

# A Maximum Yield Model for Coupled Ethanol to C4 Alkenes Based on BP Neural Network and Genetic Algorithm

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## ABSTRACT

The preparation of C4 alkenes using ethanol coupling is an important reaction in chemical production, and the catalyst combination and temperature have a significant impact on the extent and efficiency of the reaction. This paper provides a model for seeking the maximum C4 alkenes yield by designing the catalyst combination and setting the temperature. Firstly, we investigated the relationship of ethanol conversion and C4 alkenes selectivity with temperature. The correlation analysis and regression analysis were conducted. We obtained that temperature is positively correlated with ethanol conversion and C4 alkenes selectivity in a certain temperature range, and the most drastic effect point was obtained lies within the interval [350,400] °C. Moreover, we analyzed results from the perspective of the chemical reaction mechanism. Then, we analyzed the effect of different catalyst combinations and temperatures on ethanol conversion and C4 alkenes selectivity by the grey correlation model. We obtain the correlation ranking: temperature > Co loading > Co/SiO<sub>2</sub> and HAP loading ratio > drop acceleration rate of ethanol. Finally, we set the maximum C4 alkenes yield as the objective function and established a BP neural network to solve this optimization problem with the genetic algorithm used for extreme value finding. The maximum C4 alkenes yield of 0.4580 was obtained with the catalyst combination of 200 mg 1wt% Co/SiO<sub>2</sub>, 200 mg HAP, and ethanol concentration 0.9 mL/min without temperature limitation. With a limiting temperature of less than 350°C, the maximum C4 alkenes yield is 0.1982 at a reaction temperature of 348.60°C with the catalyst combination of 200 mg 1wt% Co/SiO<sub>2</sub>, 200 mg HAP, and ethanol concentration 0.9 mL/min.

**Keywords:** Correlation analysis, Grey correlation model, BP neural network, Genetic algorithm

## 1. INTRODUCTION

In the field of petrochemicals, C4 alkenes occupy an essential position. In the process of C4 alkenes preparation by ethanol coupling, the combination of temperature and catalyst has a significant degree of influence on the selectivity and yield of C4 alkenes.

Firstly, we investigate the temperature dependence of ethanol conversion and C4 alkenes selectivity for different catalyst combinations.

Then, we discuss the effect of catalyst and temperature in different combinations on ethanol conversion and C4 alkenes selectivity.

Finally, we will select the catalyst combination and temperature to maximize the C4 alkenes yield under the same experimental conditions.

## 2. MODEL ESTABLISHMENT AND SOLUTION

### 2.1. Data Analysis [1]

#### 2.1.1. Correlation Analysis

Calculate the Pearson correlation coefficients between temperature and ethanol conversion, temperature, and C4 alkenes selectivity. Moreover, the

significant level of correlation was calculated for each group under the set confidence interval of 99%. The results are listed in Table 1, where  $r$  is the correlation coefficient, and  $p$  is the significant level. Subtitles 1 and 2 represent the relationship between temperature and ethanol conversion, temperature, and C4 alkenes selectivity.

It is clear from Table 1 that the correlation coefficients between the temperature and ethanol conversion and temperature and C4 alkenes selectivity for each catalyst combination tend to be close to one, and the significance level is much less than 0.01. It indicates an extremely strong correlation between the data and that the data are all bilaterally significantly correlated at the 0.01 level. That is, the correlation analysis between the data has high reliability.

2.1.2. Regression Analysis

Scatter plots were drawn with temperature as the horizontal axis and ethanol conversion and C4 alkenes selectivity as the vertical axis. And then, the fitted curves and their functions were obtained by polynomial fitting, and the fitted functions were noted as

(1)

The coefficient of determination ( $R^2$ ) is listed in Table 1. The fitting curves of the relationship between temperature and ethanol conversion are shown in Figure 1. The relationship between temperature and C4 alkenes selectivity is shown in Figure 2.

Table 1. The Results of Correlation Analysis and Regression Analysis

|       | 1      | 2      | 3      | 4      | 5      | 6      | 7      | 8      | 9      | 10     | 11     | 12     | 13     | 14     |
|-------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| $r_1$ | 0.9992 | 0.9988 | 0.9994 | 0.9995 | 0.9997 | 1      | 1      | 1      | 1      | 1      | 0.9998 | 1      | 1      | 0.9986 |
| $p_1$ | 2.7E-5 | 5.2E-5 | 1.0E-8 | 3.4E-7 | 1.6E-7 | 8.0E-8 | 4.0E-8 | 0      | 0      | 0      | 3.5E-6 | 0      | 0      | 9.0E-8 |
|       | 0.8699 | 0.8238 | 0.9703 | 0.9763 | 0.9434 | 0.9857 | 0.9324 | 0.9999 | 1      | 1      | 0.9816 | 1      | 0.9998 | 0.9896 |
| $r_2$ | 0.9985 | 0.9998 | 0.9991 | 0.9994 | 1      | 0.9997 | 1      | 1      | 1      | 1      | 1      | 1      | 1      | 1      |
| $p_2$ | 6.7E-5 | 4.2E-6 | 5.0E-8 | 5.0E-7 | 0      | 6.4E-6 | 1.0E-8 | 0      | 0      | 6.7E-5 | 2.0E-8 | 0      | 1.0E-8 | 0      |
|       | 0.9764 | 0.9866 | 0.9963 | 0.9953 | 1      | 0.9768 | 0.998  | 0.9995 | 0.9981 | 0.9704 | 0.9727 | 0.9984 | 0.9898 | 0.9931 |

2.1.3. Conclusion

It is concluded that temperature significantly affects ethanol conversion and C4 alkenes selectivity within a specific range and both ethanol conversion and C4 alkenes selectivity increase with increasing temperature.

Solve for the maximum value of the slope of the fitted curve over a given temperature range, i.e., explore the interval where the ethanol conversion and C4 alkenes selectivity growth are maximized. A single derivative of the fitted function is conducted to find the maximum  $f'(t)$  corresponds to the temperature  $t$  in the

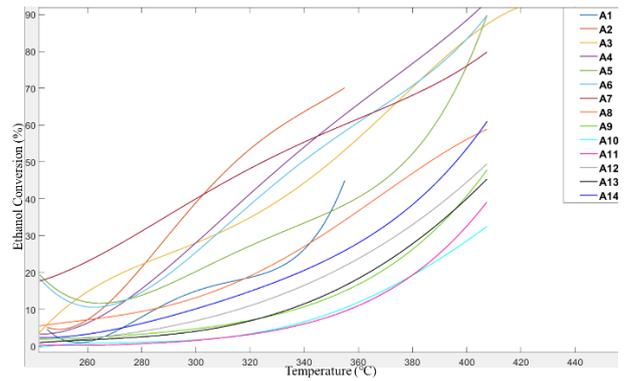


Figure 1 The fitting curves of the relationship between temperature and ethanol conversion

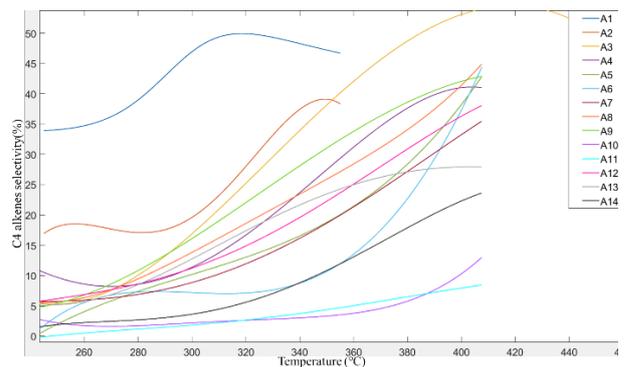
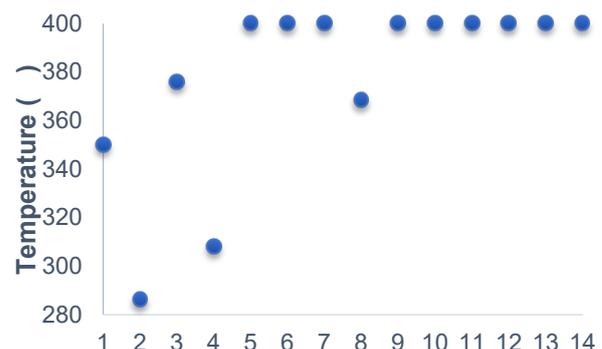
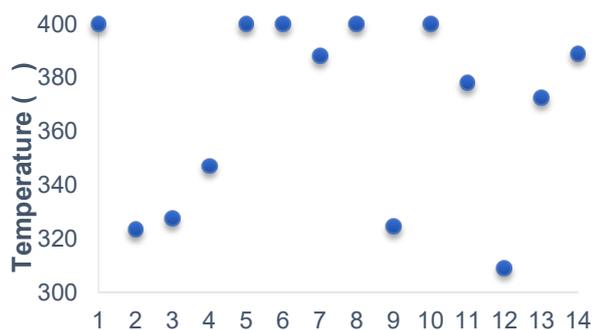


Figure 2 The fitting curves of the relationship between temperature and C4 alkenes selectivity

temperature interval. The distribution of temperature is shown in Figure 3 and Figure 4.



**Figure 3** The fitting curves of the relationship between temperature and ethanol conversion

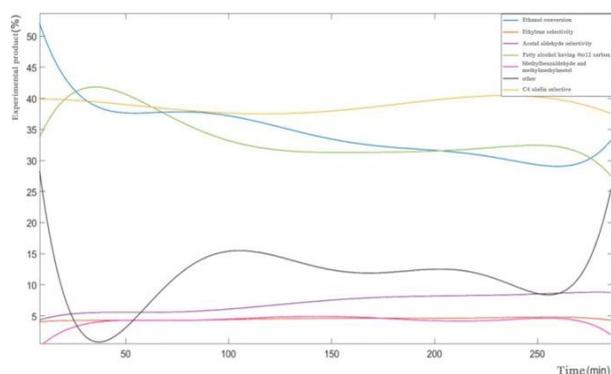


**Figure 4** The fitting curves of the relationship between temperature and C4 alkenes selectivity

## 2.2. Analysis of experimental results for a given catalyst combination under 350°C

### 2.2.1. Image analysis of change trend

Under the given combination of catalysts and temperature (350°C), with only the reaction time as a single variable, the scatter plot of the statistics of each component in the reaction against the reaction time was initially made and then fitted to them separately. We can observe the trend of the statistics of each component with the reaction time in Figure 5.



**Figure 4** The effect of time on other data

From Figure 4, it can be seen that the conversion of several major components decreases as the reaction proceeds, while the selectivity of ethylene and the selectivity of C4 alkenes are stable. In contrast, the selectivity of acetaldehyde increases to some extent, and the selectivity of fatty alcohols shows a decreasing trend.

### 2.2.2. Bias correlation analysis of ethanol conversion rate on ethylene and C4 and other related elements[3]

It is also necessary to consider the intrinsic linkage between the components, so a partial correlation analysis is required. The significance level of the test is

set at 0.05. If  $p < 0.05$ , it means that there is an excellent possibility of a linear relationship between the two variables; if  $p > 0.05$ , there is generally considered no linear relationship between the two variables. The bias correlation coefficient ( $r$ ) and significance level ( $p$ ) between the components were calculated and shown in Table 2.

From Table 2, it is known that ethanol conversion shows a weak negative correlation for ethylene and C4 alkenes selectivity at a given catalyst and temperature. Meanwhile, ethanol conversion provides a strong negative correlation for acetaldehyde selectivity. Ethanol conversion shows a strong positive correlation for fatty alcohol selectivity, and ethanol conversion shows a strong negative correlation for methylbenzaldehyde methylbenzene alcohol selectivity.

**Table 2.** Bias correlation coefficients and significant level

|  | $r$     | $p$    |
|--|---------|--------|
| Ethylene                                     | -0.1548 | 0.0008 |
| C4 alkenes                                   | -0.1470 | 0.0052 |
| Acetaldehyde                                 | -0.9627 | 0.0005 |
| C4-12 fatty alcohols                         | 0.8994  | 0.0058 |
| Methylbenzaldehyde and methylbenzene alcohol | -0.6674 | 0.1014 |

### 2.2.3. Organic chemical reaction mechanism analysis [3]

At the given environment of 350°C, it can be concluded that the reaction takes place in an isothermal environment. The isothermal equation (2) for the chemical reaction of component B at this temperature can be deduced from the fugacity of chemical component B ( ) in this environment.

$$\Delta \quad \Delta \quad \ominus \quad \ominus \quad (2)$$

Since the second term on the right in equation (2) is constant in an isothermal environment, it is known that the equilibrium constant  $K$  for this chemical reaction is constant. As the reaction time keeps increasing, the forward reaction proceeds with the addition of ethanol. The increasing air pressure in the reactor leads to the inhibition of the forward reaction. The chemical potential of ethylene and C4 alkenes tends to be stable, the chemical potential of acetaldehyde is relatively lower, and the chemical potential of fatty alcohols with C4-12 is relatively higher. Then the conversion of ethanol in the chemical reaction decreases significantly, the selectivity to ethylene and C4 alkenes are relatively stable, the selectivity to acetaldehyde increases, and the selectivity to aliphatic alcohols with C4-12 decreases continuously.

### 2.3. The influence of different catalyst combinations and temperatures

We investigated the relationship between different catalyst combinations and temperatures on the conversion of ethanol and the selectivity of C4 alkenes. Firstly, we analyzed the composition of each catalyst combination and split it into three indicators: Co loading, Co/SiO<sub>2</sub>, and HAP loading ratios, and the drop acceleration rate of ethanol. Then, the problem was transformed to investigate the effects of four independent variables, namely, Co loading, Co/SiO<sub>2</sub>, and HAP loading ratios, drop acceleration rate of ethanol, and temperature, on the conversion of ethanol and the selectivity of C4 alkenes, which are the two dependent variables. Considering the low data requirement of the grey correlation model, it is feasible to build a grey correlation model.

#### 2.3.1 Establishment of a grey correlation degree model [4-5]

According to the definition of the correlation coefficient, the correlation coefficient of the *j*th dependent variable (*x<sub>j</sub>*) to the *i*th independent variable (*v<sub>i</sub>*) is calculated as:

$$\text{Correlation Coefficient} = \frac{\sum_{k=1}^n (x_j - \bar{x}_j)(v_i - \bar{v}_i)}{\sqrt{\sum_{k=1}^n (x_j - \bar{x}_j)^2 \sum_{k=1}^n (v_i - \bar{v}_i)^2}} \quad (3)$$

Given that the values of the resolution ( $\rho$ ) are taken in the interval [0,1], since  $\rho$  can only reflect the correlation between two points, it will be integrated, then the correlation between the four independent variables and the two dependent variables can be obtained separately as

The  $|r_{ij}|$  greater than 0.7 is a strong correlation, and less than 0.3 is a weak correlation. By comparing the magnitudes of  $r_{ij}$ , the influence of the independent variables on the dependent variable can be obtained. For the  $r_{ij}$ , large ones are called dominant subfactors.

#### 2.3.2 Solution of the grey correlation model

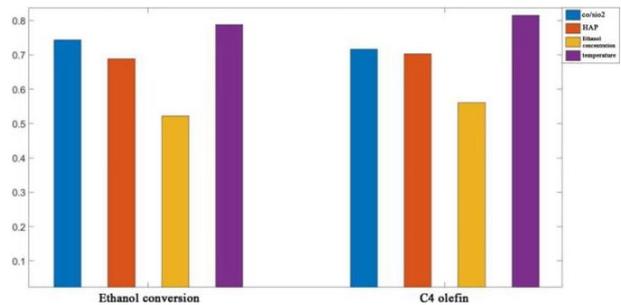


Figure 5 Correlation coefficients of each factor with ethanol conversion and C4 alkenes selectivity

From Figure 5, it is easy to analyze that the independent variable temperature is the dominant subfactor on the dependent variables ethanol conversion and C4 alkenes selectivity, which is followed by Co loading ratio, which strongly correlates with ethanol conversion C4 alkenes selectivity. Then Co/SiO<sub>2</sub> and HAP loading ratio have a slightly more significant effect on ethanol conversion and C4 alkenes selectivity. Furthermore, the drop acceleration rate of ethanol has a minor effect on ethanol. Finally, the drop acceleration rate of ethanol has a minor influence on the conversion rate and C4 alkenes selectivity. Within a certain range, all the four independent variables were significantly and positively correlated with ethanol conversion and C4 alkenes selectivity.

In order of influence: temperature on C4 alkenes selectivity > temperature on ethanol conversion > Co loading ratio on ethanol conversion > Co loading on C4 alkenes selectivity > Co/SiO<sub>2</sub> and HAP loading ratio on C4 alkenes selectivity > Co/SiO<sub>2</sub> and HAP loading ratio on ethanol conversion > drop acceleration rate of ethanol on C4 alkenes selectivity > drop acceleration rate of ethanol on ethanol conversion.

### 2.4. Select catalyst combinations and temperatures for the highest C4 alkenes yield

#### 2.4.1. Single-objective optimization model[6-8]

We will select different catalyst combinations and temperatures so that the C4 alkenes yield is as high as possible. So, a single-objective optimization model can be set up with the maximum C4 alkenes yield as the objective function, as shown in equation (4).

$$\max \text{Rate} = \eta_1 \eta_2 \quad (4)$$

$\eta_1$  is the ethanol conversion, and  $\eta_2$  is the C4 alkenes selectivity.

Next, we need to determine the constraints. Considering the four indicators of Co loading, Co/SiO<sub>2</sub>, and HAP loading ratios, the drop acceleration rate of ethanol and temperature affect C4 alkenes yield. To quantify the effect of the four indicators on C4 alkenes yield under the same reaction conditions, artificial

neural network training was performed to obtain the fitted function relationship of the four indicators on the yield of C4 alkenes. The steps are as follows.

Step 1: Select training samples for BP neural network.

Step 2: The ethanol conversion rate and C4 alkenes selectivity are used to calculate all neurons, including the input values, the implicit layer, and the output layer, respectively.

Step 3: By comparing the training samples of selected ethanol conversion and C4 alkenes selectivity data with the ethanol conversion and C4 alkenes selectivity data under the corresponding simulated output values of the network, the error functions of the predicted ethanol conversion and C4 alkenes output and the actual output of ethanol conversion and C4 alkenes selectivity are calculated respectively. The partial derivatives of the error functions are then calculated for each neuron.

Step 4: Continuously modify the weight matrix  $w$  by sample ethanol conversion and C4 alkenes selectivity data and the output values of neurons in each layer.

Step 5: Set neural network parameters.

Maximum number of training sessions=5000

The number of neurons in the hidden layer:  $lr=0.05$ .

Mean Square Error=0.00065.

#### 2.4.2. Solve single-objective optimization model by Genetic Algorithms [2]

Step 1: Determine the coding method of chromosomes.

The algorithm is designed using binary coding, and the four independent variables are formed into substrings using binary codes and then connected to form a "chromosome" string.

Step 2: Initialize the population.

After randomly generating the binary code of gene length, it is necessary to check whether the C4 alkenes yield obtained after transcoding this binary code meets the upper and lower limits in the given temperature interval for different cases. If this set of binary code meets the above requirements, it is included in the initial population. Otherwise, the randomly grown gene length binary code is re-generated and checked.

Step 3: Determine the adaptation function.

In this problem, the single optimization objective is maximum C4 alkenes yield. However, the objective function can be decomposed into a multi-objective optimization with maximum ethanol conversion and maximum C4 alkenes selectivity. A multi-objective

genetic algorithm (NWMOGA) based on weight assignment strategy is applied to solve this multi-objective optimization problem. The method weighted the two optimization objectives and then summed them and transformed them into a single-objective optimization problem.

$$\Omega \quad (5)$$

where  $\omega_1$  and  $\omega_2$  and is satisfied  $\omega_1 + \omega_2 = 1$ . The weight coefficients  $\omega_1$  and  $\omega_2$  reflect the importance of each optimization objective.

Step 4: Screening outstanding individuals.

The selection of suitable individuals is based on the roulette wheel method, in which the probability of each individual is selected for inheritance. It is proportional to the value of its fitness. The higher the fitness, the higher the probability of being selected; the lower the fitness, the lower the probability of being selected. In any selection operation of a genetic algorithm, choosing a suitable value as a wheel for adjusting the scale is necessary.

Step 5: Design of genetic operators.

(1) Crossover operation: Different from the two-point crossover operation primarily used in traditional genetic algorithms to improve convergence speed, this paper combines the genetic algorithm of a uniform two-point crossover operator (UTCGA) first generates random numbers 0 and 1. When the random number is 0, the part of the crossover two chromosomes indicates the ethanol conversion rate; when the random number is 1, the part of the crossover two chromosomes indicates the C4 alkenes selectivity.

(2) Mutation operation: First, the binary code position where the mutated gene occurs is randomly generated, and then this binary code is judged to be 0 or 1. If this binary code is 1, this binary code bit is mutated to 0 after the mutation operation, and if this binary code bit is 0, this binary code bit is mutated to 1 after the mutation operation.

Step 6: Set the relevant parameters of the genetic algorithm.

The genetic algorithm has three parameters, namely, population size ( $P$ ), crossover probability ( $P_c$ ), variation probability ( $P_m$ ), and the maximum number of genetic generations ( $P_d$ ). In this paper, set the population size  $P=100$  because the large the population size, the easier it is to find the optimal solution. Crossover probability  $P_c=0.2$  can ensure the natural evolution of the population. Mutation probability  $P_m=0.05$ , in general, the mutation is less likely to occur, and a mutation probability of 0.05 is more in line with natural laws. The maximum genetic generation  $P_d=100$  can ensure the full convergence of the optimization results.

2.4.3. Results

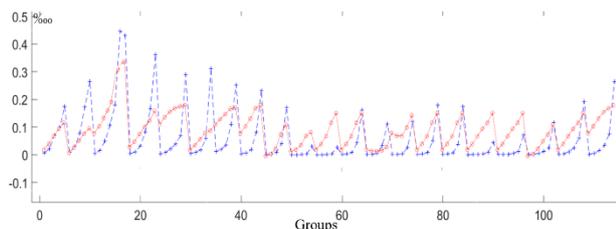


Figure 6 Comparison of learning test of neural network for C4 alkenes yield

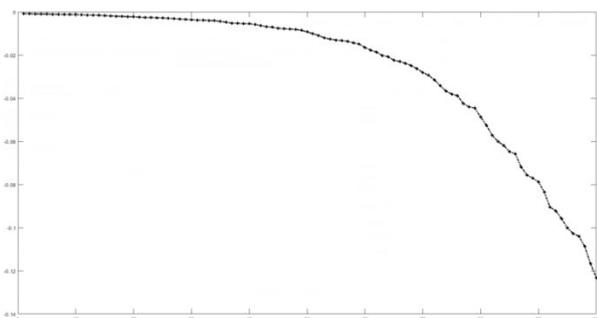


Figure 7 The convergence of the maximum fitness of the new population with the number of iterations without temperature limitation

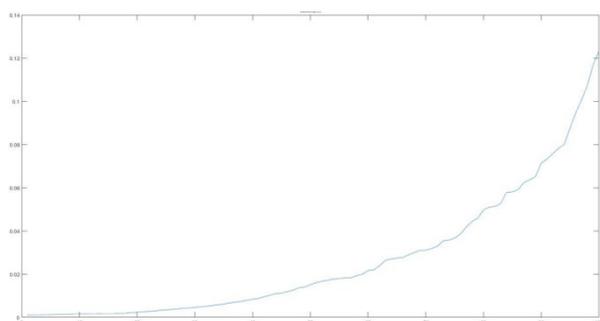


Figure 8 The convergence of maximum fitness of new populations at temperatures less than 350°C with the number of iterations

When there is no temperature limitation, the maximum C4 alkenes yield is 0.4580 at the catalyst combination of 200 mg 1wt% Co/SiO<sub>2</sub>, 200 mg HAP, and an ethanol concentration of 0.9 mL/min. Under the limitation temperature of less than 350°C, the maximum C4 alkenes yield is 0.1982 at the catalyst combination of 200 mg 1wt% Co/SiO<sub>2</sub>, 200 mg HAP, and ethanol concentration of 0.9 mL/min with the reaction temperature of 348.6°C.

Table 3. Catalyst temperature combinations with the maximum yield of C4 alkenes

|   | No temperature restriction | Restricted temperature |
|---|----------------------------|------------------------|
| Co loading (wt%)                          | 1                          |                        |
| Co/SiO <sub>2</sub> and HAP loading ratio | 200:200                    |                        |

|                       |        |        |
|-----------------------|--------|--------|
| Ethanol concentration | 0.9    |        |
| Temperature           | 378.27 | 348.60 |
| C4 alkenes yield      | 0.4580 | 0.1982 |

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3. CONCLUSION

(1) Quantified the relationship between the magnitude of the effect of the independent variables on the dependent variable using a grey correlation model.

(2) Qualitative and quantitative analyses between the data were performed through correlation and fit analyses.

(3) The search efficiency is significantly improved by using neural networks to obtain data relations with high reliability and modern optimization algorithms to solve optimization models.

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