ISSN 2616-5767 Vol.4, Issue 7: 17-21, DOI: 10.25236/AJETS.2021.040704

Study on the Optimization Process of Ethanol Coupling to C4 Olefins Based on Data Analysis and Polynomial Curve Fitting

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Abstract: *In this paper, the effects of catalyst combination and temperature on ethanol conversion and C4 olefin selectivity were studied by data analysis and mathematical model. First of all, according to the different loading methods, it is divided into an and B groups of data, and the relationship between ethanol conversion and C4 olefin selectivity and temperature under different catalyst combinations are fitted respectively. The curve reacts the relationship between ethanol conversion and C4 olefin selectivity of different catalyst combinations and temperature. Then the curves were normalized and fitted to get two curves. With the increase of temperature, the conversion of ethanol and the selectivity of C4 olefins increased linearly and nonlinearly, respectively.*

Keywords: *Curve fitting, Linear and nonlinear, Temperature, Ethanol conversion and C4 olefin selectivity*

1. Introduction

Alkenes are extremely important basic raw materials in organic chemical industry, which are widely used in the production of chemical products and medicine. With the continuous depletion of oil resources [1], the rise of oil prices, and the increasing pressure of production on the environment, it is imperative to develop the technology of preparing olefins from renewable energy. In recent years, with the development of biomass technology, in order to meet the requirements of the healthy development of chemical industry, the production process of C4 has gradually developed from petroleum cracking to ethanol coupling. As a renewable energy, ethanol has a wide range of sources and is environmentally friendly. The preparation of C4 from ethanol has a wide application prospect, which can replace the traditional olefin preparation method and reduce the dependence of olefin preparation on the petroleum industry.

The synthesis of C4 olefin by ethanol is a complex reaction process, in which the role of catalyst is very important. By controlling the related variables of catalyst and temperature, the yield of C4 olefin and the selectivity of related by-products can be adjusted. Therefore, it is of great significance to study the combination and rule of temperature and catalyst for the preparation of C4 olefin.

2. Model preparation and analysis

In this paper, firstly, the temperature is used as a single independent variable to study the experimental data [2]. By collecting the relevant experimental results, 21 kinds of catalyst combinations were obtained as independent fixed conditions, and the data were divided into 21 groups of independent data. Taking temperature as independent variable, the changes of ethanol conversion Y1 and C4 olefin selectivity Y2 with the increase of temperature were studied and analyzed, and the relationship between ethanol conversion, C4 olefin selectivity and temperature was obtained.

3. Establishment of the curve fitting model

3.1. Type of fitting curve

Considering that there are 21 kinds of catalyst combinations, which are divided into A and B categories by different charging methods [3]. Firstly, the line chart image of ethanol conversion and

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temperature is analyzed, and the type of curve used to fit the relationship between ethanol conversion and temperature is determined. For an and B data, the line chart was drawn and the change trend was observed with temperature as independent variable and ethanol conversion as dependent variable. As shown in figures 1 and 2: observing the changing trend of the image line segment, the overall trend is that the ethanol conversion rate increases with the increase of temperature, there is a small fluctuation, which does not affect the overall trend, according to empirical judgment, decided to select the polynomial curve to fit [4].

The curve type used to fit the relationship between C4 olefin selectivity and temperature was determined by examining the broken line image of C4 olefin selectivity and temperature [5]. With temperature as independent variable and C4 olefins selectivity as dependent variable, a line chart was drawn for data of A and B, and the change trend was observed. As shown in FIG. 3 and 4, the change of image line segment was observed, and the overall trend was that C4 olefins selectivity increased with the increase of temperature, with fluctuations, which did not affect the overall trend. Based on empirical judgment, polynomial curve was also selected for fitting.

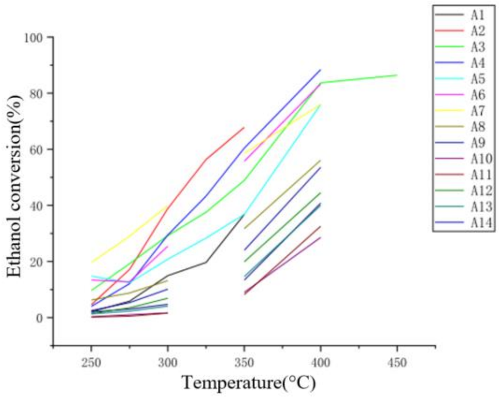

Figure 1: Type A ethanol conversion rate with temperature change

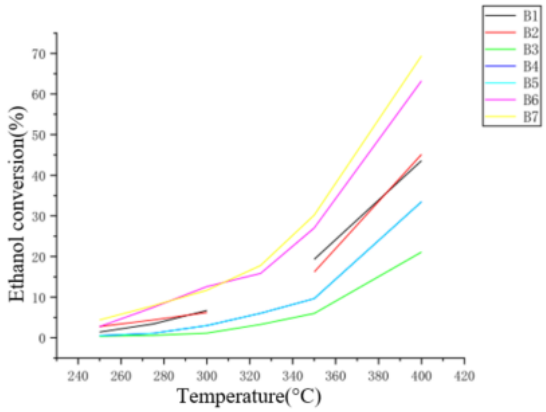

Figure 2: Type A ethanol conversion rate with temperature change

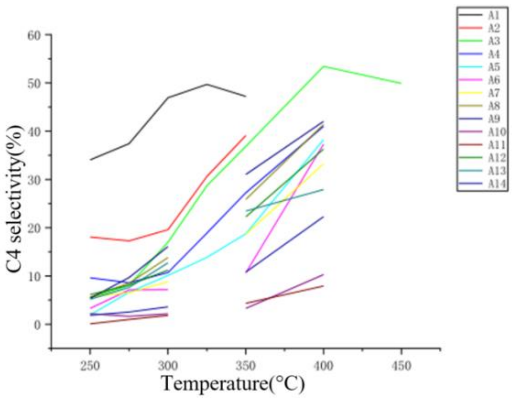

Figure 3: Assembly mode 1-C4 selectivity of each group with temperature change

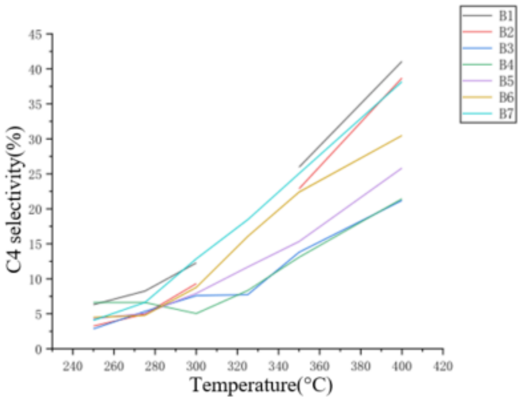

Figure 4: Assembly mode 1 C4 selectivity of each group with temperature change

3.2. Fitting of polynomial Curves

The fitting of polynomial curves is based on expressions: $\text{I}y(x,w)=\sum_{j=0}^{M}\omega_j x^j$. Goodness of fit is used to measure the degree of polynomial fitting, and the statistic measuring goodness of fit is called the determinable coefficient. The closer the value of R^2 is to 1, the better the fit is, and the value of R^2 does not exceed 1. Firstly, the goodness of fit is compared and the curve with the highest goodness of fit is selected. When the goodness of fit is the same, the sum of squares of fitting errors, the square values of correlation coefficients between measured data and inferential data, the mean square deviation and the number of coefficients of the model are compared. The process takes catalyst combination A1 as an example:

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Table 1: Coefficients and intercepts of the cubic polynomial fitting curve of catalyst combination A1

Intercept	-852.93161 ±1416.05547
B1	8.91362 ±14.35934
B2	-0.03141 ±0.04819
B3	3.7731E-5 ±5.35182E-5

The temperature of each catalyst combination and the polynomial curve of ethanol conversion can be fitted in the same way.

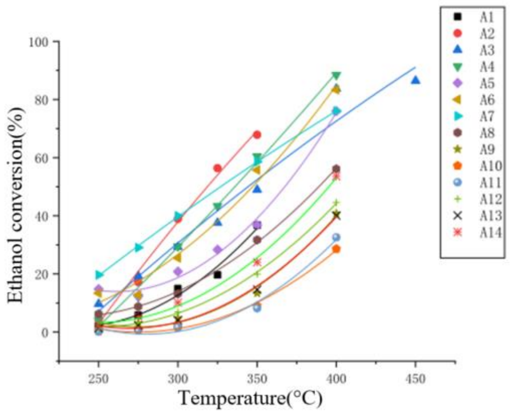

Figure 5: The polynomial fitting curve of temperature and ethanol conversion rate in groups A

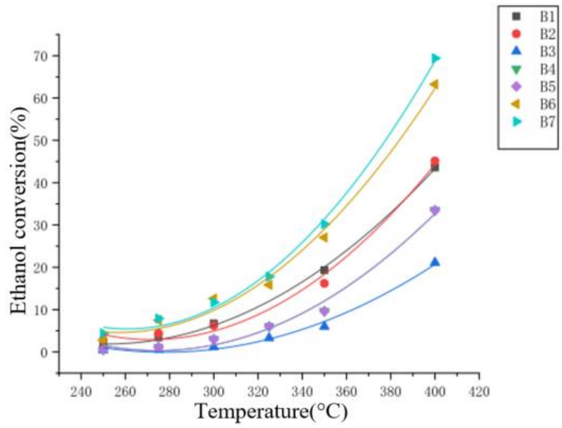

Figure 6: The polynomial fitting curve of temperature and ethanol conversion rate in groups A

Polynomial fitting curves of temperature and C4 olefins selectivity under various catalyst combinations can be obtained, as shown in the figure below. The coefficients and intercepts of the polynomial curve equation are specific.

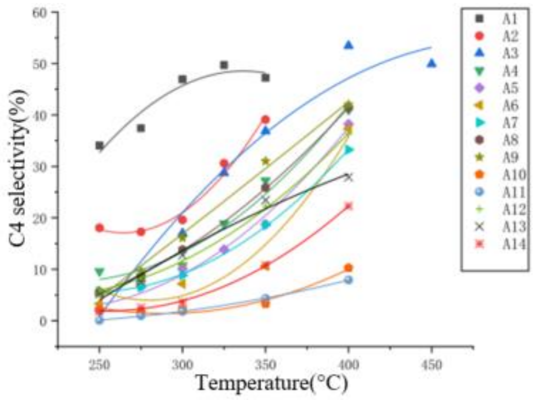

Figure 7: A group temperature and C4 selective polynomial fitting curve

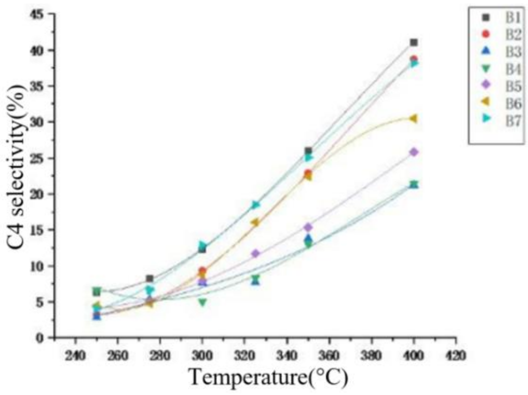

Figure 8: B group temperature and C4 selective polynomial fitting curve

4. The by-product reaction was studied by quantitative analysis of the product

Based on the collected data, this paper analyzes the test data of seven times in an experiment under the condition of a given catalyst combination at 350 degrees. The effect of residence time on the catalytic performance was investigated and the formation mechanism of the product was studied. In the process of coupling C4 olefins with ethanol as raw materials, in addition to C4 olefins, there are also ethylene, acetaldehyde, 4-12 fatty alcohols, and methyl benzaldehyde and methylbenzyl alcohol. The quantitative analysis of the products is shown in the figure.

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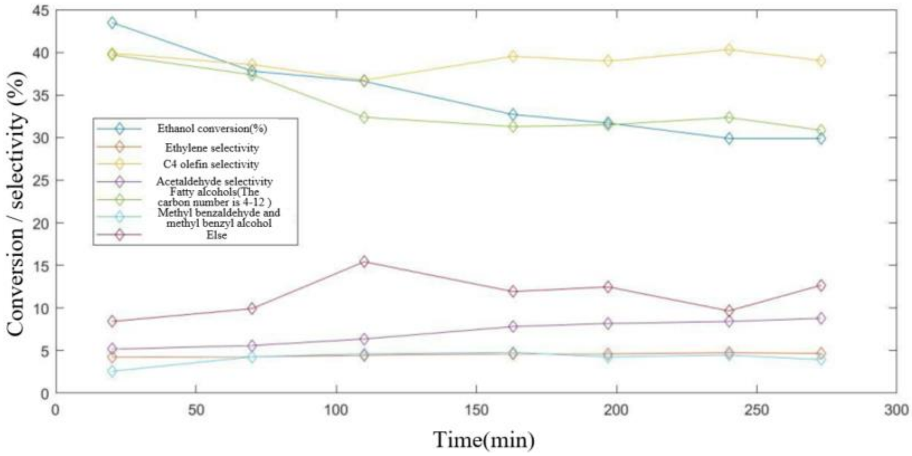

Figure 9: Quantitative analysis of product conversion/selectivity over time

When the time is in the range of 20-163min, the selectivity of aliphatic alcohols with carbon number 4-12 decreases, and acetaldehyde participates in the synthesis of aliphatic alcohols with carbon number 4-12. In the stage of 110-240min, the change trend of C _ 4 olefin and other selectivity is similar, indicating that C _ 4 fatty alcohol with carbon number 412 can be converted into C _ 4 olefin and others, while in the later stage near the end of the reaction, the conversion of ethanol is basically unchanged, while the selectivity of ethylene, C _ 4 olefin, 4-12 aliphatic alcohol, tolualdehyde and methyl benzyl alcohol decreases, while acetaldehyde and other selectivity increase. Therefore, when the conversion of ethanol basically stops, there will be further reactions, resulting in an increase in acetaldehyde and other selectivity.

5. Curve normalization and fitting

Origin software was used to try to normalize two sets of 21 fitting curves of ethanol conversion rate and C4 olefins selectivity. After the previous fitting curve was normalized to the interval [0,1], a series of discrete points were obtained, and the discrete points were fitted to obtain the results as shown in the figure and two equations y_1''', y_2'''.

Table 2: Normalized fitting curve of ethanol conversion rate

Equation	y = Intercept + B1*x^1 + B2*x^2
Intercept	3.45093 ±0.51042
B1	-0.02632 ±0.00319
B2	5.04322E-5 ±4.89664E-6
Sum of squares of residuals	0.00236
R square (COD)	0.9966

Table 3: Normalized fitting curve of C4 olefins selectivity

Equation	y = Intercept + B1*x^1 + B2*x^2
Intercept	-3.68404 ±1.22099
B1	0.01929 ±0.00716
B2	-1.9759E-5 ±1.01862E-5
Sum of squares of residuals	0.04359
R square (COD)	0.95508

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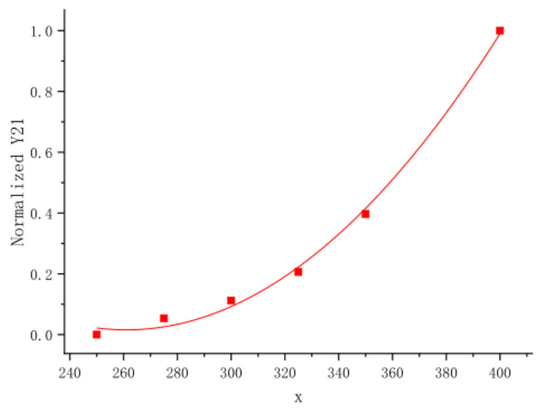

Figure 10: Fitting curve of ethanol conversion rate

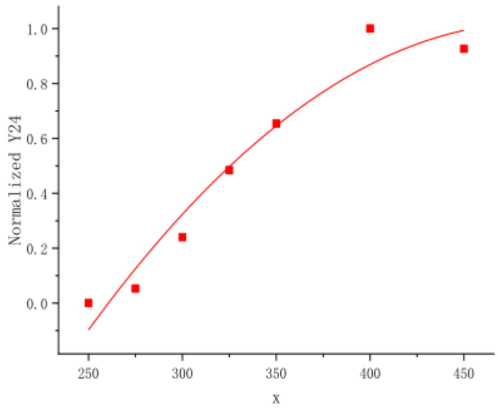

Figure 11: Fitting curve of C4 olefins selectivity

6. Conclusion

In this paper, the preparation of C4 olefins by ethanol coupling was studied, and the effects of catalyst combination and temperature on ethanol conversion and C4 olefin selectivity were discussed by establishing a mathematical model. The relationships between the conversion of ethanol, the selectivity of C4 olefins and temperature under different catalyst combinations were fitted. After the normalization of the curve, it was found that the ethanol conversion and the selectivity of C4 olefins increased linearly and nonlinearly with the increase of temperature. In this paper, by using the idea of control variable method, each factor is put into the same environment to study the relationship between ethanol conversion and C4 olefin selectivity, and the multi-factor is changed into a single factor, which makes the relationship between the factors more clear and concise. Avoid covering each other. Moreover, the polynomial fitting model and the multiple regression model verify each other, which improves the accuracy of the conclusions.

References

[1] Lu Shaopei. Synthesis of butanol and C4 olefin by ethanol coupling [D]. Dalian University of Technology, 2018.

[2] Xie Jinxing, JIANG Qiyuan, YE Jun. Mathematical Model (3rd edition) [M], Higher Education Press, 2003.

[3] Jiang Qiyuan. Mathematical experiment and mathematical modeling [J]. Practice and understanding of Mathematics, 2001 (05): 613,617.

[4] Hu Yaochi, Zhan Nina, Zhang Wen-gui, Lv Hao, Hu Yi. Journal of Nanjing university of technology (natural science), 2012, 34(01): 24-29.

[5] Xia Wei, WANG Longxiang, WANG Junguo, Qian Chen, LUO Zisheng, Chen Kun.Synthesis of low carbon olefin from ethanol catalyzed by P/ZSM-5 zeolite [J]. Experimental technology and management, 2020, 37(02): 201-204.