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Kinetic Study of Product Distribution Using Various Data-Driven and Statistical Models for Fischer–Tropsch Synthesis

Yixiao Wang, Jing Hu, Xiyue Zhang, Abubakar Yusuf, Binbin Qi, Huan Jin, Yiyang Liu, Jun He, Yunshan Wang, Gang Yang, and Yong Sun

ABSTRACT: Three modeling techniques, namely, a radial basis function neural network (RBFNN), a comprehensive kinetic with genetic algorithm (CKGA), and a response surface methodology (RSM), were used to study the kinetics of Fischer–Tropsch (FT) synthesis. Using a 29 × 37 (4 independent process parameters as inputs and corresponding 36 responses as outputs) matrix with total 1073 data sets for data training through RBFNN, the established model is capable of predicting hydrocarbon product distribution i.e., the paraffin formation rate (C₂−C₁₃) and the olefin to paraffin ratio (OPR) within acceptable uncertainties. With additional validation data sets (15 × 36 matrix with total 540 data sets), the uncertainties of using three different models were compared and the outcomes were: RBFNN (±5% uncertainties), RSM (±10% uncertainties), and CKGA (±30% uncertainties), respectively. A new effective strategy for kinetic study of the complex FT synthesis is proposed: RBFNN is used for data matrix generation with a limited number of experimental data sets (due to its fast converge and less computation time), CKGA is used for mechanism selections by the kinetic study of the complex FT synthesis is the cornerstone for sizing and process design of gas to liquid (GTL) technology. Many scholars have proposed different modeling approaches to model the kinetics. These models include (i) data regression by formulating the minimization of the sum of the square of errors through a numerical Levenberg–Marquardt (LM) algorithm, (ii) a genetic algorithm (GA) to model the product distribution of FT synthesis such as using the Anderson–Schulz–Flory (ASF) method, (iii) an explicit model based on a second-order polynomial for correlating the critical operational parameters using a response surface methodology (RSM), and (iv) data-driven soft computation machine learning techniques such as using different artificial neuron networks (ANNs) in directly correlating the product distribution and critical operational parameters.

1. INTRODUCTION

The year 2020 witnessed how weak the supply chain is in how goods (the empty grocery-store shelves and the out of stock of surgical masks) are sourced, distributed, and where they are stored. These surely ring the alarm bell for the acceleration of long-term shifts in the supply chain on various aspects. Energy security issues are also increasing as crude oil prices are intensively volatile during the pandemic as thousands of airplanes are grounded, usual commuters are working from homes, and popular tourist resorts have become deserted. Energy security issues are also increasing as crude oil prices are intensively volatile during the pandemic as thousands of airplanes are grounded, usual commuters are working from homes, and popular tourist resorts have become deserted. Although the energy demand of using crude oil is significantly falling, the petrochemical production from crude oil is still in demand as the pendulum of daily life does not stop and the consumption of fast-moving consumer goods (FMCG) bounces back quickly. The challenging issues of importing crude oils from oil-rich countries through the weak supply chain still exist. The alternative technology of using syngas to produce hydrocarbons (both for bulk/fine chemical manufacturing and energy consumption) via one of the most commercial viable process (Fischer–Tropsch, FT synthesis) shows its merit in tackling the thorny problems for many countries with poor oil reserve. The kinetic modeling of Fischer–Tropsch (FT) synthesis is the cornerstone for sizing and process design of gas to liquid (GTL) technology. Many scholars have proposed different modeling approaches to model the kinetics. These models include (i) data regression by formulating the minimization of the sum of the square of errors through a numerical Levenberg–Marquardt (LM) algorithm, (ii) a genetic algorithm (GA) to model the product distribution of FT synthesis such as using the Anderson–Schulz–Flory (ASF) method, (iii) an explicit model based on a second-order polynomial for correlating the critical operational parameters using a response surface methodology (RSM), and (iv) data-driven soft computation machine learning techniques such as using different artificial neuron networks (ANNs) in directly correlating the product distribution and critical operational parameters.
With the advancement of computation techniques, computational power has become more economical and practical, and this looms new opportunities of combining different modeling techniques to analyze the complicated kinetic system such as FT synthesis. \(^{25-27}\) Until now, there have been very rare efforts in reporting the establishment of a robust paradigm that combines the advanced calculation systems for kinetic modeling of product distribution during FT synthesis.

To achieve this goal, large experimental data sets (a 29 × 36 matrix with total 1073 data sets, of which inputs were operational parameters such as temperature (T), pressure (P), gas hour space velocity (GHSV), and syngas ratio (SR), outputs were the rate of olefin/paraffin from C\(_1\)−C\(_{15}\), respectively) were fed into different modeling techniques, namely, a radial basis function neural network (RBFNN), the comprehensive kinetics based on a genetic algorithm (CKGA) for the regional and global optimization using a genetic algorithm (GA) via the objective function (minimization of the sum of the square of errors) for mechanism selection using the Langmuir−Hinshelwood−Houghton−Watson (LHHW) approach, and the second-degree polynomial correlations through a response surface methodology (RSM), and explored and compared. Using additional validation data sets (15 × 36 matrix with total 540 data sets), the comparisons of these three techniques (RBFNN, CKGA, and RSM) were made, and a paradigm of accurate determination and prediction of reaction pathways and optimization of the system is proposed. To the best of the author’s knowledge, this novel modeling strategy for product distribution during FT synthesis has been rarely reported before.

2. THEORETICAL BACKGROUND

2.1. Radial Basis Function Neural Network (RBFNN).

Artificial neural networks (ANNs) are well-developed and applied soft computing techniques. \(^{28}\) With the advancement of computation technology, these soft computing techniques have recently remerged and begun to attract attention in both academia and industries for complex system modeling. \(^{29}\)

Inspired from the neurological system and its basic elements for handling the information, ANNs are principally constructed as an input function \(x\) of the formal neuron \(i\) corresponding to the incoming activity (e.g., synaptic input) of the biological neuron; weight \(w\) represents the effective magnitude of information transmission between neurons (e.g., determined by synapses), activation function \(z_i = f(x, w)\) describes the main computation performed by a biological neuron (e.g., spike rates), and the output function \(y_i = f(z_i)\) corresponds to the overall activity transmitted to the next neuron in the processing stream. \(^{30}\)

With the learning phase on prior representative data as a robust training and testing step, this constructed learning technique is recognized to yield good predictions in many complex systems. From configurations of neural topologies and learning procedure perspectives, different ANNs have been constructed and deployed. Among them, the multilayer perceptron (MLP) and radial basis function neural networks (RBFNNs) are one of the well-formulated and rigorous ANNs. \(^{31,32}\) In this work, we choose the RBFNN as the machine learning algorithm for product distribution predictions during FT synthesis. The rationale of using RBF lies in its relative simple neuron architecture and efficient computation. The schematic diagram of RBFNN is shown in Figure 1.

The RBFNN is unique in its neuron topology, which only possesses one hidden layer representing its nodes \(N_h\)

\[
\phi(z_i) = \exp \left[ \frac{\sum_{j=1}^{n} (x_j - c_{ijk})^2}{2\sigma^2} \right]
\]

Figure 1. Schematic diagram of RBFNN formulated from the Gaussian function.

\(\text{(including its bias term } N_b\);} \) the Gaussian function is implemented in the network, which is formulated based on its center \((c_i)\) and the spread coefficient \((d)\). The general Gaussian function is expressed as follows

\[
y_i = f(z_i) = e^{-z_i^2/2d^2}
\]
Table 1. Elementary Steps for Different Mechanisms,\textsuperscript{16,38–42} Where M1 Refers to the Carbide Mechanism, M2 Refers to the Enolic Mechanism, and M3 Refers to the CO Insertion Mechanism (with $n \geq 4$), A Refers to Alkylidene and S Refers to the Active Site on the Surface of the Catalyst

| constant | M1                  | constant | M2                  | constant | M3                  |
|----------|---------------------|----------|---------------------|----------|---------------------|
| constant | elementary          | constant | elementary          | constant | elementary          |
| $K_{M1}^H$ | $H_2 + 2S \leftrightarrow 2HS$ | $K_{M1}^H$ | $H_2 + 2S \leftrightarrow 2HS$ | $K_{M1}^H$ | $H_2 + 2S \leftrightarrow 2HS$ |
| $K_{M1}^C$ | $CO + S \leftrightarrow COS$ | $K_{M1}^C$ | $CO + S \leftrightarrow COS$ | $K_{M1}^C$ | $CO + S \leftrightarrow COS$ |
| $K_{M1}^{HCO}$ | $H_2O + S \leftrightarrow H_2O - S$ | $K_{M1}^{HCO}$ | $CO + H_2 \leftrightarrow H_2CO - S$ | $K_{M1}^{HCO}$ | $CO + H_2 \leftrightarrow H_2CO - S$ |
| $K_{M1}^O$ | $O_2 + S \leftrightarrow O_2 - S$ | $K_{M1}^O$ | $H_2C - S + CH_{2n+1} - S \rightarrow C,H_{2n+1},CH_2 - S + S$ | $K_{M1}^O$ | $H_2C - S + CH_{2n+1} - S \rightarrow C,H_{2n+1},CH_2 - S + S$ |
| $k_{M1}$ | $CO - S + S \rightarrow C - S + O - S$ | $k_{M1}$ | $CH_3 - S + H - S \rightarrow CH_4 + 2S$ | $k_{M1}$ | $CH_3 - S + H - S \rightarrow CH_4 + 2S$ |
| $k_{CH}$ | $C - S + H - S \rightarrow CH - S + S$ | $k_{CH}$ | $C,H_{2n+1} - S + H - S \rightarrow C,H_{2n+2} + S$ | $k_{CH}$ | $C,H_{2n+1} - S + H - S \rightarrow C,H_{2n+2} + S$ |
| $k_{O2}$ | $OH - S + H - S \rightarrow H_2O - S + S$ | $k_{O2}$ | $C,H_{2n+1} - S \leftrightarrow C,H_{2n} + HS$ | $k_{O2}$ | $C,H_{2n+1} - S \leftrightarrow C,H_{2n} + HS$ |
| $k_{O3}$ | $O_2 - S + S \rightarrow O_2 - S + H - S$ | $k_{O3}$ | $A \rightarrow S + S \leftrightarrow O_2 - S + H - S$ | $k_{O3}$ | $A \rightarrow S + S \leftrightarrow O_2 - S + H - S$ |
| $k_{P2}$ | $P_{n} - S + H - S \rightarrow P_{n+1} + 2S$ | $k_{P2}$ | $A \rightarrow S + S \leftrightarrow O_2 - S + H - S$ | $k_{P2}$ | $A \rightarrow S + S \leftrightarrow O_2 - S + H - S$ |
| $k_{P3}$ | $A \rightarrow S + S \leftrightarrow O_2 - S + H - S$ | $k_{P3}$ | $A \rightarrow S + S \leftrightarrow O_2 - S + H - S$ | $k_{P3}$ | $A \rightarrow S + S \leftrightarrow O_2 - S + H - S$ |
In this work, the procedure of model estimation was explored for CO initiation against experimental data. These procedures were repeated twice.

2.2. Comprehensive Kinetics with the Genetic Algorithm (CKGA). In this work, the procedure of model selection was divided into two stages. At a preliminary stage, 10 different mechanisms over 30 different chains were explored for CO initiation against experimental data. These models include carbide, \( \text{C}-\text{H}, \) and \( \text{CO} \) insertion mechanisms, respectively. The corresponding elementary steps of different mechanisms are shown in Table 1. Among these models, the direct hydrogenation of the carbide mechanism (M1) is found to be both physically and statistically relevant to the experimental results. Once the initiation mechanism is determined, the selected detailed carbide mechanism M1 was employed to further derive a comprehensive model. To account for the olefin to paraffin ratio (OPR), the 1-olefin readsorption model assuming weak Van der Waal’s interaction between olefin and the surface of the catalyst is deployed. Then, the activation energy for olefin readsorption can be written as 

\[
E^*_{\text{re}} = E^0_{\text{re}} + nE_{\text{re}}
\]

where \( E^0_{\text{re}} \) refers to the readsorption energy that is independent of the chain length (kJ mol\(^{-1}\)). \( E_{\text{re}} \) refers to the part of activation energy that is dependent on the chain length (kJ mol\(^{-1}\)), and \( n \) refers to the carbon number \( (n \geq 4) \). Then, the rate constant can be expressed as follows:

\[
k_r = k_{\text{re}} e^{-E^*_{\text{re}}/RT}
\]

\[
k^*_r = k_{\text{re}} e^{-E^0_{\text{re}}/RT} = k_{\text{re}} e^{-E^*_{\text{re}}/RT} e^{-E_{\text{re}}^*}
\]

\[
E^*_{\text{re}} = -E_{\text{re}}/RT
\]

The rate constants of chain-length-dependent (CLD) readsorption and desorption can be expressed as follows:

\[
k^*_{\text{re}} = k_{\text{re}} e^{E^*_{\text{re}}\times n}
\]

\[
k^*_d = k_d e^{E^*_{\text{re}}\times n}
\]

\[
E^*_{\text{re}} = E_d/RT
\]

where \( E^*_{\text{re}} \) and \( E^*_{\text{re}}^* \) are the constants reflecting the part of activation energy of olefin readsorption and desorption with carbon number dependency and \( R \) refers to the gas constant \((8.314 \text{ J K}^{-1}\text{mol}^{-1})\). For FT synthesis, the surface fraction of CO, \( \text{H}_2 \), and \( \text{O}_2 \) (the olefin chain-length-dependent readsorption is considering eqs 13–15, with \( n \geq 4 \)) can be expressed as follows:

\[
\theta_{\text{CO}} = \xi_{\text{CO}} \theta_S
\]

\[
\theta_{\text{HS}} = \xi_{\text{HS}} \theta_S
\]

\[
\theta_{\text{O}} = (k_{\text{CO}} P_{\text{O}_2})^{1/2}
\]

\[
K_{\text{O}} = \frac{k^*_d}{k_{\text{re}}} \text{ with } n \geq 4
\]

Calling quasi-steady-state assumption (QSSA)

\[
\theta_{\text{CS}} = \frac{k_{\text{CO}} \theta_{\text{CO}} \theta_{\text{CP}} \theta_S}{k_{\text{H}_2}^*} = \frac{\xi_{\text{CS}} \theta_{\text{CS}}}{k_{\text{CSH}}}
\]

where

\[
\xi_{\text{CS}} = \frac{k_{\text{CO}} \theta_{\text{CO}} \theta_{\text{CS}}}{k_{\text{CSH}}}
\]

\[
\theta_{\text{CS}} = \frac{k_{\text{CO}} \theta_{\text{CO}} P_{\text{O}_2} \theta_S}{k_{\text{H}_2}^*} = \frac{\xi_{\text{CS}} \theta_{\text{CS}}}{k_{\text{CSH}}}
\]

\[
The QSSA is applied with a chain number longer than 4
\]

\[
\sum_{n=1}^{\infty} \theta_{\text{CH}_n} = \frac{k_{\text{CO}} \theta_{\text{CO}} \theta_{\text{CS}}}{k_{\text{H}_2}^*} + k_{\text{CO}} \theta_{\text{CO}} P_{\text{O}_2} \theta_S = \xi_{\text{CS}} \theta_{\text{CS}}
\]

The approximate second-order polynomial expression using \( \theta_{\text{CH},S} \) as variables can be solved as

\[
A \theta_{\text{CH},S}^2 + B \theta_{\text{CH},S} + C \theta_S^2 = 0
\]

where

\[
A = \frac{k_{\text{CO}} k_{\text{A}}}{k_{\text{CO}} + k_{\text{O}_2} \theta_S}
\]

\[
B = k_{\text{CO}} \theta_{\text{CO}} P_{\text{O}_2} \left( \sum_{n=1}^{\infty} \theta_{\text{A},S} \right)
\]

\[
C = k_{\text{CO}} \theta_{\text{CO}} P_{\text{O}_2}
\]

The corresponding root could be solved as
Using QSSA in alkylidene-1-S

\[ \theta_{A-1-S} = \frac{k_{IN} \theta_{CH_2} \theta_{HS}}{k_{AS} \theta_{CH_5} + k_{CH_2} \theta_{HS}} = \frac{k_{IN} \xi_{CH_2} \theta_{HS}}{k_{IN} \xi_{CH_2} \theta_{HS} + k_{CH_2} \xi_{HS}} \]

where

\[ \xi_1 = \frac{k_{IN} \xi_{CH_2} \theta_{HS}}{k_{IN} \xi_{CH_2} \theta_{HS} + k_{CH_2} \xi_{HS}} \]

For the alkylidene-2-S intermediate

\[ \theta_{A-2-S} = \frac{k_{A} \theta_{AS} \theta_{CH_5} + k_{rev} \theta_{O_2} \theta_{HS}}{k_{AS} \theta_{CH_5} + k_{CH_2} \theta_{HS} + k_{O_2} \theta_{S}} = \frac{k_{A} \theta_{AS} \xi_{CH_5} \theta_{HS} + k_{rev} \theta_{O_2} \xi_{HS} \theta_{S}}{k_{AS} \xi_{CH_5} + k_{CH_2} \xi_{HS} + k_{O_2} \theta_{S}} \]

\[ = \sigma_1 \theta_{A-1-S} + \gamma_2 \theta_{S} \]

(23)

where

\[ \sigma_2 = \frac{k_{AS} \xi_{CH_5} \theta_{HS} + k_{CH_2} \xi_{HS} + k_{O_2} \theta_{S}}{k_{AS} \xi_{CH_5} + k_{CH_2} \xi_{HS} + k_{O_2} \theta_{S}} \]

For alkylidene-3-S

\[ \theta_{A-3-S} = \frac{k_{A} \theta_{AS} \theta_{CH_2} + k_{rev} \theta_{O_3} \theta_{HS}}{k_{AS} \theta_{CH_2} + k_{CH_2} \theta_{HS} + k_{O_3} \theta_{S}} = \frac{k_{A} \theta_{AS} \xi_{CH_2} \theta_{HS} + k_{rev} \theta_{O_3} \xi_{HS} \theta_{S}}{k_{AS} \xi_{CH_2} + k_{CH_2} \xi_{HS} + k_{O_3} \theta_{S}} \]

\[ = \sigma_1 \theta_{A-2-S} + \gamma_2 \theta_{S} \]

(24)

where

\[ \sigma_2 = \frac{k_{AS} \xi_{CH_2} \theta_{HS} + k_{CH_2} \xi_{HS} + k_{O_3} \theta_{S}}{k_{AS} \xi_{CH_2} + k_{CH_2} \xi_{HS} + k_{O_3} \theta_{S}} \]
\[ \sigma_1 = \frac{k_{\text{CHS}}}{k_{\text{CHS}} + k_{\text{HS}} + k_{\text{O}}} \] and \[ \gamma \]

For the alkylidene-n-S intermediate
\[ \theta_{\lambda-n-S} = \frac{k_{\text{CHS}}}{k_{\text{CHS}} + k_{\text{HS}} + k_{\text{O}}} \] with \[ n \geq 4 \] (25)

The following linear algebra will be casted
\[ \nu_1 = \xi \theta_s \]
\[ \nu_2 = \sigma_1 \theta_s + \gamma \theta_s \]
\[ \nu_3 = \sigma_2 \nu_1 + (\sigma_2 \nu_3 + \gamma \theta_s) \]
\[ \nu_n = \sigma_{n-1} \nu_1 + (\sigma_{n-1} \nu_3 + \gamma \nu_{n-1} + \gamma \nu_3) + \ldots + \gamma \nu_n \]
\[ \prod \sigma_{n-i}! \left( \sum_{i=1}^{n} \prod \sigma -1, \gamma \right) \theta_s \] (26)

With assumption of \[ \sigma = \sigma_i = \ldots = \sigma_n \] and \[ \gamma = \gamma_i = \ldots = \gamma_n \] alkylidene-n-S can be given as follows (\( n \geq 4 \))
\[ \theta_{\lambda-n-S} = \frac{k_{\text{CHS}}}{k_{\text{CHS}} + k_{\text{HS}} + k_{\text{O}}} \] with \[ n \geq 4 \] (27)

Thus, the site balance is expressed as the following
\[ \theta = 1 + \xi \theta_s + \xi \theta_s + \xi \theta_s + \theta \left( 1 + \sum_{i=4}^{n} \prod \sigma_{n-i}, \gamma \right) \theta_s \] (28)

The schematic diagram of model selection using a genetic algorithm for data regression is shown in Figure 2. Finally, the rate expressions of the reagent and different products are then expressed as follows with \( n \geq 4 \)
\[ r_{CH_4} = k_{CH_4} \xi \theta_s/\text{DEM} \] (29)
\[ r_{\text{H}_2} = k_{\text{H}_2} (\sigma_{\text{H}_2} + \gamma) \xi \theta_s/\text{DEM} \] (30)
\[ r_{\text{H}_2} = k_{\text{H}_2} (\sigma_{\text{H}_2} + \gamma) \xi \theta_s/\text{DEM} \] (31)
Graph columns

![Graph columns](image)

**Figure 3.** Schematic diagram of response surface methodology (RSM) for significance analysis, where NPR refers to a normal plot of residues, RVP refers to residues versus predictions, BCP refers to the Box–Cox plot for power transform, and CD refers to Cook’s distance.

2.3. Response Surface Methodology (RSM). In statistics, response surface methodology explores the relationships between several explanatory variables and one or more response variables.\(^\text{43}\)

The main idea of RSM is to use a sequence of designed experiments to obtain an optimal response. In addition, it can also be used to directly correlate the influential operational parameters with responses using the most widely deployed second-degree polynomial expressions to find out the offset, linear, quadratic, and interactive terms as follows

\[
Y_i = b_0 + \sum_{i=1}^{4} b_i X_i + \sum_{i=1}^{4} b_i X_i^2 + \sum_{i=1}^{4} b_i X_i X_j
\]  

(41)

where \(Y_i\) is the responded value (in this work, there are 36 different responses including \(X_{CO2}, S_{CH4}, r_{CO}, S_{CO2}, S_{C2-C4}, r_{pyr}, r_{Oa}\) with \(n \leq 15\)), \(X_{ij}\) is the binary parameter of the investigated operational parameters \((T, P, \text{GHSV}, \text{S.R})\), and \(b_0, b_i, b_i, (b_{ij})\) are coefficients from the polynomial expression. Although it does not shed any insightful lights upon the kinetic mechanism, it does provide the useful statistical indications for the significances of responses that are caused by the variations of process variables (either singular or binary). With experimental results (Table 4 in the Experimental Part section), the RSM is capable of calculating the corresponding formation rate of olefin and paraffin with different carbon numbers (Figure 3).

3. RESULTS AND DISCUSSION

3.1. Model Comparisons. Once experimental data (Table 4 from the Experimental Part section) were fed into different models (RBFNN, CKGA, and RSM), model predictions against validation results (Table S1) were used to test the performances of constructed models. Because of a range of differences, the parameters, i.e., \(X_{CO2}, S_{CH4}, r_{CO}, S_{CO2}\) and \(S_{C2-C4}\) and the formation rate of olefin and paraffin with different carbon numbers \((r_{pyr}, r_{Oa}\) with \(n \leq 15\)) are plotted in Figure 4a,b, respectively. Clearly, with different models, data present appreciably different aggregating patterns both in Figure 4a1–c1 and a2–c2, respectively.

Taking the center aggregation (purple circle with the range from 0 to 0.0006 for both axis), for instance, the percentage of different carbon numbers (Figure 3).
Figure 4. Comparisons between the experiment and model prediction when the rate is in mole·h⁻¹ for (a) RBFNN model, (b) comprehensive kinetics based on the genetic algorithm (CKGA) model, and (c) RSM-based model, where Exp_rH₂ and rCO refer to the experimental hydrogen and CO consumption rate (mole·h⁻¹), Calcd_rH₂ and rCO refer to the calculated hydrogen and CO consumption rate (mole·h⁻¹), Exp_rPi and rOi refer to the experimental paraffin and olefin rate with the carbon number i (mole·h⁻¹), and Calcd_rPi and rOi refer to calculated paraffin and olefin rates with the carbon number i (mole·h⁻¹).
data falling out of this range from RBFNN, CKGA, and RSM models is 14.2, 16.6, and 18.9%, respectively. Apparently, the patterns of data distribution using different modeling approaches are not same, which will lead to the variation of relative errors between the experiment and predictions. To further assess the deviations between the experimental results and model predictions, the corresponding standard deviations were calculated as follows

$$\bar{x} = \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} (x_i - \bar{x})^2}$$

(42)

where \(N\) represents the numbers of experimental runs, \(\bar{x}\) represents the averaged values of each parameters (\(X_{\text{CO}}\), \(S_{\text{CH}4}\), \(r_{\text{CO}}\), \(C_{\text{CO}2}\), \(C_{\text{C2-C4}}\), \(r_{\text{On}}\) with \(n \leq 16\)), and \(x_i\) refers to corresponding specific value. Then, the standard error (SE) of each experimental value is defined as follows

$$\text{SE} = \frac{\bar{x}}{\sqrt{N}}$$

(43)

The errors between experiment and model predictions using three different models are shown in Figure 5, with the color bar from blue to red indicating the variations of standard errors from ±5 to ±20% in validation tests. The standard errors for majority data are less than ±10% with the presence of some exceptionally high errors (over ±20%) for all of three models (RBFNN, CKGA, and RSM). The RBFNN model approach is found to have relatively fewer standard errors within an experimental data range of 0–0.001 (mol·h⁻¹), while the CKGA model presents the largest deviation among the three investigated models. The possible reasons could be more additional conditions needed to be met for constant regressions during the mechanism selection (both in statistical and physical relevance such as meeting Arrhenius and Van’t Hoff criteria).

In addition, regarding to those data leading to large discrepancies (SE > ±10%), the calculations in RBFNN are found to undershoot, while the calculations from CKGA and RSM overshoot with more larger errors being observed from CKGA model. The comparison of experimental data and model predictions for \(C_1-C_{15}\) at the baseline condition are shown in Figure 6 (the run baseline with best data fit was chosen). Different model approaches provide different accuracies during data regression. Because of direct computation (using training data for RBFNN and second-degree polynomial expression for RSM), both RBFNN and RSM tend to provide predictions with relatively higher accuracy and less computational time.

On the other hand, CKGA does provide elementary mechanism (using the Langmuir–Hinshelwood–Hougen–Watson approach for elementary reaction pathway derivation) that sheds insightful lights on the CO hydrogenation mechanism at the investigated experimental conditions, even though the accuracy of the CKGA model tends to be lower during predictions at some experimental runs (over ±30%). Therefore, RBFNN is found to be the most robust (computational time and accuracy) to make predictions among the investigated models, if sufficient training data were fed.
relatively big uncertainties C5 in Figure 6a might lie in the vaporization and loss of C5 during trap swap. With the CKGA model, the kinetic expressions (constants in the kinetic expression Table 2) could be obtained through data regressions. The obtained constants can be compared with reported values from literature reports. For instance, the values of $k_p$ and $k_n$ are quite close to each other, suggesting the reactivity of alkylidene to paraffin being stable as the carbon number increases over 4. The FT activation energy is close to the typical cobalt-based catalyst indicating the validity of constructed reaction pathways.38,39,45

One of major challenges of using CKGA lies in compromising the computational time and accuracy using GA for both regional and global optimization to converge the
objective functions. As a dimension of tensor increase, the demand for computational time and internal memories increases significantly. Clearly, it might not be the best choice of obtaining kinetic constants via direct data regression through the elementary mechanisms using quasi-steady state assumption (QSSA) if the goal is for process optimization. Instead, CKGA might be more meaningful in exploring possible reaction pathways during mechanism selections. With regard to optimizing and sizing the reaction system, the RSM surely shows its inherent advantage, even though it does not provide any insightful descriptions between process parameters and the responses. With RSM, the polynomial correlations are able to provide a very accurate correlation with those investigated critical process parameters. For instance, correlations are able to provide a very accurate correlation with the selectivity: 

\[ Y_f = b_0 + b_1T + b_2P + b_3GHSV + b_4SR + b_5T \times P + b_6P \times GHSV + b_7T \times SR + b_8P \times GHSV + b_9P \times SR + b_{10}T^2 + b_{11}P^2 + b_{12}GHSV^2 + b_{13}SR^2 \]  

(44)

For instance, the established coefficients for all \((C_3-C_1)\) paraffin formation rates can be found from Table S2 with less than ±10% experimental uncertainties.

3.2. Strategy for Kinetic Modeling and Process Optimization. For sizing and designing a reactor system, the key challenge still lies in constructing accurate and reliable kinetic expressions.47,49,50 Albeit, the LHHW approach has been successfully and widely employed to derive kinetic models for FT synthesis; the inherent limitations such as yielding the debatable mechanistic elementary reactions and tediously computational times still need to be substantially improved in the practical applications.17,48 Because of the flexibility for learning the information and a pertinence for pattern recognition in the complex system, the applied soft computing technique such as using RBFNN has been widely used for modeling and control tools for a complex system.50

However, quite a few research studies either focus on kinetic constant correlations by simply using ANNs or generate the central composite design (CCD) matrix through the RBFNN simulations, followed by statistical analysis through RSM.50-62 The critical limitation lies in its lacking understanding of kinetic mechanisms.61 As discussed before, the best strategy is
to maximize the merits of each model (RBFNN, CKGA, and RSM); the hybrid approach of using a small number of data points to cost-effectively generate more representative data sets through RBFNN, followed by CKGA (for mechanism selection) and RSM (performance evaluation to scrutinize the effects of process parameters upon the investigated responses) will show more promising prospects. The schematic diagram of the strategy of kinetic modeling is shown in Figure 9. With the advancement of computation technologies, the consideration of a hybrid paradigm of using RBFNN, CKGA, and RSM has become more attractive. The necessity of combining inherent merits of RBFNN, CKGA (mechanistic kinetic), and RSM (statistical analysis) secures both accuracy of predictions and insightful understanding of the reactions (Table 4).

4. CONCLUSIONS

Three different types of modeling frameworks, namely, RBFNN, CKGA, and RSM, were explored and compared to model the product distribution for FT synthesis using a Ru-promoted Co/Al₂O₃ catalyst in a conventional packing bed reactor (PBR). A new strategic modeling paradigm for olefin/
paraffin rate expressions during FT synthesis was proposed by considering both accuracy and intrinsic understanding of FT kinetics. The proposed new strategy possesses appealing features of modeling the rates of different hydrocarbons (olefin, paraffin with \( C_2 - C_{15} \)), olefin to paraffin ratio (OPR), and statistical analysis of the key operational parameters upon responses (selectivity, olefin, and paraffin with different \( C_2 - C_{15} \) carbon numbers). The accuracy and data patterns of using

Figure 9. Schematic diagram of the strategies of kinetic modeling from different models (RBFNN, CKGA, and RSM).
Table 4. Experimental Designs for Kinetics During Fischer–Tropsch Synthesis, Where $X_{CO}$ is CO Conversion, $S_{CH_4}$ is Methane Selectivity, $S_{CO_2}$ is CO Selectivity, $S_{C_2-C_4}$ is Alkene, TOS is Time on Stream (h) Selectivity, * is Baseline Conditions, T is Temperature (°C), P is Pressure (Bar), GHSV is Gas Hour Space Velocity (L·h$^{-1}$), and SR is Syngas Ratio, Respectively

| runs | $T/°C$ | $P/bar$ | GHSV/L·h$^{-1}$ | SR | experimental $X_{CO}$ | experimental $S_{CH_4}$ | experimental $S_{CO_2}$ | experimental $S_{C_2-C_4}$ | TOS/h |
|------|---------|---------|-----------------|----|-----------------------|-------------------------|-----------------------|---------------------------|------|
| 0*   | 215     | 20      | 3000            | 1.5| 0.3201                | 0.1238                  | 0.0054                | 0.2103                    | 48   |
| 1    | 215     | 20      | 2790            | 2.2| 0.5560                | 0.1570                  | 0.0481                | 0.2540                    | 60   |
| 2    | 215     | 17      | 2795            | 1.5| 0.4850                | 0.1082                  | 0.0183                | 0.2768                    | 72   |
| 3    | 215     | 15      | 1380            | 1.7| 0.5707                | 0.0865                  | 0.0513                | 0.1247                    | 84   |
| 4    | 200     | 17      | 2796            | 1.2| 0.3371                | 0.0495                  | 0.0067                | 0.1024                    | 96   |
| 5    | 200     | 17      | 1380            | 1.2| 0.5503                | 0.0774                  | 0.0484                | 0.0520                    | 108  |
| 6    | 215     | 15      | 2796            | 1.2| 0.4388                | 0.0958                  | 0.0083                | 0.2780                    | 120  |
| 7*   | 220     | 20      | 3001            | 1.5| 0.3199                | 0.1238                  | 0.0054                | 0.2103                    | 132  |
| 8    | 215     | 17      | 1380            | 1.2| 0.5146                | 0.0760                  | 0.0422                | 0.0443                    | 144  |
| 9    | 215     | 17      | 3003            | 1.7| 0.4850                | 0.1082                  | 0.0183                | 0.2768                    | 156  |
| 10   | 215     | 20      | 1380            | 1.7| 0.5567                | 0.0792                  | 0.0495                | 0.0618                    | 168  |
| 11   | 220     | 20      | 4202            | 1.5| 0.2214                | 0.1900                  | 0.0321                | 0.1361                    | 180  |
| 12   | 230     | 17      | 1380            | 1.7| 0.5707                | 0.0870                  | 0.0515                | 0.1233                    | 192  |
| 13   | 230     | 17      | 2792            | 2.2| 0.5905                | 0.0763                  | 0.0515                | 0.2647                    | 204  |
| 14   | 215     | 15      | 2791            | 2.2| 0.5841                | 0.0766                  | 0.0507                | 0.2701                    | 216  |
| 15   | 200     | 17      | 3000            | 2.2| 0.5290                | 0.1245                  | 0.0374                | 0.2682                    | 228  |
| 16   | 230     | 17      | 2796            | 1.2| 0.4536                | 0.0958                  | 0.0074                | 0.2793                    | 240  |
| 17   | 215     | 17      | 1380            | 2.2| 0.5705                | 0.0871                  | 0.0518                | 0.1186                    | 252  |
| 18   | 230     | 20      | 2796            | 1.7| 0.5107                | 0.1458                  | 0.0345                | 0.2693                    | 264  |
| 19   | 215     | 17      | 2807            | 1.7| 0.4850                | 0.1082                  | 0.0183                | 0.2768                    | 276  |
| 20   | 230     | 15      | 2797            | 1.7| 0.5608                | 0.0804                  | 0.0466                | 0.2766                    | 288  |
| 21   | 215     | 17      | 4212            | 1.2| 0.2819                | 0.0865                  | 0.0173                | 0.0879                    | 300  |
| 22   | 215     | 17      | 2799            | 1.5| 0.4850                | 0.1082                  | 0.0183                | 0.2768                    | 312  |
| 23   | 200     | 20      | 2796            | 1.7| 0.3543                | 0.1130                  | 0.0045                | 0.2317                    | 324  |
| 24   | 200     | 15      | 2800            | 1.5| 0.4760                | 0.0769                  | 0.0094                | 0.2796                    | 336  |
| 25   | 215     | 17      | 4210            | 2.2| 0.3046                | 0.1592                  | 0.0402                | 0.2146                    | 348  |
| 26   | 220     | 17      | 3000            | 1.7| 0.4850                | 0.1082                  | 0.0183                | 0.2768                    | 360  |
| 27   | 200     | 17      | 4200            | 1.5| 0.2729                | 0.0752                  | 0.0195                | 0.0643                    | 372  |
| 28   | 215     | 15      | 4210            | 1.7| 0.1327                | 0.2579                  | 0.0502                | 0.1442                    | 384  |
| 29   | 230     | 17      | 4212            | 1.5| 0.2222                | 0.2163                  | 0.0463                | 0.1851                    | 396  |
| 30*  | 220     | 20      | 2989            | 1.5| 0.3027                | 0.1127                  | 0.0044                | 0.2055                    | 408  |

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sets of coefficients can be found from previous reports.\textsuperscript{59} \( R_0 \) is the reaction rate of formation (mol·h\(^{-1}\)) of the \( i \)th component, refers to molar flow rate of species \( i \) (mol·h\(^{-1}\)), and refers to the mass of catalyst (g). The partial pressure of the \( i \)th compound

\[
P_i = \frac{m_i}{\sum_{i=1}^{N_c} m_i} P_i (i = i - N_c)
\]

where \( N_c \) refers to the total numbers of components, \( P_i \) refers to partial pressure of the \( i \)th compound (bar), \( m_i \) refers to the mass of components (g), and \( P_t \) refers to the total pressure of the system (bar). The gases and liquid (both cold trap setting at 10 °C and hot trap setting at 110 °C) were collected and analyzed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC–MS), respectively. Before systematically exploring the different experimental conditions, the baseline condition (0\textsuperscript{th}) was maintained for about 48 h. At the end of the experiment, the condition was adjusted back to the baseline condition (30\textsuperscript{th}) for about 12 h and deactivation was relatively less than 6%.

It must be noted that FT synthesis yields a wide range of products (C\(_1\)–C\(_{50}\)), for the simplicity of kinetic modeling, C\(_2\)–C\(_{5}\), olefin and n-paraffin (ignoring all branched hydrocarbons) were usually taken into account due to the fact that the rate of the hydrocarbons with a larger carbon number was not simply governed by the kinetics at the experimental conditions. To validate the established model, additional 15 runs were conducted, which is shown in Table S1. Therefore, the overall procedure for model establishment and validation are as follows: (i) data in Table 1 were used to establish the model (RBFNN—data train, CKGA—data regression, RSM—data design in the matrix) and (ii) data in Table S1 were used to validate three constructed models (RBFNN, CKGA, RSM).

### ASSOCIATED CONTENT

1. **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c03851.

Tables S1–S3 for additional information such as validation experimental results for kinetics during Fischer–Tropsch synthesis, kinetic expressions for detailed product distribution derived from the CKGA model, and coefficients of the quadratic polynomial expression for paraffin formation rate from C\(_1\) to C\(_{15}\).

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**Notes**

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