlation coefficient is used to measure the linear relationship between variables, and the correlation equation is obtained by regression. The person correlation coefficient formula is as follows [2]:

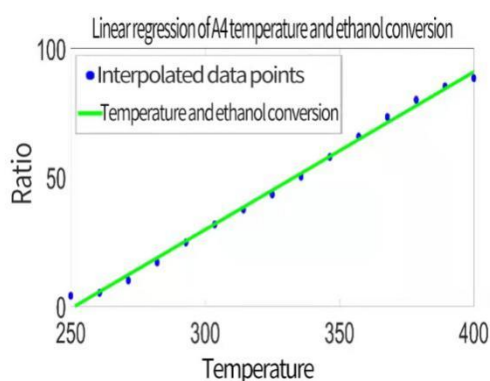
$$r = \frac{\sum_{i=1}^n (X_i - \bar{X})(Y_i - \bar{Y})}{\sqrt{\sum_{i=1}^n (X_i - \bar{X})^2} \sqrt{\sum_{i=1}^n (Y_i - \bar{Y})^2}} \quad (2)$$

Using MATLAB to calculate the regression equation and correlation coefficient shows the results in Table 1.

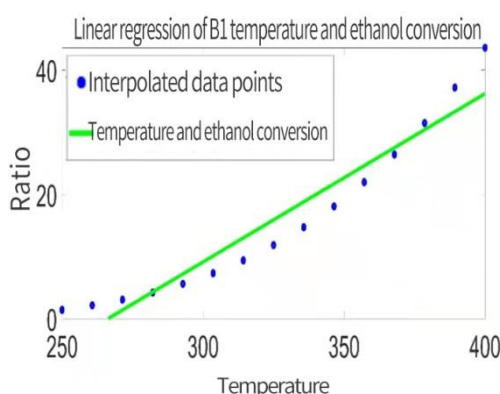
Table 1. Temperature-Ethanol Group A and B Linear Regression Equations and Correlation Coefficients

catalyst combination	regression equation	r value
A1	$y = 0.3173x - 80.5400$	0.975
A2	$y = 0.6968x - 172.0348$	0.995
A3	$y = 0.4579x - 107.4401$	0.984
A4	$y = 0.6173x - 153.9603$	0.998
A5	$y = 0.3903x - 94.0655$	0.973
A6	$y = 0.5260x - 128.5545$	0.989
A7	$y = 0.3773x - 74.0611$	0.999
A8	$y = 0.3423x - 86.1559$	0.976
A12	$y = 0.2773x - 73.8638$	0.983
A13	$y = 0.3173x - 65.5400$	0.930
B6	$y = 0.3803x - 99.6901$	0.995
B1	$y = 0.2709x - 72.1540$	0.975

Using MATLAB to draw the images of A4 and B1 as shown in Fig.2 (a) and (b).



(a)



(b)

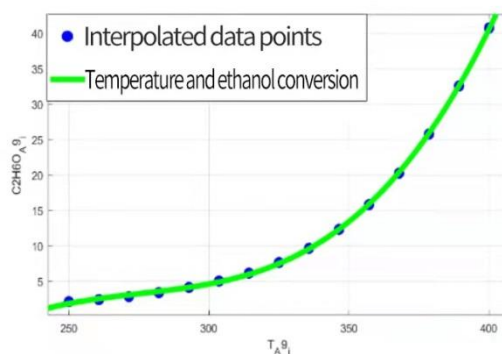
Figure 2. (a), (b). A 4, B1 linear regression graph of temperature and ethanol conversion.

To sum up, it can be seen that the correlation between temperature and ethanol conversion is affected by the assembly method. For group A, which tends to be more linear, the increase in temperature has a more significant effect on the improvement of ethanol conversion. In the range of 250-400 degrees, the growth rate of ethanol conversion was higher than that of group B after increasing the temperature.

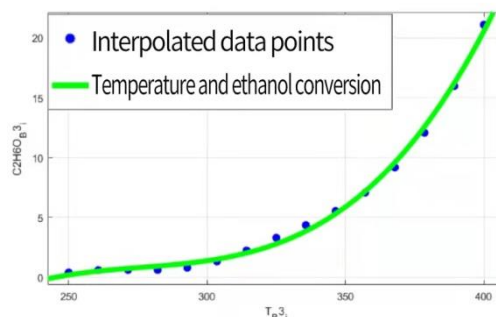
When choosing the number of fits, consider the following parameters: residual sum of squares SSE sum and goodness of fit, where the residual sum of squares is calculated as:

$$SSE = \sum y_i^2 \quad (3)$$

The effect of fitting A9 and B3 is shown in Fig. 3 (a) and (b).



(a)



(b)

Figure 3. (a)、(b). A9 and B3 fitting regression diagram of temperature and ethanol conversion rate.

The time-dependent response data at 350 degrees for an unknown catalyst combination is depicted in Fig.4.

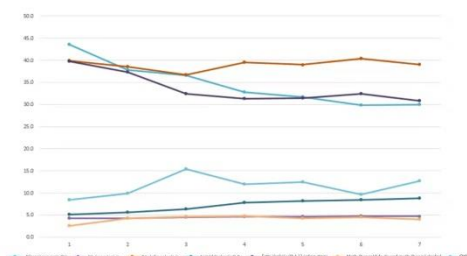


Figure 4. The plot of conversion rate over time.

2.3. Results analysis of ethanol conversion and C4 olefins at different times

The conversion rate of ethanol and the selectivity of C4 olefins are the most important for the preparation of C4 olefins, so it is necessary to fit these two indicators and predict the results at 280 degrees 290 degrees, and 300 degrees to achieve the analysis of the experimental results. The cubic spline interpolation method was used to supplement the data points, and at the same time to ensure the same temperature gradient in the same group of experiments, the number of samples was expanded to 15, and polynomial fitting was adopted for the first 12 data after interpolation processing, and the latter three data were verified.

The regression equation of temperature-ethanol conversion is:

$$y = 0.0001496x^2 - 0.0941x + 44.32 \quad (4)$$

The temperature-C4 olefin selectivity regression equation is:

$$y = -9.637 \times 10^{-12}x^4 + 3.982 \times 10^{-6}x^3 - 0.042x + 41.38 \quad (5)$$

The goodness of fit of the two fitting functions is 0.971 and 0.980, respectively, and the test points selected for the fitted data all fall on the fitted curve. Using this model to predict the time-ethanol conversion rate and C4 olefin selectivity at 280min, 290min, and 300min, the prediction effect is shown in Fig.5 (a) and (b).

From Fig.5 (a) and (b), after 270min, the conversion rate of ethanol will stabilize at around 30, and the C4 olefin selectivity has a slow decline trend in a short time.

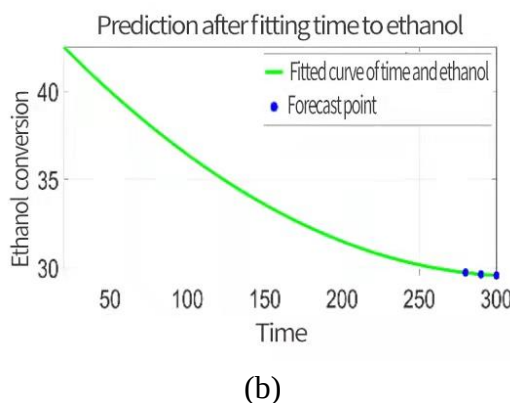
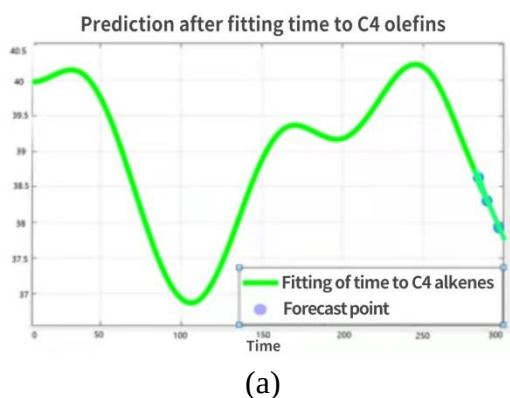


Figure 5. (a)、(b). Time and C4 olefins, ethanol prediction images.

The person correlation coefficient is used to calculate the correlation between two variables, and the obtained correlation coefficient matrix is shown in Fig.6.

	Ethanol conversion	Ethylene selectivity	C4 Olefins	Acetaldehyde selectivity	4-12 fatty alcohol	Methylbenzene	Other
Ethanol conversion	1	-0.954787	-0.146963	-0.962659	0.8994468	-0.667393	-0.357593
Ethylene selectivity	-0.954787	1	0.2514576	0.9718462	-0.897112	0.5780375	0.3207078
C4 Olefins	-0.146963	0.2514576	1	0.2681882	0.1510709	-0.345119	-0.797908
Acetaldehyde selectivity	-0.962659	0.9718462	0.2681882	1	-0.886218	0.4901143	0.3090905
4-12 fatty alcohol	0.8994468	-0.897112	0.1510709	-0.886218	1	-0.732984	-0.684681
Methylbenzene	-0.667393	0.5780375	-0.345119	0.4901143	-0.732984	1	0.5785772
Other	-0.357593	0.3207078	-0.797908	0.3090905	-0.684681	0.5785772	1

Figure 6. Correlation coefficient matrix color scale.

Fig. 6 has good visibility and can more intuitively observe the magnitude of the correlation between the indicators. The darker the color, the closer $|r|$ is to 1, and the stronger the correlation. When $|r|$ is greater than 0.7, it represents a strong correlation between variables.

3. SVR Model

The linear regression function established by projecting the data into a high-dimensional space is:

$$f(x) = w\varphi(x) + b \quad (6)$$

Where $\varphi(x)$ is the mapping function, and the optimal values of w and b are the regression coefficients and constant terms of each variable in the expression after regression.

Defining ε as a linear insensitive loss function, and its solution is characterized by function minimization, which can ensure the sparseness of dual variables and ensure the existence of the global minimum solution and the optimization of reliable generalization bounds, and minimize the error through planning. Introducing the Lagrangian function and converting it to the dual form [4].

The radial basis function (RBF) is the most commonly used kernel function for SVR, and the specific formula is as follows:

$$f(x) = w^*\phi(x) + b^* = \sum_{i=1}^l (a_i - a_i^*) K(x_i, x) + b^* \quad (7)$$

The execution structure of the SVR model is shown in Fig. 7.

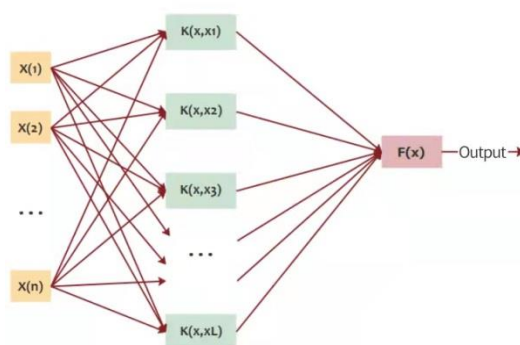


Figure7. SVR model structure diagram.

For the ethanol conversion rate, the regression equation can be written from the obtained regression coefficient and constant term as:

$$y_{\text{ethanol}} = -0.0438x_1 + 0.1385x_2 + 0.1517x_3 - 8.7454x_4 + 0.3394x_5 - 56.59 \quad (8)$$

For the selectivity of C4 olefin, the regression equation can be written from the regression coefficient and constant term obtained from the solution as:

$$y_{\text{olefin}} = 0.1477x_1 - 3.2144x_2 - 0.0625x_3 + 2.7806x_4 + 0.1875x_5 - 25.0706 \quad (9)$$

By observing the coefficients, it can be found that the effects of Co loading, loading ratio, HAP mass, and ethanol addition rate on C4 olefins are opposite to their effects on ethanol conversion, while the effect of temperature on C4 olefins is also positive. Therefore, both the ethanol conversion and the selectivity to C4 olefins will increase as the temperature increases.

4. Influencing Factors

The effects of ethanol conversion, C4 olefin selectivity, and different catalyst combinations were solved by the SVR model, and the relevant regression equations were obtained by taking the two as independent variables. The expression for the yield of C4 olefins is:

$$\text{Yield } i\% = \text{ethanol conversion} \times \text{C4 olefin selectivity} \times 100\% \quad (10)$$

where $y_{\text{yield}} = y_{\text{ethanol}} \times y_{\text{olefin}}$.

The olefin yield was made as high as possible by varying the catalyst combination and temperature under the same experiment. Under the constraints of real-life experimental conditions, the preset values of Co loading, Co/SiO₂, HAP charging ratio, and ethanol concentration are usually selected within certain specific value ranges. $x_1 \sim x_5$ represents the Co loading, charge ratio, HAP mass, ethanol addition rate, and temperature.

According to the optimum loading capacity of Co and the optimum loading ratio of Co, and the combination of such conditions as the catalyst, a gradient division of temperature was carried out. Five groups of experiments were set at 325°C, 400°C, 500°C, 700°C and 1000°C respectively. It was assumed that various experimental conditions were reasonable and appropriate. Inappropriate reaction time timely detection of C4 olefin yields and record, compare the five groups of experiment results, looking for a larger temperature gradient under the optimum reaction temperature range, and the calculation before the measurement of the range of the optimum temperature experiment, supporting results accuracy, in the case of the yield of mutation, to further explore of catalyst activity [5]. It was found that under the given temperature limit, the yield of C4 olefin increased with the increase of temperature, so we believe that temperature is an essential factor affecting the yield of C4 olefin. In order to improve the production efficiency of C4 olefin, it is necessary to study the optimal preparation temperature in actual production. In addition, the use of catalysts in the chemical process has an important value. It can reduce the activation energy of chemical reactions greatly improve the reaction rate. Although the catalyst is good, its use conditions are sometimes very harsh. For biocatalysts, such as enzymes, too low or too high temperature will reduce their activity or even deactivate them. The catalyst used in the chemical process is the chemical catalyst of metal oxide. Combining with the actual situation, high temperature may also lead to the decomposition of the chemical components of the catalyst and lead to its failure, which greatly reduces the efficiency of production. Therefore, it is of great significance to study the influence of temperature on catalyst activity.

5. Conclusion

In this paper, we analyzed the change rule of ethanol conversion rate and C4 olefin selectivity under different times, but also through analyzing the relative time trend of each product, the side effects of the reaction were speculated, and the influence of chemical balance in the reaction was analyzed. In addition, we use the SVR equation, and kernel function can solve nonlinear classification. Finally, the effect of temperature on catalyst activity was studied.

References

- [1] M. Samanta, C. J. Schwarz, "The shapiro-wilk test for exponentiality based on censored data," Journal of the American Statistical Association, 1988, 83(402): 528-531.
- [2] S. Shoukui, S. X. Jing, "Mathematical modeling algorithm and application," Beijing: National Defense Industry Press, 2008.
- [3] S. P. Lu, "Synthesis of butanol and C4 olefin by ethanol coupling," Dalian University of Technology, 2018.
- [4] D. S. Fei, Q. B. Juan, T. H. Yan, "A review of support vector machine theory and algorithm research," University of Electronic Science and Technology of China Report, 2011, 40(01): 2-10.
- [5] Y. D. Hong, L. W. Huai, Y. S. Wen, Z. Bing, P. S. Yi, "Research progress of fischer-tropsch catalyst for hydrocarbon synthesis," Progress in Chemistry, 201(02): 118-127.