

Study on Preparation of C4 Olefin by Ethanol Coupling Based on Polynomial Fitting Analysis

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Abstract: In this paper, firstly, according to different catalyst combinations, in order to explore the relationship between ethanol conversion, C4 olefin selectivity and temperature, the non-linear relationship between temperature and ethanol conversion and C4 olefin selectivity can be predicted by polynomial fitting. According to the correlation analysis of the change data of components at different times under a given condition, the best reaction temperature is 421.1°C. Under this condition, the expected value of ethanol conversion is 88.4% and the predicted value of olefin selectivity is 46.78%. Then the conversion function is defined according to the reaction principle, and the parameters that influence the sensitivity of the variables to the properties of the catalyst are determined, which can better reflect the influence degree of the parameters. Finally, by fitting the established function model and calculating the parameters, we can get the functional expression about the selectivity of C4 olefins. By bounding the expression, including the selection range of the independent variables c_r , M_{cr} , h_r , M_{hr} , T_r (. As well as the restriction on the selectivity of olefins, the selectivity should be as high as possible but not higher than the actual realizable value. The actual realizable value can be roughly determined by fitting and consulting the literature. The standardized data can be imported into the expression to find the global optimal solution.

Keywords: Ethanol conversion, C4 olefin selectivity, Polynomial fitting

1. Introduction

Ethanol is a kind of clean energy, which can be obtained through biomass fermentation. The raw material sources are very wide. Ethanol is the raw material for the production and preparation of C4 olefin, so now most processes use ethanol to prepare C4 olefin. However, there are many kinds of products involved in the preparation of C4 olefin by ethanol, which results in low selectivity and poor economic applicability of the target product. Therefore, in this process, the selection of catalytic materials and the selection of preparation methods and conditions are very important, in order to improve product selectivity under the same experimental conditions, to achieve the optimal combination, so it is of great significance and value to explore the technological conditions of ethanol catalytic coupling to prepare C4 olefin. Therefore, the selection of catalytic material combination and temperature has become the core element, and how to carry out the optimal combination has become the problem we consider [1].

2. Effect of temperature on ethanol conversion and C4 olefin selectivity

2.1. Model preparation

According to different catalyst combinations, we first made a preliminary analysis of 21 groups of data, and obtained the preliminary trend form. In this paper, we try the linear and nonlinear simulation, and adopt the strategy from low to high degree in the nonlinear fitting. The use of fourth-power fitting can be as close as possible to the original data, and individual data sets are fitted to the fifth power. The specific fitting analysis involves the following four items, namely: SSE, R-square, AdjustedR-square and RMSE.

SSE and variance: A data processing method in which discrete points on a plane are approximated or compared by continuous curves [2] in order to express functional relations between coordinates. R Square fitting coefficient: The normal value range of the "fitting coefficient" is [0-1], and the closer it is to 1, the stronger the variable of the equation is in explaining y, and the better the model fits the data. The fitting

coefficient Adjusted by Adjusted R Square.

2.2. Model result

From the model fitting results, the temperature changes of catalyst combinations A1, A3, A4 and A5 are very likely to be different from those of other combinations 5: the maximum value of ethanol conversion may exist in catalyst combination A3 at 400-450 °C [3]. There may be a local decrease and then an increase in the combination A4 between 250 and 300 °C, and there may also be a maximum value of ethanol conversion between 350 and 400 degrees Celsius. Similarly, the combination A1 and A5 may decrease at first and then rise at 250-300 °C; The other related combinations are similar, showing a change and increase, here A8 as the experimental representative [4].

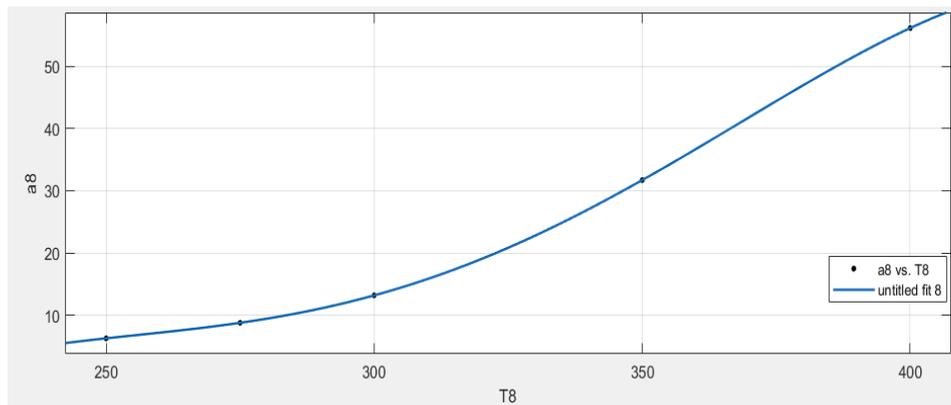


Figure 1: Under the condition of catalyst combination A8, the relationship between ethanol conversion and temperature fits the curve.

The relationship between C4 olefin selectivity and temperature can be obtained by the same method. The trend of similar catalyst combinations can be classified into the following two cases, the selectivity increases with the temperature, and its growth rate slows down and increases gradually.

3. The relationship between C4 olefin selectivity and temperature

Because different combinations of catalysts only affect the reaction rate, thus affecting the stage of the reaction, but not on the reaction itself, there is only one independent variable, that is, temperature change. C4 olefin selectivity and ethanol conversion are dependent variables under this independent variable. There is only one degree of freedom, so the comprehensive consideration of the three can be further fitted. In the three-dimensional space, the relationship between the three can be presented as a rising curve. The following is the relationship curve of the scattered data of the three through MATLAB fitting.

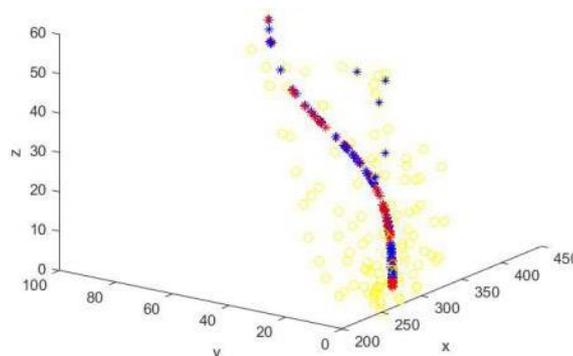


Figure 2: The fitting results of the relationship between ethanol conversion, C4 olefin selectivity and temperature

According to the fitting results, the optimum reaction temperature is 421.1 °C. Under this condition, it is estimated that the ethanol conversion can reach 88.4% and the olefin selectivity of C4 can reach 46.78%.

4. Quantitative analysis of different catalyst combinations

4.1. Model building

The conversion equation of reactants can be expressed as:

$$X = 1 - e^{-k\tau} \quad (1)$$

K is the reaction rate coefficient and τ is the duration of the reactants in the catalyst layer. When the conditions do not completely meet the above conditions, the conversion rate equation can be written as:

$$X = 1 - e^{-k \times f(T, p, y, \tau)} \quad (2)$$

Where $f(T, p, y, \tau)$ is the function of reaction conditions, T is reaction temperature, P is reaction pressure, y is the initial molar fraction of each reactant. In general, the reaction rate coefficient K satisfies Arrhenius' law

Assuming that $k_0 e^{\frac{-E_a}{RT}} f(T, p, y, \tau)$ is small, the above equation can be simplified as:

$$X = A' e^{\frac{-E_a}{RT}} \quad (3)$$

$$A' = k_0 f(T, p, y, \tau) \quad (4)$$

After simultaneous can get:

$$\ln X = \ln A' - \frac{E_a}{RT} \quad (5)$$

By visualizing the catalyst groups at different temperatures, we can obtain groups of nearly parallel straight lines. Therefore, we can assume that the reaction activation energy of the catalyst is constant at different times. The specific data processing process is as follows: firstly, the range of temperature T is normalized as Tr, 1/Tr is the abscissa, and 100ln(X is the ordinate) is plotted, and the following results are obtained:

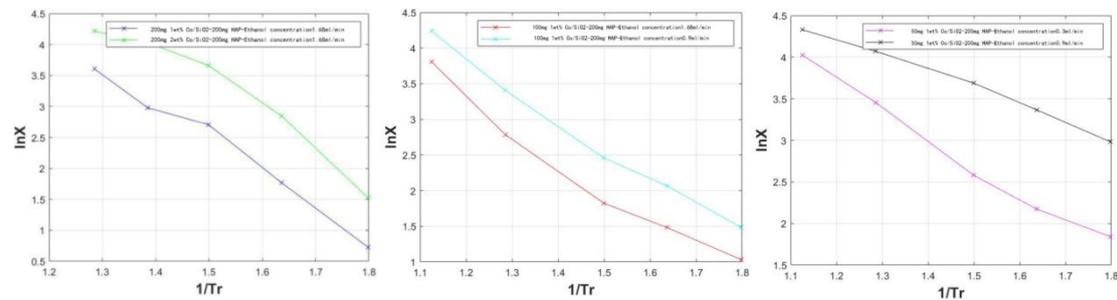


Figure 3: Relationship between conversion and reaction temperature

The results show that it can be approximated that the apparent activation energy hardly changes with the carrier in the catalytic process, so we set the activation energy term as constant. It is considered that the main factor affecting ethanol conversion is pre-exponential factor K0, and the quantitative correspondence between catalyst and pre-exponential factor is further established.

The factors affecting the conversion and direction of the transformation are temperature T, concentration C of Co/SiO2, mass Mc of Co/SiO2, concentration H of ethanol and HAP mass Mh. The mass ratio of two mixtures can be reflected by their respective masses, so no additional variables are set in this paper.

Let the property exponent G satisfy

$$g = Y^{\alpha_1} Y^{\alpha_2} Y^{\alpha_3} Y^{\alpha_4} Y^{\alpha_5} \quad (6)$$

Y represents the properties that affect the properties of the catalyst

$$\sum_i \alpha_i = 1 \quad (7)$$

$$0 \leq \alpha_i \leq 1$$

It is assumed that the property index g satisfies the following relation with the pre-exponential factor k_0 :

$$k_0 = B_0 g^\beta \geq 0 \quad (8)$$

Table 1: Standardized definition of variables

Original variable	Variable meaning	Standardized variable
c(1/C)	Co/SiO2 reciprocal of concentration	cr
Mc	Mass ratio of Co/SiO2 to HAP	Mcr
h(1/H)	Reciprocal of ethanol concentration	hr
Mh	Quality of ethanol	Mhr
T	Temperature	Tr

Then standardize the variables:

$$X = 1 - e^{(-A_0 \cdot cr^{n_1} \cdot Mcr^{n_2} \cdot hr^{n_3} \cdot Mhr^{n_4} \cdot Tr^{n_5})} \quad (9)$$

The above equation can be deformed into:

$$\ln[-\ln(1-X)] = \ln A_0 + n_1 \ln cr + n_2 \ln Mcr + n_3 \ln hr + n_4 \ln Mhr + n_5 \ln Tr \quad (10)$$

4.2. Model solving

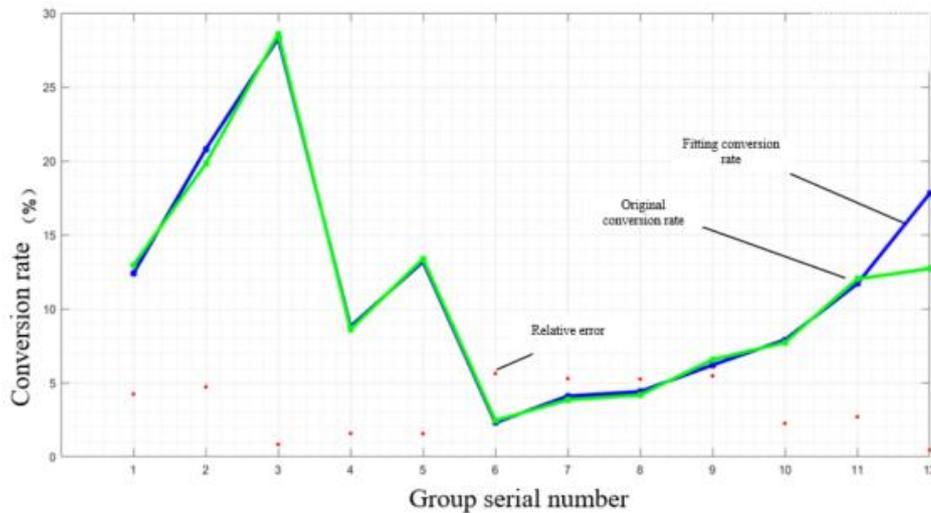


Figure 4: Original conversion and fitting conversion can be viewed-ethanol

If all the values are weighted and averaged, you can get

Table 2: Model calculation parameter-ethanol

Parameter name	Data	Parameter name	Data
β	4.6468	A_0	106.12
n_1	0.6575	α_1	0.074
n_2	1.0331	α_2	0.116
n_3	1.0165	α_3	0.115
n_4	0.8668	α_4	0.098
n_5	5.3120	α_5	0.600
Average relative error ARD (%)		3.3302	

The table lists the relevant model parameters obtained by fitting, and the average relative deviation of fitting is 3.3302%, indicating that the fitting degree of the proposed mathematical model is high. Among them, in order to facilitate the comparison, the fitting conversion calculated by each catalyst is

listed in the table, which is in good agreement with the original conversion obtained by the experiment.

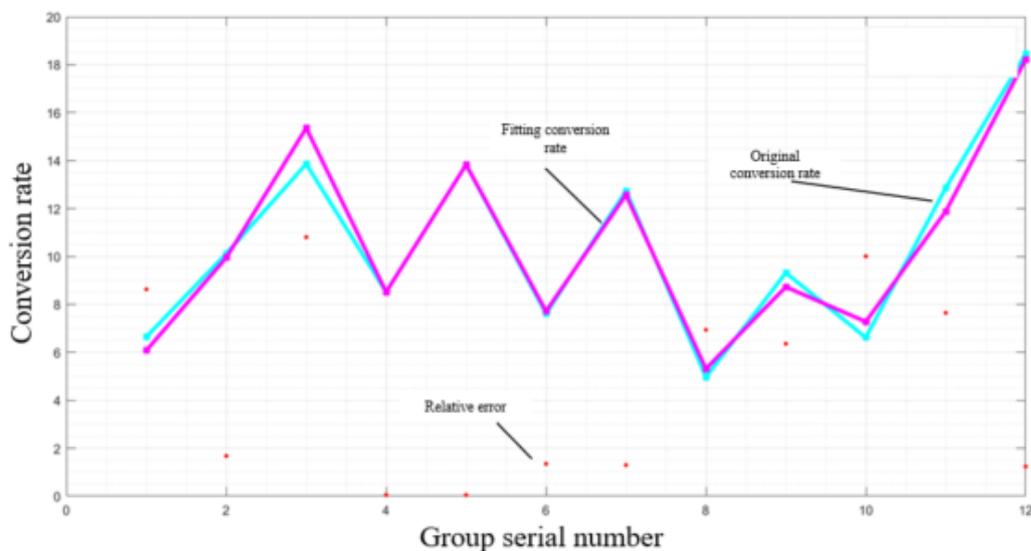


Figure 5: Visual View of original conversion and fitting conversion-C4 Olefins

5. Conclusion

There are many kinds of products involved in the process of preparing C4 olefins from ethanol, and different catalyst combinations will have different effects on the process. Firstly, according to different catalyst combinations, the relationship between ethanol conversion, C4 olefin selectivity and temperature was studied. According to the correlation analysis of the change data of components at different times under a given condition, the optimum reaction temperature is 421.1 °C. Under this condition, the expected value of ethanol conversion is 88.4% and the predicted value of olefin selectivity is 46.78%. Then 12 groups of different catalyst ratio and ambient temperature were obtained. By fitting the established function model and calculating the parameters, we can get the functional expression about the selectivity of C4 olefins. By limiting the boundary of the expression, including the selection range of independent variables cr , Mcr , hr , Mhr and Tr , the standardized data is imported into the expression and the global optimal solution is obtained. When there are additional conditions, the local optimal solution can be obtained by adding additional boundary restrictions.

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