Experimental Modeling, Analysis, and Solution of Ethanol Coupling for C4 Olefin Production Based on Cubic Spline Interpolation Algorithm

Yuhan Huang [1], Xiaoyu Zhang [2, *], Xueya Song [3], Jing Cheng [4], and Junjie Li [5]

[1] School of Resource and Environmental Engineering, Wuhan University of Science and Technology, Wuhan, China

[2] School of Machinery and Automation, Wuhan University of Science and Technology, Wuhan, China

[3] School of Public Health, Wuhan University of Science and Technology, Wuhan, China

[4] School of Chemistry and Chemical Engineering, Wuhan University of Science and Technology, Wuhan, China

[5] School of Computer Science and Technology, Wuhan University of Science and Technology, Wuhan, China

* Corresponding Author Email: 3271964285@qq.com

Abstract. This paper presents an analysis of ethanol coupling to prepare C4 olefins based on the cubic spline interpolation algorithm. Firstly, the cubic spline interpolation was utilized to fit and plot the trends of temperature, catalyst combination, ethanol conversion rate, and C4 olefin selectivity. Additionally, a polynomial fitting model was established to determine the functional relationships of ethanol conversion rate and C4 olefin selectivity with different catalysts and temperatures, thereby identifying their dependencies on temperature. Subsequently, interpolation fitting was conducted for the variables over time. As the reaction is reversible, a dynamic equilibrium was observed after 273 minutes, allowing for predictive function modeling. Discrepancy analysis between predicted values and experimental data revealed prediction errors of 4.19% and 2.11% for A8 and B7 ethanol conversion rates, and 0.03% and 4.48% for A2 and A3 C4 olefin selectivity, respectively. Combining these errors led to the inference of the catalyst in Appendix II as 200mg1wt%Co/SiO2-200mgHAP with an ethanol concentration of 0.9ml/min.

Keywords: C4 olefins; Cubic spline interpolation; Polynomial fitting model.

1. Introduction

Olefins are hydrocarbons containing C=C bonds, and C4 olefins are one of them, a single olefin with one double bond in four carbons. As an important chemical raw material, C4 olefins are widely used in the production of chemical products and pharmaceutical intermediates. Fossil energy is generally used to prepare olefins in industry, but due to the pollution of the ecological environment and the shortage of resources, there is an urgent need for a green energy source. As a new clean energy source, ethanol has a very wide range of sources and low cost, which can achieve the purpose of saving energy consumption and reducing pollution from the source. Therefore, it is crucial to explore the optimal reaction conditions for the preparation of C4 olefins from ethanol by coupling.

Shi Wang et al [1] designed relevant experiments with different catalysts and temperatures for the coupling preparation of ethanol and C4 olefins to study the relationship between ethanol conversion, C4 olefin selectivity and temperature, and to explore the effects of different catalyst combinations and temperatures on ethanol conversion and C4 olefin selectivity. Based on the experimental data, logistic and neural network models were used to classify and discuss the different catalyst combinations. The results of Michał Patrzałek et al [2] showed that the water-soluble Ru catalyst could be eliminated by the addition of thiocyanate ions (with or without the support of charcoal additives) after AHOM in pure water. The developed purification method makes the aqueous decomposition method more practical and the used water-soluble catalysts easier to separate from the

aqueous decomposition products.P. Oliveira et al [3] analyzed the effect of the acidity of the ZSM-5 catalyst on the catalytic reforming of various short-chained olefins (ethylene, propylene and 1-butene). Four ZMS-5 catalysts with different acid strength distributions were studied at different temperatures and partial pressures. The results were fitted using a kinetic model based on a network mechanism that describes the products in detail by product type (olefins, paraffins, and aromatics) and by number of carbon atoms. A study by Xuefei Wang et al [4] concluded that the Mgsingle - bond - single - bond - si interface formed by the strong interaction of MgO and SiO2 at low ZnO loading structure is crucial for the formation of 1,3-butadiene, thanks to the equilibrium dehydrogenation and the good performance of the Csingle - bond - dc bond coupling.S.P. Wrigley et al [5] further explored the heavy-atom-blocking of the internal energy transfer within the excited state through the chemical activation studies of 4-(trimethyllead)-2-butyl and 5-(trimethyltin)-2-pentyl radicals Possibilities.

The production of C4 olefins from ethanol coupling is a significant process with applications in various industries. Understanding the complex relationships between process variables such as temperature, catalyst combinations, and reaction outcomes is crucial for optimizing production efficiency and product quality. This study employs the cubic spline interpolation algorithm and multivariate nonlinear regression model to analyze and model the experimental data. By utilizing these methods, we aim to establish functional relationships between temperature, catalyst combinations, ethanol conversion rate, and C4 olefin selectivity. Additionally, the study delves into the reversible nature of the reaction, identifying dynamic equilibrium and utilizing predictive modeling to assess the reaction state. Furthermore, the investigation categorizes catalysts based on loading methods, leading to the introduction of a new variable to capture the intricate impact of loading ratios on the reaction outcomes. The evaluation of these relationships provides insights into the dependencies of ethanol conversion rate and C4 olefin selectivity on various process variables, ultimately contributing to a comprehensive understanding of the ethanol coupling process.

2. Determination of transformation relations based on polynomial fitting models

2.1. Model 1

In this paper, polynomial fitting was used to develop fitting models for ethanol conversion, C4 olefin selectivity and temperature for different catalyst combinations:

$$\hat{y}_1 = a_1\hat{x}^3 + b_1\hat{x}^2 + c_1\hat{x} + d_1 \quad (1)$$

$$\hat{y}_2 = a_2\hat{x}^3 + b_2\hat{x}^2 + c_2\hat{x} + d_2 \quad (2)$$

Where x is the temperature of this reaction, y_1 is the ethanol conversion variable, and y_2 is the C4 olefin selectivity variable. The fitted equations and coefficients are shown in Table 1:

Table 1. Fitted equations on ethanol conversion, selectivity of C4 olefins

No.	Fitted equations on the ethanol conversion rate variable ($y_1=a_1x^3+b_1X^2+c_1\times+d_1$)	R^2	Fitted equations on C4 olefin selectivity variables ($y_2=a_2x^3+b_2X^2+c_2\times+d_2$)	R^2
Al	$0.0025x^2-1.194x+141.8$	0.9797	$-6.069\cdot10-5x^3+0.05251x^2-14.84x+1409$	0.9844
A2	$-8.052\cdot10-5x^3+0.0717x^2-20.46x+1895$	0.9993	$-3.013\cdot10-5x^3+0.0302x^2-9.718x+1029$	0.9890
A3	$-2.037\cdot10-5x^3+0.0210x^2-6.607x+671.5$	0.9873	$-1.862\cdot10-5x^3+0.0185x^2-5.707x+565.6$	0.9980
A4	$-1.866\cdot10-5x^3+0.0186x^2-5.478x+505$	0.9987	$-2.106\cdot10-5x^3+0.0218x^2-7.136x+763.7$	0.9985
A5	$5.399\cdot10-6x^3-0.0021x^2+0.0158x+54.84$	0.9945	$1.382\cdot10-5x^3-0.0124x^2+3.816x-395.6$	1
A6	$-3.473\cdot10-5x^3+0.0355x^2-11.37x+1183$	0.9988	$3.224\cdot10-5x^3-0.0292x^2+8.782x-873.5$	0.9999
A7	$-1.613\cdot10-6x^3+0.0013x^2-50.06x+0.0555$	0.9998	$-2.034\cdot10-6x^3+0.0031x^2-1.197x+141$	1
A8	$-5.782\cdot10-6x^3+0.0074x^2-2.598x+285.2$	0.9998	$-2.118\cdot10-^6x^3+0.0028x^2-0.9026x+88.8$	0.9997
A9	$1.602\cdot10-5x^3-0.0131x^2+3.635x-335.6$	0.9999	$-1.097\cdot10\sim5x^3+0.0107x^2-3.19x+303.9$	1
A10	$9.187\cdot10-6x^3-0.0071x^2+1.867x-163.6$	0.9999	$4.752\cdot10-6x^3-0.0039x^2+1.073x-95.06$	0.9957
A11	$1.555\cdot10-5x^3-0.0129x^2+3.558x-328.7$	0.9998	$6.035\cdot10-7x^3-0.0004x^2+0.12x-14.07$	0.9998
A12	$5.421\cdot10-6x^3-0.0034x^2+0.7297x-55.05$	1	$-3.199\cdot10-6x^3+0.0040x^2-1.377x+149.5$	0.9999
A13	$9.635\cdot10-^6x^3-0.0071x^2+1.783x-149.5$	1	$-1.339\cdot10-5x^3+0.0128x^2-3.818x+371.9$	0.9998
A14	$1.084\cdot10-5x^3-0.0084x^2+2.285x-215.1$	0.9998	$-3.965\cdot10-7x^3+0.0014\ x^2-0.6171x+77.78$	0.9995
B1	$5.871\cdot10-6x^3-0.0038x^2+0.8754x-70$	1	$-7.716\cdot10-5x^3+0.0084x^2-2.762x+290.4$	0.9999
B2	$1.651\cdot10-5x^3-0.0136x^2+3.765x-349.6$	1	$-7.11\cdot10-6x^3+0.0079x^2-2.612x+272.9$	1
B3	$7.823\cdot10-6x^3-0.0062x^2+1.671x-149.7$	0.9993	$1.711\cdot10-6x^3-0.0012x^2+0.3438x-35.17$	0.9768
B4	$1.469\cdot10-5x^3-0.0123x^2+3.456x-326.6$	0.9982	$-6.409\cdot10-6x^3+0.0073x^2-2.549x+291.3$	0.9824
B5	$1.639\cdot10-5x^3-0.0135x^2+3.76x-351.8$	0.9998	$-2.428\cdot10-6x^3+0.0030x^2-1.034x+112$	0.999
B6	$2.246\cdot10-5x^3-0.0191x^2+5.566x-546.7$	0.9986	$-1.965\cdot10-5x^3+0.0195x^2-6.153x+632.3$	0.9994
B7	$1.472\cdot10-5x^3-0.0111x^2+2.885x-254.3$	0.9996	$-6.14\cdot10-6x^3+0.0064x^2-1.977x+191.6$	0.9990

R2 is the degree of linear fit, and 0.75 is used as the reference standard. From Table 1, it can be seen that by fitting out all the

Equations, the value of R2 coefficient tends to be close to 1, indicating that the equation is well-fitted and can express the relationship between the two.

In order to make the expression of the equations more intuitive, therefore, the interpolation and fitting method was used to fit the graphs of ethanol conversion, C4 olefin selectivity and temperature.

Interpolation and fitting are to construct an approximation function based on a set of known data, and then the approximation function can be used to find the point corresponding to the unknown point and estimate its approximation value. This method is suitable for when the amount of sample data is not enough, the need to supplement the data of the situation, but also can reflect the pattern of change of the data, and the prediction of the unknown situation. With the method parameter indicating the method used for interpolation, the commonly used method has 4 kinds of value, this paper uses spline 3 times spline interpolation, the specific process for each segment within the construction of a third-degree polynomial, and each node out of a continuous first or second order derivatives, so that its function to meet the interpolation conditions.

Since there are twenty-one catalyst combinations, there is a certain sample size that is combined and analyzed together so that the results have some validity. A partially fitted graph was made from the data as shown in Figure 1.

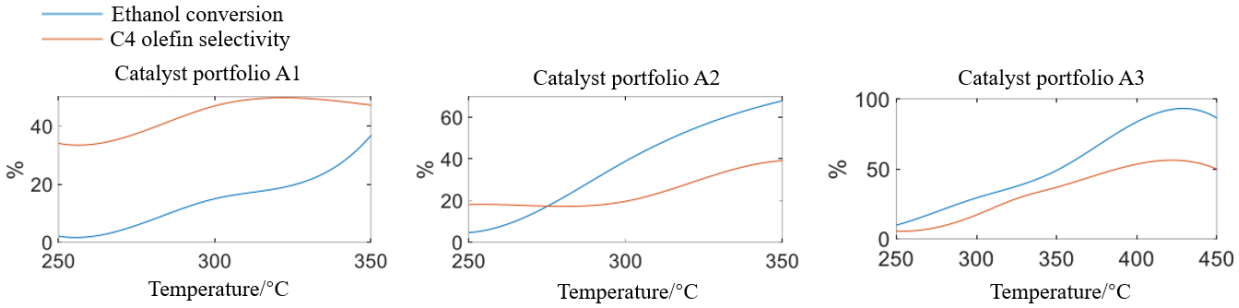

Fig 1. Interpolated fitted plots for different catalyst combinations.

Observing Fig. 1, it can be seen that in general, the ethanol conversion and C4 olefin selectivity of the reaction increase with increasing temperature, and only a very small portion of the data decreases with increasing temperature. It is concluded that ethanol conversion and C4 olefin selectivity are positively correlated with temperature.

2.2. Model 2

Ethanol conversion, ethylene selectivity, C4 olefin selectivity, acetaldehyde selectivity, carbon number 4-12 aliphatic alcohols, methyl benzaldehyde versus methyl benzyl alcohol, and other product selectivities were measured and calculated as a percentage of different time points. In order to investigate the analysis of the test results at different times for a given catalyst combination and temperature of 350 °C, the paper also starts with polynomial fit modeling.

Table 2. Fitting equations for the indicators at 350°C versus time.

Indicators	simultaneous equations	R^2
Ethanol conversion rate	$-1.652\cdot10^{5}x^{5}+1.386\cdot10\text{-}7x^{4}-4.259\cdot10\text{-}5x^{3}+0.005933x^{2}-0.4216x+49.91$	0.9960
Ethylene selectivity	$-2.042\cdot10\text{-}11x^{5}+1.563\cdot10\text{-}^{8}x^{4}-4.436\cdot10\text{-}^{6}x^{3}+0.0005613x^{2}-0.02674x+4.574$	0.9899
C4 olefin selectivity	There is no suitable fitting equation due to too much variation and irregularity	
Acetaldehyde selectivity	$4.831\cdot10\text{-}11x^{5}-3.113\cdot10\text{-}8x^{4}+6.434\cdot10\text{-}6x^{3}-0.0004306x^{2}+0.01708x+4.956$	0.9991
Carbon numbers 4-12 aliphatic	$2.249\cdot10\text{-}5x^{5}-2.035\cdot10\text{-}7x^{4}+6.582\cdot10\text{-}5x^{3}-0.008897x^{2}+0.4005x+34.77$	0.9957
Aliphatic Alcohols	$-3.488\cdot10\text{-}9x^{4}+2.515\cdot10\text{-}6x^{3}-0.000686x^{2}+0.081x+1.209$	0.9691

Looking at Table 2, it can be seen that the R2 coefficients of the fitted equations tend to be 1 for all the indicators, except for the selectivity of C4 olefins for which there is no suitable fitting equation due to the irregularity in the variation of the nodes, thus concluding that the model is well fitted.
The metric of C4 olefin selectivity was then excluded and a fitted image was made for several other metrics, as shown in Figure 2:

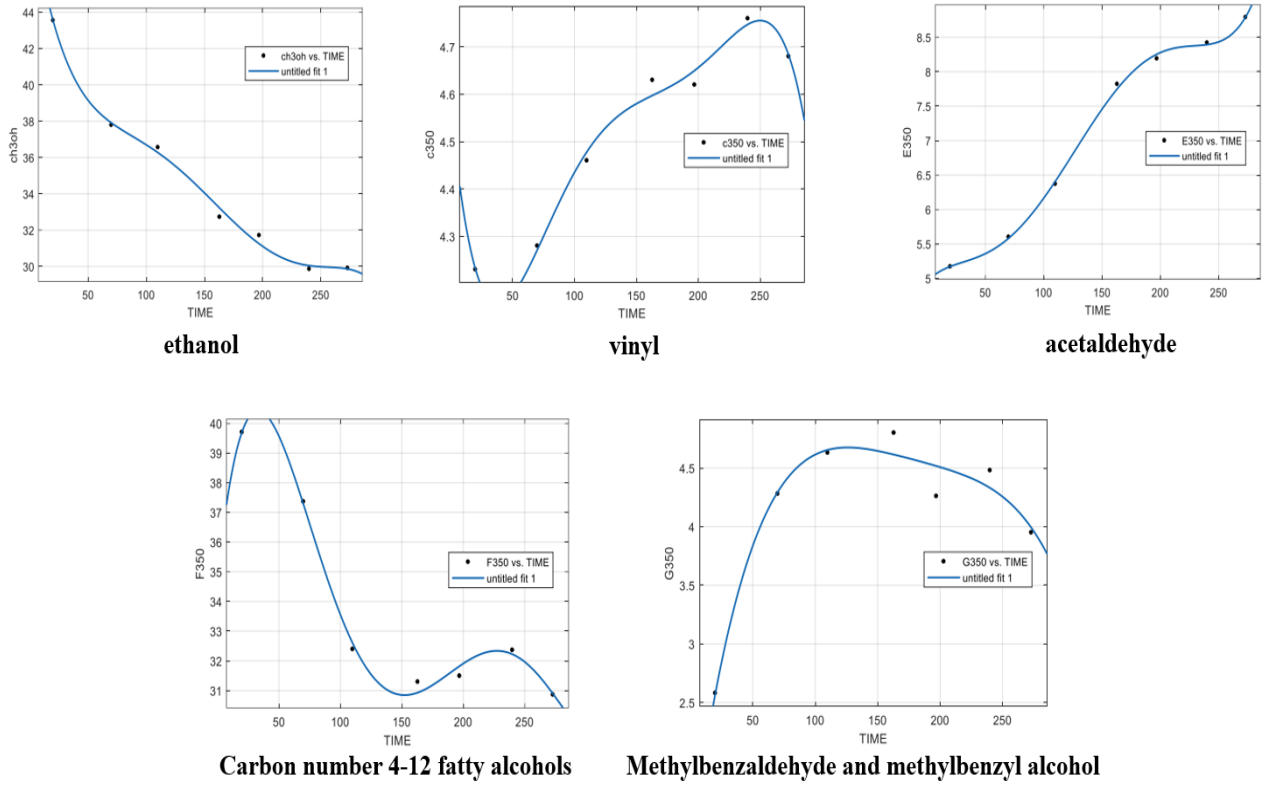

Fig 2. Fit chart.

The analysis of Fig. 2 shows that: the conversion rate of ethanol decreases with the increase of time; the selectivity of ethylene shows a tendency to decrease, then increase and then decrease; the selectivity of acetaldehyde increases slowly with time; the curve of the selectivity of fatty alcohols with the carbon number of 4-12 shows the curve of increasing, then decreasing sharply to 30.86%, and then floating in a small band; the curves of the selectivities of methyl benzaldehyde and methyl benzene methanol are similar to the parabolic line, and show the curve of increasing and then decreasing firstly. The selectivity curves of methyl benzaldehyde and methyl benzyl alcohol were similar to parabolic curves, first increasing and then decreasing.

With the longer reaction time, most of the indicators tend to be stable, especially the ethanol conversion rate, ethylene selectivity, methyl benzaldehyde and methyl benzyl alcohol in 243min-273min basically remain unchanged, through the information and previous knowledge, it can be presumed that when the reaction is carried out to 273min, the reaction rate of the coupling reaction is roughly unchanged to reach the equilibrium point, and after the equilibrium of the reactant and the product are in dynamic equilibrium. After equilibrium, the reactants and products are in dynamic equilibrium. After equilibrium, the reactants and products are in dynamic equilibrium. It is concluded that the catalyst at 350℃ has an ethanol conversion of 29.9% and a C4 olefin selectivity of 39.04%.

3. Speculation on a given catalyst

The values of ethanol conversion and C4 olefin selectivity at 350 °C for a given catalyst are known, and in order to infer the catalyst composition in this case, the proportional content and charging mode of the most similar catalyst components were inferred based on the characteristics of the different catalyst combinations in Annex I. The catalyst composition for the given catalyst combination was calculated as follows.

Firstly, the relative error $E1$, $E2$ (relative error = absolute error / true value) between the given catalyst combination and the combination of 21 catalysts for the two metrics was calculated with the formula:

$$E_1 = \frac{|\hat{y}_1 - y_1|}{y_1} \times 100\% \quad (3)$$

$$E_2 = \frac{|\hat{y}_2 - y_2|}{y_2} \times 100\% \quad (4)$$

The results of the calculations are shown in Table 3:

Table 3. Relative error between the two indicators.

Catalyst combination number	Relative error on the ethanol conversion rate variable	Relative errors on C4 olefin selectivity variables
A1	19.27%	16.27%
A2	129.53%	0.03%
A3	78.21%	4.48%
A4	100.76%	29.49%
A5	28.81%	52.79%
A6	90.89%	73.38%
A7	96.37%	52.58%
A8	4.19%	33.56%
A9	53.65%	19.35%
A10	70.00%	90.93%
A11	73.39%	88.92%
A12	33.29%	43.37%
A13	51.19%	40.12%
A14	18.61%	72.38%
B1	35.45%	33.30%
B2	46.02%	41.83%
B3	79.39%	67.67%
B4	63.27%	67.70%
B5	47.76%	60.09%
B6	13.55%	42.22%
B7	2.11%	35.51%

When the relative error value is smaller, it means that the ratio content of catalyst combination components is closer at this time. From Table 3, it can be seen that each group of catalysts cannot achieve both indicators close to the value of the given catalyst at the same time, therefore, the two indicators are discussed separately in this paper.

For the variable of ethanol conversion, it can be observed that the relative errors of catalysts A8 and B7 are smaller, and comparing the proportional contents of the two catalysts, it is found that all the other parts are the same except for the different masses, which leads to the common point of the catalyst combinations of the two groups:

$$1\text{wt\%Co/Si02} - \text{HAP} - \textit{ethanol concentration}\ 0.9\text{ml/min} \quad (5)$$

For the variable of C4 olefin selectivity, it can be observed that the catalysts in the A2 and A3 groups have a relatively small error, and then comparing the proportional content of the two groups, it is found that, in contrast to the previous one, except for the same mass, the rest of the parts are not the same, which leads to the conclusion that the two groups have a common point in the combination of the catalysts:

$$200\text{mg} - 200\text{mg} \quad (6)$$

From this, the catalyst combination is surmised to be:

$$200\text{mg}1\text{wt\%Co/Si02} - 200\text{mgHAP} - \textit{ethanol concentration}\ 0.9\text{ml/min} \quad (7)$$

Since, the combination is exactly the same as A3, but the specific values are quite different, it can be deduced that the combination is likely to be loaded by loading mode II.

4. Summary

In conclusion, the study successfully utilized cubic spline interpolation to analyze the ethanol coupling process for C4 olefin production. By establishing functional relationships between process variables and reaction outcomes, the study elucidated the dependencies of ethanol conversion rate and C4 olefin selectivity on temperature and catalyst combinations. The identification of dynamic equilibrium and the prediction of reaction states further enhanced the understanding of the reversible nature of the reaction. The comprehensive analysis presented in this study provides valuable insights for optimizing the ethanol coupling process, ultimately contributing to the advancement of C4 olefin production techniques.

References

[1] S. Wang, Z. Jiang, J. Yang, Y. Tang, and B. Liu, "Design and research on preparation of C4 olefins by ethanol coupling based on logistic," Energy Reports, vol. 8, pp. 370–376, Jul. 2022.

[2] M. Patrzałek et al., "Testing diverse strategies for ruthenium catalyst removal after aqueous homogeneous olefin metathesis," Journal of Organometallic Chemistry, vol. 965–966, p. 122320, May 2022.

[3] P. Oliveira et al., "Light olefin transformation over ZSM-5 zeolites with different acid strengths – A kinetic model," Applied Catalysis A: General, vol. 384, no. 1, pp. 177–185, Aug. 2010.

[4] X. Wang, Y. Men, J. Wang, S. Liu, Q. Song, and M. Yang, "The influence of zinc loadings on the selectivity control of bio-ethanol transformation over MgO-SiO2 catalysts," Applied Catalysis A: General, vol. 598, p. 117565, May 2020.

[5] S. P. Wrigley, D. A. Oswald, and B. S. Rabinovitch, "On the question of heavy-atom blocking of intramolecular vibrational energy transfer," Chemical Physics Letters, vol. 104, no. 6, pp. 521–525, Feb. 1984.