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Modeling and optimization of industrial Fischer–Tropsch synthesis with the slurry bubble column reactor and iron-based catalyst☆

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ABSTRACT

To optimize industrial Fischer–Tropsch (FT) synthesis with the slurry bubble column reactor (SBCR) and iron-based catalyst, a comprehensive process model for FT synthesis that includes a detailed SBCR model, gas liquid separation model, simplified CO₂ removal model and tail gas cycle model was developed. An effective iteration algorithm was proposed to solve this process model, and the model was validated by industrial demonstration experiments data (SBCR with 5.8 m diameter and 30 m height), with a maximum relative error < 10% for predicting the SBCR performances. Subsequently, the proposed model was adopted to optimize the industrial SBCR performances simultaneously considering process and reactor parameters variations. The results show that C₅₊ yield increases as catalyst loading increases within 10–70 ton and syngas H₂/CO value decreases within 1.3–1.6, but it doesn't increase obviously when the catalyst loading exceeds 45 ton (about 15 wt% concentration). Higher catalyst loading will result in higher difficulty for wax/catalyst separation and higher catalyst cost. Therefore, the catalyst loading (45 ton) is recommended for the industrial demonstration SBCR operation at syngas H₂/CO = 1.3, and the C₅₊ yield is about 402 ton" per day, which has an about 16% increase than the industrial demonstration run result.

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1. Introduction

Fischer–Tropsch (FT) synthetic fuels have very beneficial properties, such as low sulfur content and near-zero aromatics, which make them good candidates as alternative and/or complementary sources of fuel. FT synthetic fuels can be produced from coal or natural gas. Two types of catalysts are commercially used in FT synthesis, namely iron-based (Fe) and cobalt-based (Co) catalysts. Iron catalyst is cheaper and has a higher water gas shift (WGS) activity, and therefore it is best suited for CO rich syngas produced from coal gasification. Three types of FT reactors are in commercial use at present time: they are fixed bed reactor, fluidized bed reactor and slurry phase reactor [1]. Slurry bubble column reactor (SBCR) possesses many advantages such as better heat & mass transfer, lower manufacture cost and higher yield of single set. Therefore, it is an active research area for a lot of researchers in modeling, scale-up and optimization of the SBCR for FT synthesis.

Industrial scale SBCR (diameter 5–10 m, height 30–50 m) was simulated and investigated using the SBCR model by the researchers [2–10]. Recent work on the intensification of the Sasol SPD (Slurry

Phase Distillate) reactor presented by Sasol [9] shows that the scope exists to potentially double the volumetric conversion of Sasol's existing G1 commercial slurry phase reactors through the relative increases in gas velocity and catalyst concentration. Sehabiague [10] used the double bubble SBCR model to assess the performance of an industrial SBCR for FT synthesis, and predicted and optimized the performance of an industrial scale (ID-5.8 m SBCR) operating with iron-based catalyst for FT synthesis, with emphasis on catalyst deactivation.

In previous works, most researchers investigated and optimized the SBCR performance using their reactor models at a fixed inlet gas composition to the SBCR. However, in the industrial FT synthesis process, due to the single pass conversion not too high, a lot of tail gas will be returned to the SBCR. It will change the inlet gas composition when the reaction performance changes. Therefore, the optimal results obtained at fixed inlet gas composition to the SBCR may not be reasonable. To solve this problem, a process model integrated with a SBCR model for FT synthesis should be used. This work developed a comprehensive process model for FT synthesis that includes a detailed SBCR model, gas liquid separation model, simplified CO₂ removal model and tail gas cycle model, and used the model to investigate and optimize the performances of an industrial FT synthesis process with the SBCR and iron-based catalyst.

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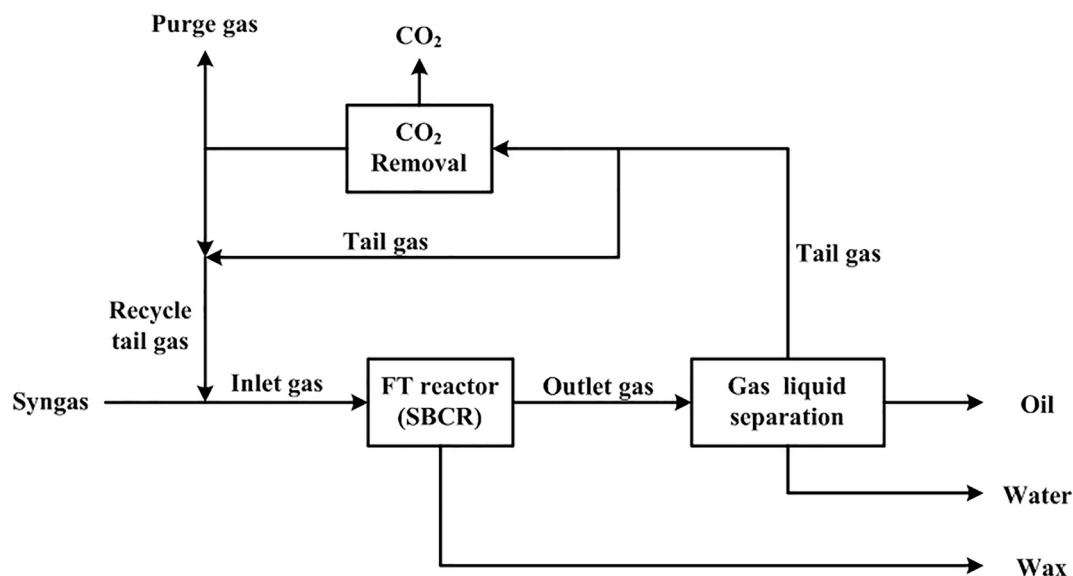


Fig. 1. Schematic graph for the FT synthesis process with the SBCR and iron-based catalyst.

2. Process Description of FT synthesis

A typical FT synthesis with the iron-based catalyst includes FT synthesis reaction, gas liquid separation, CO₂ removal and tail gas cycle, as shown in Fig. 1. Syngas (CO + H₂) is mixed with the recycled tail gas to feed into the FT reactor (SBCR). Under the reaction conditions (230–280 °C, 2–4 MPa) and with the presence of the iron-based catalysts, most CO is converted into hydrocarbon, and small amount of CO is converted into CO₂. The reaction tail gas is then cooled and fed into the gas liquid separator, and oil and water are separated from the tail gas. Because the single pass conversion in the FT reactor is not too high, a lot of tail gas (about 1–3 times of syngas flowrate) will be recycled into the FT reactor. To control the CO₂ content of the inlet gas to the reactor, part of the tail gas (about 10%–30% of total tail gas) needs to remove CO₂ before recycling into the FT reactor, and the rest of the tail gas is directly recycled into the FT reactor. In addition, some tail gas is released to control the reaction pressure.

3. Mathematical Model for FT Synthesis Process

The comprehensive mathematical model for FT synthesis process mainly includes: a detailed SBCR model, a gas liquid separation model, a simplified CO₂ removal model and a tail gas cycle model.

3.1. SBCR model

Modeling research work on the SBCR for FT synthesis began from 1950s [11]. According to bubble characters, the models were divided into homogeneous state consisting of single bubble and heterogeneous state consisting of two-class or multi-class bubbles [12], and the most models are zero dimension and one dimension. Zero dimension models, which do not consider axial and radial direction, can only predict the varied trend of the parameters [13–16] and the typical physical phenomena such as jump change of gas holdup [17,18]. Typical one dimension model includes single bubble model [19–21], double bubble model [2,4,5,22–25] and multi-stage series CSTR model [26,27]. Deckwer *et al.* [19], Stern *et al.* [20], and Saxena *et al.* [21] proposed the single bubble model and Van der Laan *et al.* [2], Maretto *et al.* [22], De Swart *et al.* [23], Rados *et al.* [24], Sehabiague *et al.* [4], and Wang *et al.* [5] proposed and improved the double bubble model. These models above were used for the design of the large scale SBCR. Ghasemi and Sohrabi [25] compared the single bubble model with the double bubble model, and the

results show that increasing reactor diameter and decreasing solid concentration both lead to major impact, while bubble breakup and coalescence minimize their difference.

The objective of this work is to develop a process model for industrial FT synthesis with the SBCR and optimize its performance, and one dimension SBCR model is adopted here, which includes material balance equations, hydrodynamic and mass transfer correlations, FT and WGS reaction kinetic equations and hydrocarbon distribution model.

3.1.1. Material balance equations

The SBCR model is essentially based on the axial dispersion model in conjunction with the two-class of gas bubble model [4,10]. The catalyst particle suspension was modeled using the Sedimentation-Dispersion model. The following key assumptions were considered: (1) the mass-transfer resistances in the gas-film and in the liquid-solid film are negligible and (2) the slurry temperature is constant. According to these assumptions and model features, the mass balances of each component in the different phases over a differential element of the reactor can be derived as shown in Table 1; and the boundary conditions for solving these equations are given in Table 2.

Table 1
Material balance equations [10]

Phase	Material balance equations
Liquid	$\frac{d}{dh} \left(\varepsilon_L D_L \frac{dC_{iL}}{dh} \right) - \frac{d(U_L C_{iL})}{dh} + \varepsilon_L (k_L a)_i^{LB} \left(\frac{C_{iG}^{LB}}{K_i^{LB}} - C_{iL} \right) + \varepsilon_L (k_L a)_i^{SB} \left(\frac{C_{iG}^{SB}}{K_i^{SB}} - C_{iL} \right) + \varepsilon_L \varepsilon_p \rho_p \sum_{j=1}^n v_{ij} r_j = 0$
Small bubbles	$\frac{d}{dh} \left(\varepsilon^{SB} D^{SB} \frac{dC_{iG}^{SB}}{dh} \right) - \frac{d(U_G^{SB} C_{iG}^{SB})}{dh} - \varepsilon^{SB} (k_L a)_i^{SB} \left(\frac{C_{iG}^{SB}}{K_i^{SB}} - C_{iL} \right) + \frac{K_T}{H} (U_G^{SB} - U_G^{LB}) (C_{iG}^{SB} - C_{iG}^{LB}) = 0$
Large bubbles	$\frac{d}{dh} \left(\varepsilon^{LB} D^{LB} \frac{dC_{iG}^{LB}}{dh} \right) - \frac{d(U_G^{LB} C_{iG}^{LB})}{dh} - \varepsilon_L (k_L a)_i^{LB} \left(\frac{C_{iG}^{LB}}{K_i^{LB}} - C_{iL} \right) + \frac{K_T}{H} (U_G^{SB} - U_G^{LB}) (C_{iG}^{LB} - C_{iG}^{SB}) = 0$
Solid suspension	$\frac{d}{dh} (\varepsilon_L D_S \frac{dC_{iW}}{dh}) + \frac{d}{dh} ((\varepsilon_L U_p - U_L) C_W) = 0$

3.1.2. Hydrodynamic and mass transfer coefficient correlations

The hydrodynamic parameters are quite important for scale-up and optimization on the SBCR. Sehabiague and Morsi [10,13,14] have done lots of works on this area at actual FT synthesis conditions. The

Table 2
Boundary conditions [10]

Phase	Boundary conditions at bottom	Boundary conditions at top
Liquid	$U_L C_{iL} - \varepsilon_L D_L \frac{dC_{iL}}{dh} = 0$	$\frac{dC_{iL}}{dh} = 0$
Small bubbles	$U_G^{SB} C_{iG}^{SB} - \varepsilon^{SB} D^{SB} \frac{dC_{iG}^{SB}}{dh} = U_G^{SB} C_{iG}^{IN}$	$\frac{dC_{iG}^{SB}}{dh} = 0$
Large bubbles	$U_G^{LB} C_{iG}^{LB} - \varepsilon^{LB} D^{LB} \frac{dC_{iG}^{LB}}{dh} = U_G^{LB} C_{iG}^{IN}$	$\frac{dC_{iG}^{LB}}{dh} = 0$
Solid suspension	$\int_0^H C_W dh = \bar{C}_W$	$U_L C_W^{IN} = U_L C_W^{OUT}$

hydrodynamic and mass transfer coefficient correlations in the latest literature published by Sehabiague [10] were adopted in this work (Appendix), which have the best prediction accuracy for gas the holdup and mass transfer coefficient.

3.1.3. Reaction kinetic equations

The reaction kinetic equations were developed specially for the iron-based catalyst used in the industrial demonstration reactor, shown as in Table 3.

Table 3
FT iron-based catalyst kinetic used in the model

Kinetic rate expression	Parameters (255 °C)
$r_{CO} = \frac{k_{FT} P_{CO} P_{H_2}}{P_{CO} + a_{FT} P_{H_2O} + b_{FT} P_{CO_2}}$	$k_{FT} = 0.118 \text{ mol} \cdot \text{kg}^{-1} \cdot \text{s}^{-1} \cdot \text{MPa}^{-1}$ $a_{FT} = b_{FT} = 5.9$
$r_{CO_2} = \frac{k_{WGS} (P_{CO} P_{H_2O} - P_{H_2} P_{CO_2} / K_{P,WGS})}{(P_{CO} + a_{WGS} P_{H_2O} + b_{WGS} P_{CO_2})^2}$	$k_{FT} = 0.083 \text{ mol} \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$ $a_{WGS} = b_{WGS} = 1.9$ $K_{P,WGS} = 79.7$

3.1.4. Hydrocarbon distribution model

In the FT synthesis, the product yield decreases exponentially with increasing chain length. The so-called Anderson–Schulz–Flory (ASF) distribution describes the entire product range by a single parameter α , the probability of the addition of a carbon intermediate to a chain [28,29]. However, significant deviations from the ASF distribution were reported in literature. The usual deviations of the distribution of α -olefins and paraffins are a relatively high yield of methane [30–32] and a relatively low yield of ethene [30,31,33] in comparison to the ASF distribution. Some authors described the total hydrocarbon yield with two different catalytic sites with different chain growth probabilities, since the total hydrocarbon distribution could be fitted by addition of two individual ASF distributions [34,35]. However, such double-models cannot explain the decrease of the olefin to paraffin ratio. The hydrocarbon product distribution is calculated by the α -olefin re-adsorption model proposed by Van der Laan [3]. Some α -olefin re-adsorption product distribution model were revised according to the industrial demonstration run data, shown as in Table 4.

Table 4
Parameters value for α -olefin re-adsorption product distribution model

Parameters	This work	Original model ³
t_p^1	3.9	6.5
k_R	$2.00 \times 10^{-3} \frac{P_{H_2}^{1.2} P_{CO}^{-0.47}}{\bar{O}_{v,0}/W}$	$8.00 \times 10^{-5} \frac{P_{H_2}^{1.2} P_{CO}^{-0.47}}{\bar{O}_{v,0}/W}$

3.1.5. Physical properties and flash calculations

The physical properties (density, viscosity, surface tension and saturated vapor pressure) of the wax produced from the industrial demonstration reactor were measured with experiments close to the actual reaction temperature [10], and the physical properties of the wax at

528 K are: density 693 kg m^{-3} , viscosity 0.0015 Pa s , surface tension 0.017 N m^{-1} and saturated vapor pressure 5685 Pa .

Henry constants for CO, CO₂, H₂, H₂O, N₂ and light hydrocarbons (C₁–C₃) were obtained from Marano- and Holder [36]. The multicomponent VLE model of Marano and Holder [36] was applied. However, ideal gas behavior of the gas phase is assumed because under the reaction conditions applied, the fugacity coefficients (up to C₃₀) as calculated with the Peng–Robinson equation of state are between 0.95 and 1.01 [3]. The equilibrium constants between vapor and liquid for non-hydrocarbons and C_{1–3} hydrocarbons were calculated from:

$$K_i \equiv \frac{y_i}{x_i} = H_i^\infty \phi_i / P \quad (1)$$

For the other hydrocarbons, the K -value is given by:

$$K_i = \gamma_i^\infty P_{i,sat} \phi_i / P \quad (2)$$

A flash calculation using these K -values gives the final composition of the liquid and gas phase outlet of the SBRC:

$$\rho_P \bar{\varepsilon}_L \varepsilon_P V_{RRFT} \sum_i \frac{m_i}{n m_i} = U_G^H A y_i C_G + U_S A x_i C_L \quad (3)$$

$$N_i^{OUT} = U_G^H y_i A C_G \quad (4)$$

3.2. Gas–liquid separation model

In the gas liquid separation unit, the reaction tail gas is cooled to about 35 °C, and almost all C₅₊ and water are condensed. Then the gas liquid mixture is fed into a separator to separate oil and water from the tail gas. The equilibrium constants between vapor and liquid oil for non-hydrocarbons and hydrocarbons were calculated from Eqs. (3) and (4), and the equilibrium constants between vapor and liquid water for non-hydrocarbons and light hydrocarbons can be calculated by the Henry coefficients in the water. A flash calculation using these K -values gives the final composition of the liquid and gas phase outlet of the separator:

$$N_i^{OUT} = N_i^{TG} y_i + N_i^{oil} x_i^{oil} + N_i^{water} x_i^{water} \quad (5)$$

3.3. CO₂ removal model

In the industrial FT synthesis process with the iron-based catalyst, the hot potassium carbonate method is preferred to remove CO₂. Hot potassium carbonate solution (about 80 °C, 20 wt%–35 wt%) is fed into the top of the scrubber, and counters current contact with the tail gas and absorbs CO₂. A simplified model was used for CO₂ removal unit. CO₂ concentration in the tail gas is controlled to a constant value from the CO₂ removal unit, and the loss of other components (CO, H₂, N₂, C_{1–4}) were estimated by the Henry coefficients in water.

$$N_i^{RTG} = (1 - \delta_i) \beta N_i^{TG}, i \neq \text{CO}_2 \quad (6)$$

$$N_i^{RTG} = y_{CO_2}^{RTG} \frac{\sum_{i=0}^n N_i^{RTG}}{1 - y_i^{IN}}, i = \text{CO}_2 \quad (7)$$

$$y_i^{RTG} = \frac{N_i^{RTG}}{\sum_{i=0}^n N_i^{RTG}} \quad (8)$$

$$N_i^{DTG} = (1 - \beta) N_i^{TG} \quad (9)$$

3.4. Tail gas cycle model

The recycle tail gas is usually given a proportion of the syngas flowrate, shown as follows.

$$N^{RG} = \lambda N^{FG} \quad (10)$$

For the purge gas

$$N^{PG} = N^{DTG} + N^{RTG} - N^{RG} \quad (11)$$

$$y_i^{PG} = y_i^{RTG} \quad (12)$$

$$N_i^{PG} = N^{PG} y_i^{PG} \quad (13)$$

For the recycle tail gas

$$N_i^{RG} = N_i^{RTG} + N_i^{DTG} - N_i^{PG} \quad (14)$$

$$y_i^{RG} = \frac{N_i^{RG}}{N^{RG}} \quad (15)$$

For the inlet gas to the SBCR

$$N^{IN} = N^{RG} + N^{FG} \quad (16)$$

$$N_i^{IN} = N_i^{RG} y_i^{RG} + N_i^{FG} y_i^{FG} \quad (17)$$

$$y_i^{IN} = \frac{N_i^{IN}}{\sum_{i=0}^n N_i^{IN}} \quad (18)$$

3.5. Algorithm for the model

The presented mathematical model is complex due to the tail gas cycle. An effective iteration algorithm was proposed to solve this model, as shown in Fig. 2.

In the iteration process, the initial value and step are shown as Eqs. (19)–(21).

$$N_{i,0}^{RG} = N_i^{RG} y_i^{FG} \quad (19)$$

$$\Delta N_{i,k}^{RG} = N_{i,k+1}^{RG} - N_{i,k}^{RG} \quad (20)$$

$$N_{i,k+1}^{RG} = N_{i,k}^{RG} + a \Delta N_{i,k}^{RG} \quad (21)$$

where $a = 0.1-1$, $\epsilon = 0.001$.

4. Industrial Demonstration Experiment and Simulation Results

The model and algorithm were verified by the experiment data from Shenhua FT industrial demonstration unit in Erdos (SBCR with 5.8 m diameter and 30 m height).

4.1. Process description of the industrial demonstration unit

The schematic process flowsheet diagram of the industrial demonstration unit is shown as Fig. 3. Syngas ($\text{CO} + \text{H}_2$) is mixed with the recycled tail gas to feed into the FT reactor (SBCR with 5.8 m diameter and 30 m height), and occurs FT synthesis reaction at 255 °C and 2.8 MPa. The reaction tail gas exchanges heat with the recycled tail gas, and then it is cooled to about 35 °C and fed into gas liquid separator. In the gas liquid separator, the liquid (oil and water) are separated from the tail gas. Some reaction tail gas is directly recycled into the FT reactor, and other tail gas needs to remove CO_2 before recycling into the reactor

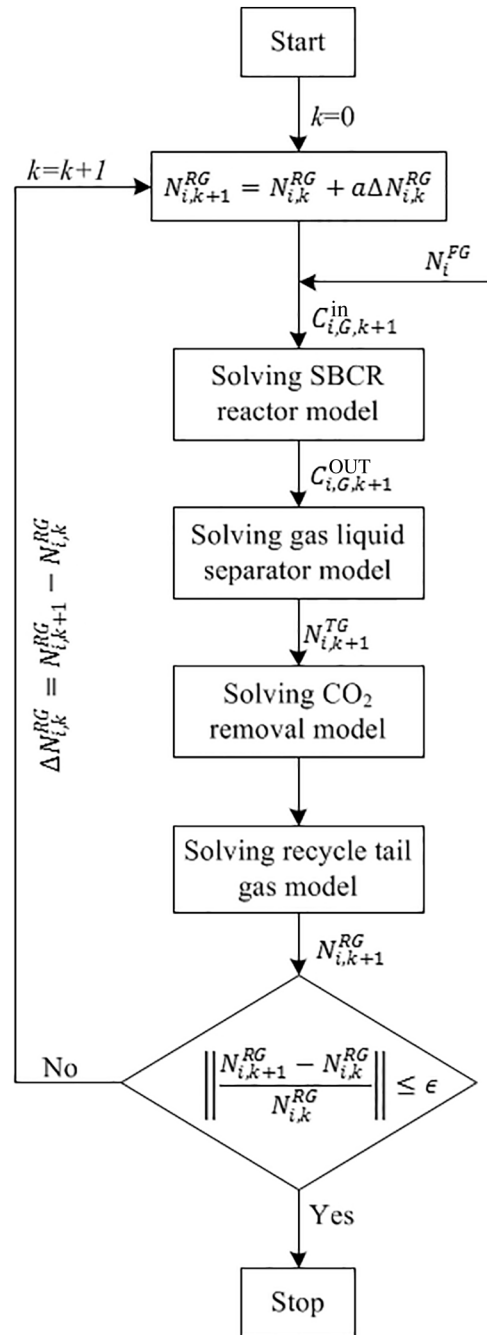


Fig. 2. Algorithm for the process model for FT synthesis.

to control the CO_2 content of the cycled tail gas. In the CO_2 removal unit, hot potassium carbonate solution (about 80 °C, 30 wt%) is used to absorb CO_2 from the tail gas, and CO_2 mole content of the tail gas is controlled to about 2% from this unit. In addition, some tail gas is released to control the reaction pressure.

4.2. Experiment and simulation results

For the industrial demonstration unit, the syngas produced by Shell gasifier is used, and the composition of the syngas is shown as Table 5 and main operation conditions are listed in Table 6.

The experiment and simulation results for the performance of the industrial demonstration unit are shown as Table 7 and Table 8. The maximum relative error of predicting CO total conversion, CO single pass

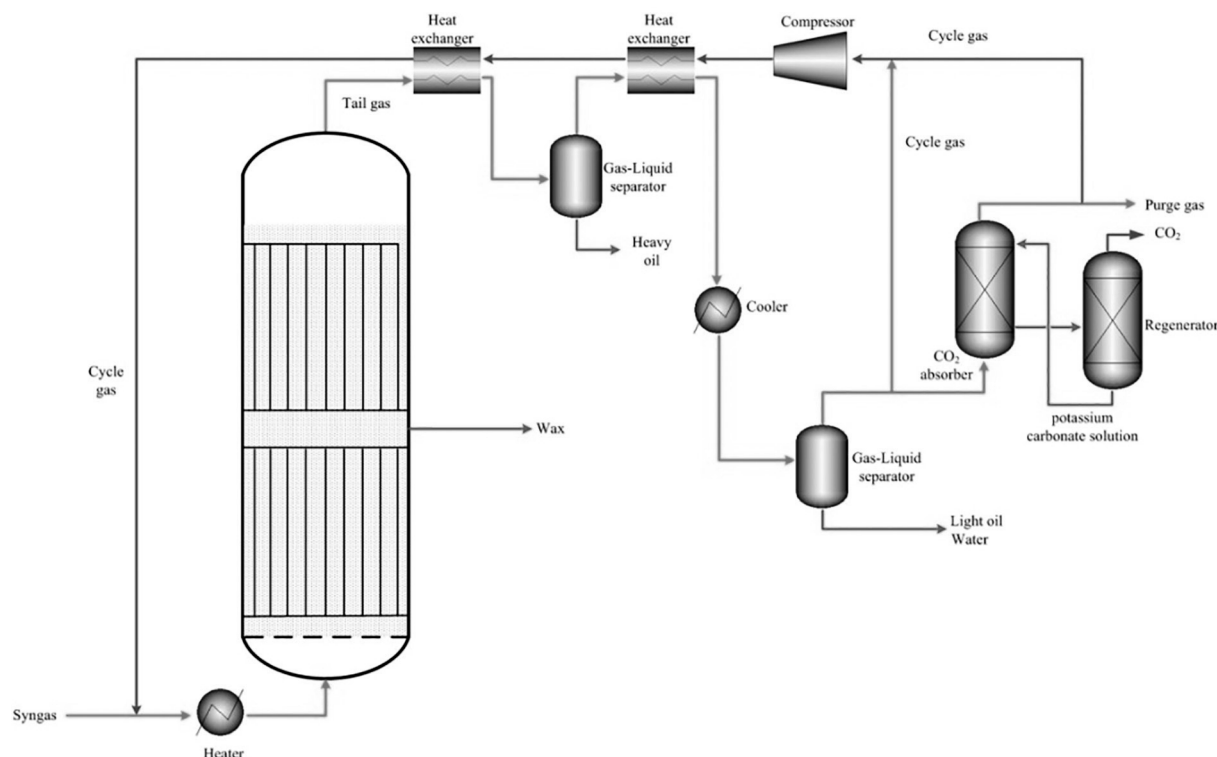


Fig. 3. Schematic graph for Shenhua FT industrial demonstration unit.

Table 5
Composition of syngas

Components	Mole fraction
H ₂	0.5247
CO	0.3446
CO ₂	0.0002
N ₂	0.1272
Ar	0.0027
CH ₄	0.0003
H ₂ S	<0.02 mg·Nm ⁻³

Table 6
Operation conditions for the industrial demonstration unit

Process parameters	Values
Reaction temperature/°C	255
Reaction pressure/MPa	2.8
Recycle ratio	1.75
Ratio of tail gas to CO ₂ removal/%	25
Syngas flowrate/Nm ³ ·h ⁻¹	120,000
Superficial gas velocity of the reactor/m·s ⁻¹	0.23
Catalyst loading in the reactor/t	20

Table 7
SBCR performances in the industrial demonstration unit

Items	Experiment	Simulation ^①	Relative error/%	Simulation ^②	Relative error/%
CO total conversion/%	72.3	75.4	4.2	73.4	1.5
CO single pass conversion/%	36.3	36.4	0.3	35.4	-2.5
CO ₂ selectivity/%	18.8	18.6	-1.1	18.9	0.5
CH ₄ selectivity/%	2.50	2.64	5.6	7.97	218.8
C ₅₊ yield/t·d ⁻¹	345.6	327.6	-5.3	215.0	-37.9

^① Use the revised parameter values (Table 4) for α -olefin re-adsorption product distribution model;

^② Use the original parameter values (Table 4) for α -olefin re-adsorption product distribution model.

conversion, CO₂ selectivity, CH₄ selectivity and C₅₊ yield is <10%. The experiment and simulation results for mole fraction of inlet gas to FT reactor are listed in Table 8, with a maximum relative error <10% for main components. In the inlet gas to reactor, the inert gas (N₂) content exceeds 20% due to tail gas cycle, which limits the reactor performance. The original parameter values for α -olefin re-adsorption product distribution model were also used to compare the simulation results with the revised parameter values in this work. The simulation results with the original parameter values for α -olefin re-adsorption product distribution model show the larger relative errors for the CH₄ selectivity (218.8%) and C₅₊ yield (-37.9%) (seeing Table 7).

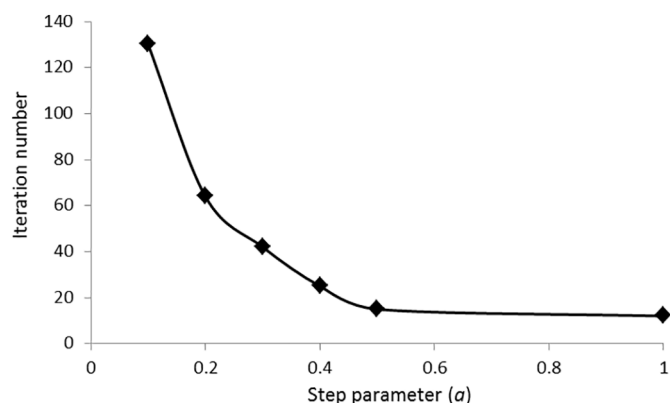
4.3. Algorithm investigation

To investigate the performance of the algorithm to the model, different values of step parameter (a) were selected to solve the model, and the iteration numbers required are presented in Fig. 4. The results show that iteration number will decrease as the step parameter increases, especially when $a < 0.5$. However, the larger the step parameter, the lower the stability of the algorithm; a larger step parameter easily makes the algorithm not convergent. Thus, $a = 0.5$ is preferred in the algorithm.

Table 8

Experiment and simulation results for mole fraction of the inlet gas to the SBCR

Components	Experiment/%	Simulation/%	Relative error/%
H ₂	45.1	42.6	−5.5
CO	25.2	26.3	4.4
CO ₂	6.2	5.8	−6.5
C _{1–4}	2.1	1.9	−9.5
N ₂	21.2	22.8	7.5

**Fig. 4.** Iteration number changes as the step parameter of iteration algorithm ($\epsilon = 0.001$).

5. Optimization Results on the SBCR Performance

For the industrial demonstration unit, syngas flowrate ($120,000 \text{ Nm}^3 \cdot \text{h}^{-1}$), recycle ratio (1.75), reaction temperature (255°C) and reaction pressure (2.8 MPa) are almost constant due to the designed coal gasifier, cycle gas compressor and SBCR. However, the H_2/CO of syngas and catalyst loading could be adjusted and optimized to obtain maximum productivity for the SBCR.

The effect of catalyst loading on the SBCR performances was investigated at different H_2/CO value of syngas. Fig. 5 shows that C_{5+} yield increases as catalyst loading increases within 10–70 ton and syngas H_2/CO value decreases within 1.3–1.6. However, it is noted that the C_{5+} yield doesn't increase obviously as catalyst loading increases when the catalyst loading exceeds 45 ton (about 15 wt% concentration). Although higher catalyst loading will increase C_{5+} yield, it will result in higher

difficulty for wax/catalyst separation and higher catalyst cost. Therefore, the catalyst loading (45 ton) is recommended for the industrial demonstration unit operation at syngas $\text{H}_2/\text{CO} = 1.3$, and C_{5+} yield is about 402 t/d for the case, which has an about 16% increase than the industrial demonstration run results.

6. Conclusions

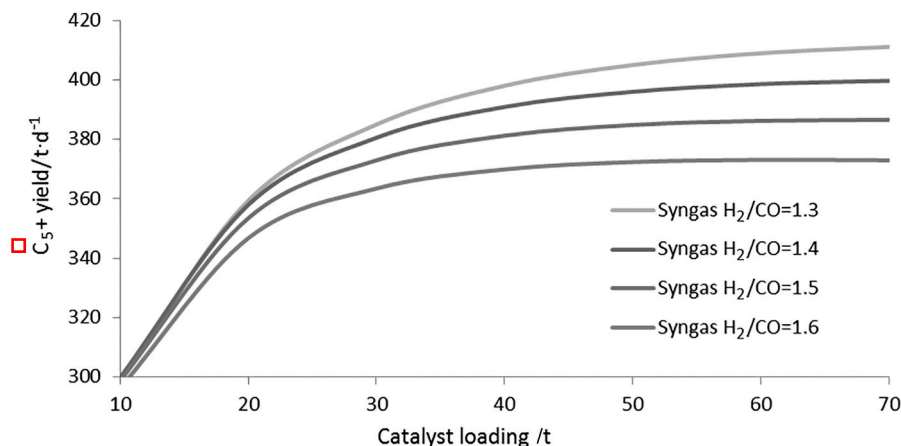
This work developed a comprehensive process model for FT synthesis that includes a detailed SBCR model, gas liquid separation model, simplified CO_2 removal model and tail gas cycle model. The SBCR model is a one dimension double bubble model that consists of mass balance equations of multi-components in the large bubble, small bubble and liquid, FT and WGS kinetic equations, α -olefin re-adsorption product distribution model and hydrodynamic correlations. Subsequently, an effective iteration algorithm was proposed to solve this process model. The model was validated by the industrial demonstration experiments (SBCR with 5.8 m diameter and 30 m height) data, and the maximum relative error of predicting CO total conversion, CO single pass conversion, CH_4 selectivity, CO_2 selectivity, space time yield and main component contents is less than 10%.

Finally, the proposed model was adopted to optimize the performance of the industrial demonstration SBCR simultaneously considering process and reactor parameters variations. The results show that C_{5+} yield increases as catalyst loading increases within 10–70 ton and syngas H_2/CO value decreases within 1.3–1.6, but the C_{5+} yield doesn't increase obviously as catalyst loading increases when the catalyst loading exceeds 45 ton (about 15 wt% concentration). Although higher catalyst loading will increase C_{5+} yield, it will result in higher difficulty for wax/catalyst separation and higher catalyst cost. Therefore, the catalyst loading (45 ton) is recommended for the industrial demonstration unit operation at syngas $\text{H}_2/\text{CO} = 1.3$, and the C_{5+} yield is about $402 \text{ t} \cdot \text{d}^{-1}$, which has an about 16% increase than the industrial demonstration run results.

For a new FT synthesis unit in design, the model developed in this work could be used better for simultaneously optimizing SBCR parameters and process parameters (*i.e.* reactor diameter and height, syngas flowrate and H_2/CO value, recycle ratio, catalyst loading) to obtain maximum productivity.

Nomenclature

A	Reactor area, m^2
C	Concentration, $\text{mol} \cdot \text{m}^{-3}$
C_p	Solid concentration in slurry phase, kg m^{-3}
C_w	Solid mass concentration, wt%

**Fig. 5.** Effect of catalyst loading on the SBCR productivity at different H_2/CO value of syngas (Syngas flowrate $120,000 \text{ Nm}^3 \cdot \text{h}^{-1}$, recycle ratio 1.75, reaction temperature 255°C , reaction pressure 2.8 MPa).

D	Diffusion coefficient, $\text{m}^2 \cdot \text{s}^{-1}$
D_R	Diameter of reactor, m
H	Reactor height, m
H^∞	Henry constant at infinite dilution
K	Gas liquid equilibrium constants
K_T	Pseudo kinetic constant
K_P	Reaction equilibrium constant
$k_L a$	Volumetric mass transfer coefficient, s^{-1}
k_L	Liquid mass transfer coefficient, $\text{s}^{-1} \cdot \text{m}^{-2}$
m	Molar selectivity
M_W	Molar weight, $\text{kg} \cdot \text{kmol}^{-1}$
N	Molar flowrate, $\text{mol} \cdot \text{s}^{-1}$
P	Pressure, MPa
P^{sat}	Saturated vapor pressure, MPa
r	Reaction rate, $\text{mol} \cdot (\text{kgcat})^{-1} \cdot \text{s}^{-1}$
R	Gas constant, $8.31 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
T	Temperature, K
U	Superficial velocity, $\text{m} \cdot \text{s}^{-1}$
V_R	Reactor volume, m^3
W	Catalyst weight, kg
X_W	weight fraction of the primary liquid in the mixture (0.5 ≤ X_W ≤ 1.0) (w/w)
x	Molar fraction in liquid phase
y	Molar fraction in gas phase
β	Proportion of tail gas to CO_2 removal unit
δ	Loss ratio in the CO_2 removal unit
ρ	Density, $\text{kg} \cdot \text{m}^{-3}$
μ	Viscosity, $10^{-3} \text{ Pa} \cdot \text{s}$
σ	Surface tension, $\text{N} \cdot \text{m}^{-1}$
ϵ	Tolerance of relative error
ε	Volumetric fraction
$\bar{\varepsilon}$	Average volumetric fraction
ν	Stoichiometric coefficient
λ	Recycle ratio
γ^∞	Activity coefficient at infinite dilution
ξ	Opening ratio of sparger, %
$\emptyset$	Poynting factor
$\emptyset_{v,0}$	Flow rate at normal conditions, $\text{m}^3 \cdot \text{h}^{-1}$
Γ	Gas distributor parameter

Superscripts

SB	Small bubble
LB	Large bubble
oil	Liquid oil
water	Liquid water
IN	Inlet gas to reactor
OUT	Outlet gas from reactor
TG	Tail gas from gas liquid separator
RG	Recycle tail gas to reactor
FG	Feed syngas
RTG	Tail gas after CO_2 removal
DTG	Directly recycle tail gas
PG	Purge gas

Subscripts

G	Gas phase
i	Species
j	Reaction
L	Liquid phase
p	Particle
S	Solid phase
SL	Slurry phase

Appendix A

Hydrodynamic and mass transfer coefficient correlations [10]

$$\varepsilon_G = 1.235 \times 10^4 \left(\frac{\rho_G^{0.174} U_G^{0.553} \Gamma^{0.053}}{\rho_L^{1.59} \mu_L^{0.025} \sigma_L^{0.105}} \right) \left(\frac{P}{P - P_L^{\text{sat}}} \right)^{0.203} \left(\frac{D_C}{D_C + 1} \right)^{-0.117} \\ \times e^{-0.00015C_P - 1.78 \times 10^{-6} C_P^2 - 433.9d_P - 0.434X_W}$$

$$k_L a = 9.34 \times 10^{-9} \left(\frac{\rho_L^{1.82} \rho_G^{0.27} U_G^{0.387} \Gamma^{0.173}}{M_{W,G}^{0.02} \mu_L^{0.25} \sigma_L^{0.976}} \right) \left(\frac{P}{P - P_L^{\text{sat}}} \right)^{0.241} \left(\frac{D_C}{D_C + 0.3} \right)^{0.1} \\ \times e^{-8 \times 10^{-9} C_P - 1.6 \times 10^{-6} C_P^2 - 0.8C_P + 1675.7d_P + 0.176X_W}$$

α -Olefin re-adsorption product distribution model [3].

$$m_{\text{CH}_4} = t_p^1 \theta_1.$$

$$m_{\text{C}_2\text{H}_6} = t_p^2 \alpha_2 \theta_1$$

$$m_{\text{C}_2\text{H}_4} = \frac{t_o^2}{1 + k_R^2} \alpha_2 \theta_1$$

$$m_{\text{C}_n\text{H}_{2n+2}} = \theta_1 \prod_{i=2}^n \alpha_i, n > 2$$

$$m_{\text{C}_n\text{H}_{2n}} = \frac{t_o}{1 + k_R e^{\alpha_2 n}} \theta_1 \prod_{i=2}^n \alpha_i, n > 2$$

$$\alpha_2 = \frac{p}{\frac{t_o^2}{1 + k_R^2} + t_p^2 + p}$$

$$\alpha_i = \frac{p}{\frac{t_o}{1 + k_R e^{\alpha_2 n}} + 1 + p}, i > 2$$

$$\sum_{i=1}^n m_i = 1$$

Where $p = 14.4 P_{\text{H}_2}^{-0.26} P_{\text{CO}}^{0.40}$, $t_o = 3.71 P_{\text{H}_2}^{0.5}$, $k_R = 8.00 \times 10^{-5} \frac{P_{\text{H}_2}^{1.2} P_{\text{CO}}^{0.47}}{\emptyset_{v,0} / W}$, $t_p^1 = 6.5$, $t_p^2 = 1.7$, $c = 0.35$, $k_R^2 = 17.6 k_R e^2$, $t_o^2 = t_p^2 t_o$

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