

# Industrial Regenerator Model for SMTO Technology

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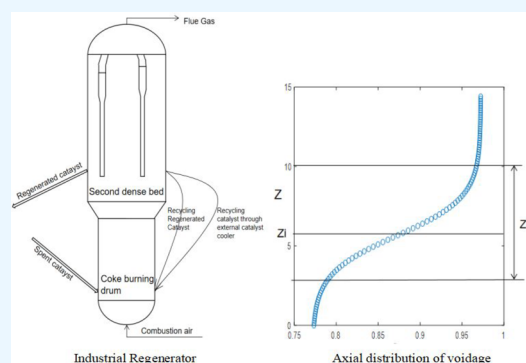
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**ABSTRACT:** In order to alleviate the current domestic oil shortage, China has studied the technology of using coal as the source to produce low carbon olefins, among which methanol to olefin (MTO) is an important process. Since the coke deposition of MTO catalyst is inevitable, the deactivated MTO catalysts need to be regenerated by continuous coke combustion to recover the activity. This paper used the actual industrial data to study the gas–solid two-phase fluidized bed of a SMTO regenerator and the coke combustion kinetics of the deactivated SAPO-34 catalyst, and established the mathematical model of the SMTO industrial regenerator. The kinetic parameters in the model were obtained and validated with different data, which showed that the model is reliable and can accurately predict the industrial reaction results and provide guidance for the SMTO production operation.



## 1. INTRODUCTION

Low-carbon olefins are important basic chemical raw materials. The traditional steam cracking process for olefin production needs a large amount of naphtha from crude oil, but China is a country short of petroleum resources. In order to alleviate the current oil shortage, China has studied the technology of using coal as the source to produce low carbon olefins,<sup>1</sup> among which methanol to olefin (MTO) is an important process. The MTO reaction was first reported by Mobil in the early 1970s.<sup>2</sup> During the research and development of methanol to gasoline production, it was found that intermediate products such as C2–C4 olefins would be formed during the production process, and the reaction conditions and catalyst composition could be reasonably controlled to keep the reaction at the stage of light olefins, which led to the formation of the MTO process. Now there are four typical methanol to olefin technologies, including UOP/Hydro MTO process; DMTO process from Dalian Institute of Chemical Physics (DICP), Chinese Academy of Sciences; SMTO process from Shanghai Research Institute of Petrochemical Technology, Sinopec Co. Ltd.; and MTP process from Lurgi which produces propylene as the destination product. Most of the catalysts applied in methanol to olefin technology use SAPO-34 molecular sieve as the active component.<sup>3</sup> SAPO-34 molecular sieve has a suitable pore size and acid strength to convert methanol to low carbon olefins with high selectivity and limit the generation of macromolecular hydrocarbon products, on the other hand, SAPO-34 molecular sieve is prone to coke deposition and then deactivates due to its small pore size.<sup>4,5</sup> Therefore a continuous catalyst regeneration in the MTO industrial regenerator is required to maintain the reactivity in the reactor. For MTO reactions, a certain amount of carbon deposition on the

catalyst helps to shorten or avoid the induction period of the reaction. How to control the carbon content of regenerated catalysts by adjusting the coke combustion intensity is a question to be considered in the MTO industrial operation.

Aguayo et al.<sup>6</sup> studied the deactivation of MTO catalysts and showed that the coke deposited on the catalysts mainly consisted of alkanes, naphthalenes, phenanthrenes, and pyrenes from C9 to C13. Haw et al.<sup>7</sup> found that the type of coke deposition on the MTO catalysts was related to the reaction time. The coke composition was mainly a small amount of methylbenzene with occasional methylnaphthalene in the early stage of the reaction, a large amount of methylbenzene and methylnaphthalene in the middle stage of the reaction, and a large amount of polycyclic aromatic hydrocarbons in the later stage.

The MTO industrial regenerator is similar to the regenerator for catalytic cracking.<sup>8</sup> The engineering design types of industrial fluidized bed regenerator can be divided into three categories: single-stage regeneration, two-stage regeneration, and circulating fluidized bed regeneration.<sup>9</sup> The regenerator studied in this paper is the circulating fluidized bed regeneration, which combines the advantages of two-stage regeneration and fast fluidized bed regeneration. The structure type of the regenerator is different from that of the single-stage regeneration and two-stage regeneration, mainly consisting of a

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fast fluidized bed reactor, commonly known as a coke burning drum, and a dense bed reactor, which is a buffer vessel for completing the final coke combustion. Li and Kwauk<sup>10</sup> demarcated the transition from turbulent fluidization to fast fluidization, in which particles need to be continuously recycled to the bottom of the bed to maintain dense bed operation, by a critical velocity, above which dilute-phase upflow with continuous solids feed becomes possible. The characteristics of fast fluidization are no distinguishable upper bed surface; particles are transported out from the top and must be replaced by adding solids near the bottom; and clusters or strands of particles descend, mostly near the wall, while gas and dispersed particles move upward in the interior.<sup>11</sup>

The circulating fluidized bed model has been studied by many scholars. Wei<sup>12</sup> studied the industrial fluidized catalytic cracking process and analyzed the gas–solid mixing of the coke burning drum, which is a fast fluidized bed. The axial voidage distribution of the coke burning drum was calculated using the four-parameter model proposed by Guo et al.<sup>13</sup>

Xu et al.<sup>14</sup> studied the desulfurization process of circulating fluidized bed and calculated the reactor flow field which conforms to the fast fluidization condition. He proposed a model for the distribution of axial voidage as follows:

$$1 - \varepsilon = 14 \frac{G_s}{\rho_p} e^{-2.61h/H} \quad (1)$$

The kinetic model of coke combustion on molecular sieve catalysts has been studied in detail by many researchers in China and abroad.<sup>17–19</sup>

In the regeneration of MTO catalyst, the following reactions exist:<sup>15</sup>



Within the normal regeneration temperature range, the reaction rates of reactions 5 and 6 can be considered as no occurrence. In the presence of the additive for CO combustion, the oxidation rate of CO is fast and the coke combustion products are only CO<sub>2</sub> and H<sub>2</sub>O.<sup>16</sup> In this paper only reactions 2 and 3 are considered.

Chang et al.<sup>17</sup> studied the coke combustion regeneration of FCC gasoline aromatization catalysts with particle size of 1000 μm in a fixed-bed microreactor, and established an apparent regeneration kinetic model to calculate the molar ratio of CO<sub>2</sub> and CO in the products, aiming to provide guidance for the optimization of process operating conditions. Their established reaction rate equation for coke combustion is as follows:

$$-\frac{dC}{dt} = kC^m P_{\text{O}_2}^n \quad (7)$$

Gayubo et al.<sup>18</sup> investigated the relationship between the recovery of catalyst activity and the coke combustion time in an isothermal reactor, as well as the relationship between the recovered activity and the coke content. The rate of coke combustion on the catalyst was considered as a first order

relationship with the concentration of reactants (coke and oxygen). The kinetic equation was expressed as follows:

$$-\frac{dC}{dt} = -k e^{-(E/R)(1/T-1/723)} C P_{\text{O}_2} \quad (8)$$

Yan et al.<sup>19</sup> used a fluidized bed reactor with a computerized online measurement system to study the coke combustion regeneration of molecular sieve catalysts. The amount of carbon dioxide produced by the reaction is measured online by a highly sensitive and fast-response conductivity computer system. The kinetic model for coke combustion is

$$-\frac{dC_C}{dt} = kP(C_C)^{n_1}(Y_{\text{O}_2})^{n_2} \quad (9)$$

Based on coke regeneration kinetics and fluidization theory, this paper established a mathematical model suitable for SMTO industrial regenerator, and validated the mathematical model with industrial data. Finally, the mathematical model was used for simulation, analysis, and optimization of the SMTO industrial regenerator, which provided guidance for industrial unit production.

## 2. SMTO REGENERATOR DESCRIPTION

The SMTO process was developed by Shanghai Research Institute of Petrochemical Technology, Sinopec Co. Ltd. The SMTO process uses a fast fluidized bed reactor which can achieve a methanol conversion of 99.8% and a total olefin yield of more than 80%, and its regenerator uses a combination of a coke burning drum and a dense phase fluidized bed for incomplete catalyst regeneration.<sup>20</sup>

**2.1. Regenerator.** The research object of this paper is the regenerator in the SMTO unit of a coal chemical company. The regenerator adopts coke burning drum in the lower part plus dense bed regeneration in the upper part, which is a two-stage regeneration as shown in Figure 1. The regenerator structure includes inner gas collection chamber, first and second cyclone separation system, coke burning drum, cooling steam distribution ring, low pressure drop distribution plate, main air distribution pipe, etc. The main function of the regenerator is to burn off the coke on the spent catalyst to recover the activity of the catalyst. Its structural parameters are listed in Table 1.

The air and hot nitrogen enters from the main air distribution pipe at the bottom of the coke burning drum, and comes into contact with the spent catalysts from the reactor, burning off the coke on the spent catalysts to recover the activity of the catalysts. The recovered catalysts enters the reactor through the sloped pipe of the regenerator together with the catalysts separated from the cyclone separator, while the separated flue gas leaves the regenerator after passing through the tristage cyclones in the inner collection chamber.

The main part of catalyst coke combustion happens in the coke burning drum. The spent catalyst enters the coke burning drum and mixes with the high temperature catalyst from the circulating sloped pipe, which raises the starting temperature of coke combustion. The gas linear velocity is high in the coke burning drum, which makes the catalyst flow nearly like a plug flow during the regeneration process, with better gas–solid contact and high coke combustion efficiency.

**2.2. Catalysts.** SMTO catalysts use SAPO molecular sieves as the main active component, with alumina, silicon oxide, diatomaceous earth, or Kaolin as the carrier. SAPO molecular

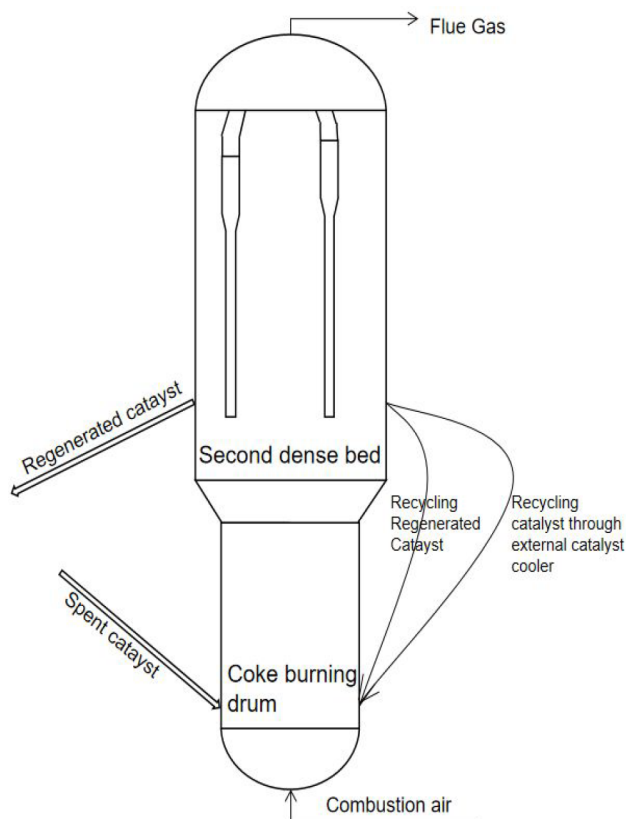


Figure 1. Schematic diagram of regenerator.

Table 1. Structural Parameters of Regenerator

Height of coke burning drum, m	Coke burning drum diameter, m	Second dense bed height, m	Diameter of second dense bed, m
14.40	4.66	4.00	5.96

sieves are crystalline silica–alumina phosphates made by the process of molding, drying, and roasting under the synergistic effect of binder and other processing aids so that its skeleton is interconnected by the tetrahedra of  $[\text{SiO}_4]$ ,  $[\text{AlO}_4]$ ,  $[\text{PO}_4]$ ,<sup>21</sup> thus yielding a negatively charged skeleton with exchangeable cations and protonic acidity. Due to the contribution of the CHA topological structure with a large cavity (9.4 Å in diameter) and small 8-ring pore (3.8 Å × 3.8 Å), the SAPO-34 catalyst exhibits excellent performance in the MTO reaction, achieving exceptionally high selectivity toward light olefins<sup>22</sup> as the narrow 8-ring pore openings could impose diffusion limitations on large molecules and make light olefins the dominant products.<sup>23</sup> It has been demonstrated that the catalytic performance, especially the deactivation behavior in the MTO reaction, is strongly related to the diffusion limitation.<sup>24</sup> Table 2 shows the properties of catalysts used for the SMTO reaction.

**2.3. Operating Conditions.** The data source for the regenerator modeling is a 1.8 million t/a SMTO industrial unit in a coal chemical company, and a total of 27 sets of data were collected. The specific operating conditions of the regenerator are as follows: the inlet mixing temperature of coke burning drum is 500–540 °C, the inlet pressure of coke burning drum is 0.17–0.19 MPa, the air flow rate is 50000–60000 N m<sup>3</sup>/h, the coke of the spent catalyst is between 2.6–3.3 wt %, the carbon of regenerated catalyst is between 0.03–0.2 wt %, the

Table 2. SMTO Catalyst Properties

Projects	Unit	Indicators
Shape		Microspherical
Skeleton density	kg/m <sup>3</sup>	2100–2500
Particle density	kg/m <sup>3</sup>	1400–1700
Stacking density	kg/m <sup>3</sup>	690–810
Pore volume	mL/g	0.18–0.28
Specific surface area	m <sup>2</sup> /g	190–270
Specific heat	kJ/kg·°C	1
Particle size composition		
<20 μm	vol%	1.0–2.0
20–40 μm	vol%	2.0–10.0
40–60 μm	vol%	20.0–25.0
60–80 μm	vol%	25.0–35.0
80–100 μm	vol%	20.0–25.0
>100 μm	vol%	15.0–20.0

flow rate of the spent catalyst is 105–150 t/h, and the flow rate of the recycling regenerated catalyst (including those returned from external heat exchanger) of the regenerator is 400–600 t/h.

**2.4. Analysis Methods.** The industrial data include catalyst coke deposition, temperature, pressure, and flue gas composition, where temperature and pressure can be read directly from temperature and pressure gauges, flue gas composition is determined by an online analysis system, and catalyst carbon deposition is measured by TGA.

### 3. MODELING

The coke combustion in the SMTO regenerator is largely influenced by the bed flow state,<sup>25</sup> which must be combined with a fluidization theory and combustion reaction kinetics to establish a mathematical model conforming to the industrial SMTO regenerator.

Solid particles are suspended in a moving fluid, so that a small group of solid particles under the action of the fluid can flow like a fluid. This is called fluidization of solids. How to make the solid catalyst flow like a fluid, and contact, separate, react, and regenerate with the feedstock is the core problem of fluidization. Fluidization of catalysts is the technical core for the methanol to olefin process to achieve industrial production.

**3.1. Basic Assumptions.** Based on the feature of SMTO technology and the analysis above, the following assumption are proposed for the SMTO regenerator model:

- At the bottom inlet of the coke burning drum, the combustion air, the spent catalyst, and the recycling catalyst from the second dense bed are rapidly mixed and thermally balanced.
- Considering the combustion of the spent catalyst and the regenerated catalyst from the second dense bed separately, the carbon combustion reaction rates of the two catalyst streams are different, and hydrogen combustion occurs only on the spent catalyst.
- The hydrogen combustion reaction rate is fast, and almost all of the hydrogen in the coke is burned off within the coke burning drum.
- Coke combustion is under the control of reaction kinetics, ignoring the effect of radial gas–solid dispersion effect on the regeneration effect.
- The regenerator is well insulated and assumed to be an adiabatic reactor.

- (f) Gases and catalysts in the second dense bed reach thermal balance and full backmixing.
- (g) In the presence of the additive for CO combustion, the oxidation rate of CO is fast and the coke combustion products are only CO<sub>2</sub> and H<sub>2</sub>O.
- (h) The coke burning drum flow pattern and the voidage distribution conforms to the four-parameter model proposed by Guo et al.<sup>13</sup>

The combustion reactions of the regeneration process are as follows:



The reaction kinetic equations are

$$r_{\text{C}} = -k_{\text{C}}P_{\text{O}_2}w_{\text{C}} \quad (12)$$

$$r_{\text{H}} = -k_{\text{H}}P_{\text{O}_2}w_{\text{H}} \quad (13)$$

$$k_{\text{C}} = k_{\text{C},0} \exp\left(-\frac{E_{\text{C}}}{RT}\right) \quad (14)$$

$$k_{\text{H}} = k_{\text{H},0} \exp\left(-\frac{E_{\text{H}}}{RT}\right) \quad (15)$$

### 3.2. Mathematical Model of Coke Burning Drum.

According to the analysis of industrial operating conditions, the regenerator's coke burning drum is a fast fluidized bed. The fast fluidized bed is characterized by the disappearance of the dilute-dense phase interface, the bed density exists in the state of dilute upper and dense lower, good gas–solid contact, fast transfer rate, small gas–solid backmixing, high equipment utilization.

The calculation of axial voidage distribution for a fast fluidized bed adopts the four-parameter model proposed by Guo et al.<sup>13</sup>

$$\varepsilon = \left[ \varepsilon_{\text{d}} + \varepsilon_{\text{e}} \exp\left(-\frac{Z - Z_{\text{i}}}{Z_0}\right) \right] \left[ 1 + \exp\left(-\frac{Z - Z_{\text{i}}}{Z_0}\right) \right]^{-1} \quad (16)$$

In eq 16,

$$\varepsilon_{\text{e}} = 1 - (1 + 0.318(u_{\text{g}}/u_{\text{s}})^{0.5}((\rho_{\text{s}} - \rho_{\text{g}})/\rho_{\text{g}})^{-0.082})\varepsilon_{\text{s}} \quad (17)$$

$$\varepsilon_{\text{d}} = 1 - (1 + 0.116(u_{\text{g}}/u_{\text{s}})^{1.13}((\rho_{\text{s}} - \rho_{\text{g}})/\rho_{\text{g}})^{-0.013})\varepsilon_{\text{s}} \quad (18)$$

$$Z_{\text{i}} = 1.6 \ln((\varepsilon^* - \varepsilon_{\text{e}})/(\varepsilon^* - \varepsilon_{\text{d}}))/(-\gamma) \quad (19)$$

$$Z_0 = 500 \exp(-30(\varepsilon_{\text{e}} - \varepsilon_{\text{d}})) \quad (20)$$

In eqs 17–20,  $\varepsilon_{\text{s}} = \frac{G_{\text{s}}}{\rho_{\text{s}}(u_{\text{g}} - u_{\text{i}})}$ ,  $u_{\text{s}} = \frac{G_{\text{s}}}{\rho_{\text{s}}}$ ,  $\varepsilon^* = 1 - \frac{G^*}{\rho_{\text{s}}(u_{\text{g}} - u_{\text{i}})}$ ,  $G^* = 0.125Fr^{1.85}Ar^{0.63}((\rho_{\text{s}} - \rho_{\text{g}})/\rho_{\text{g}})^{0.44}$ ,  $\gamma = (0.88 - 420d_{\text{p}})/((u_{\text{g}} - u_{\text{i}})^2d^{0.6})$ .

Based on the fluidized bed model above, we can obtain the axial distribution of the voidage along the height of the coke burning drum as shown in Figure 2, which shows a “S” profile ranging from 0.77 on the bottom to 0.98 on the top. There is a transition zone between the dilute and the dense phases, with a turning point in the voidage distribution.

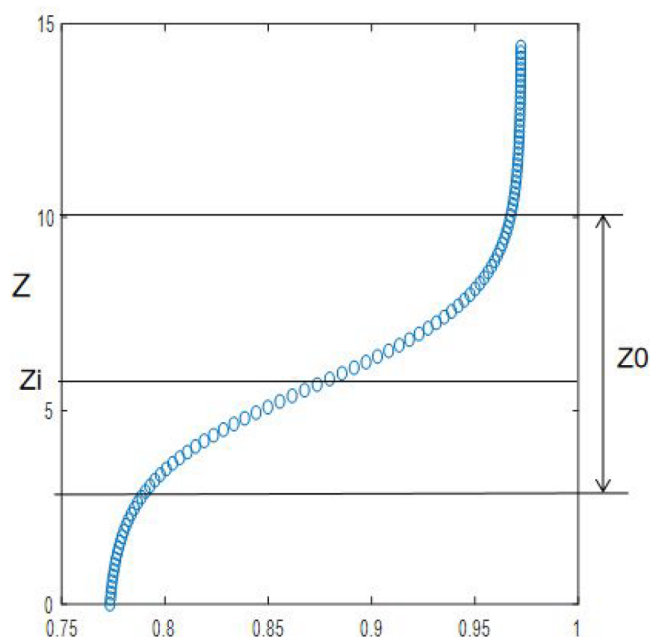


Figure 2. Axial distribution of voidage.

At the bottom inlet of the coke burning drum, the carbon content of the spent catalyst and the recycling regenerated catalyst from the second dense bed are different, and the carbon content affects the reaction rate of the carbon combustion reaction, so the spent catalyst and the regenerated catalyst are considered separately in this paper, and the carbon combustion reactions rate of the two streams are the following formula 21 and 22. And the hydrogen combustion only occurs on the spent catalyst, because only the coke of the spent catalyst contains hydrogen.

$$r_{\text{C}1} = -k_{\text{C}}P_{\text{O}_2}w_{\text{C}1} \quad (21)$$

$$r_{\text{C}2} = -k_{\text{C}}P_{\text{O}_2}w_{\text{C}2} \quad (22)$$

Based on the mass, heat, and momentum balance for the microelement height of the coke burning drum, we can obtain the differential equations for carbon and hydrogen content of the catalyst, molar flow rate of flue gas, regeneration reaction temperature  $T$  (K), and regeneration pressure  $P$  (Pa) along the height of the coke burning drum.

$$\frac{d(w_{\text{C}1}fs_1)}{dh} = \rho_{\text{s}}(1 - \varepsilon) \frac{fs_1}{fs_1 + fs_2 + fs_3} r_{\text{C}1}A \quad (23)$$

$$\frac{d(w_{\text{C}2}(fs_2 + fs_3))}{dh} = \rho_{\text{s}}(1 - \varepsilon) \frac{fs_2 + fs_3}{fs_1 + fs_2 + fs_3} r_{\text{C}2}A \quad (24)$$

$$\frac{d(w_{\text{H}}fs_1)}{dh} = \rho_{\text{s}}(1 - \varepsilon) \frac{fs_1}{fs_1 + fs_2 + fs_3} r_{\text{H}}A \quad (25)$$

$$\frac{dF_{\text{CO}_2}}{dh} = -\left( \frac{d(w_{\text{C}1}fs_1)}{dh} + \frac{d(w_{\text{C}2}(fs_2 + fs_3))}{dh} \right) \quad (26)$$

$$\frac{dF_{\text{H}_2\text{O}}}{dh} = -0.5 \frac{d(w_{\text{H}}fs_1)}{dh} \quad (27)$$

$$\frac{dF_{O_2}}{dh} = \frac{d(w_{C_1}fs_1)}{dh_{12}} + \frac{d(w_{C_2}(fs_2 + fs_3))}{dh_{12}} + 0.25 \frac{d(w_H fs_1)}{dh} \quad (28)$$

$$\frac{dT}{dh} = \frac{-\left(\frac{dF_{CO_2}}{dh} \Delta H_{CO_2} + \frac{dF_{H_2O}}{dh} \Delta H_{H_2O}\right)}{F_{CO_2} C_{P,CO_2} + F_{O_2} C_{P,O_2} + F_{H_2O} C_{P,H_2O} + F_{N_2} C_{P,N_2} + fs C_{P,cat}} \quad (29)$$

$$\frac{dP}{dh} = -(\rho_s(1 - \varepsilon) + \rho_g \varepsilon)g \quad (30)$$

The differential equations were solved by the Runge–Kutta method<sup>26</sup> which is a high-precision single-step algorithm widely used in numerically solving that the initial conditions of the differential equations are the inlet composition and temperature of the coke burning drum according to the industrial data.

**3.3. Mathematical Model of Second Dense Bed.** The dense phase zone of the second dense bed is a shallow bed layer with low air velocity, which is considered as full backmixing. This paper assumes that gases and catalysts in the second dense bed reach thermal balance and full backmixing, so the following equations are obtained based on mass and heat balance for the second dense bed.

$$w_{C_0} = \frac{w_{C_1}fs_1 + w_{C_2}(fs_2 + fs_3)}{fs} \quad (31)$$

$$r_C = -k_C P_{O_2} w_C \quad (32)$$

Mass balance:

$$(w_{C_0} - w_C)fs = -r_C \rho_s (1 - \varepsilon) A_1 h_1 \quad (33)$$

Heat balance:

$$\frac{-(w_{C_0} - w_C)fs}{12} \Delta H_{CO_2} = F_{CO_2} C_{P,CO_2} + F_{O_2} C_{P,O_2} + F_{H_2O} C_{P,H_2O} + F_{N_2} C_{P,N_2} + fs C_{P,cat} \quad (34)$$

$$\Delta H_{CO_2} = -406909.11 + 43.26T + 0.00575T^2 \quad (35)$$

$$\Delta H_{H_2O} = -252111.38 + 34.39T + 0.000315T^2 \quad (36)$$

$$C_{P,CO_2} = 0.983 + 0.00026T \quad (37)$$

$$C_{P,H_2O} = 1.91 + 0.000035T \quad (38)$$

$$C_{P,O_2} = 1.081 + 0.000034T \quad (39)$$

$$C_{P,N_2} = 0.971 + 0.00015T \quad (40)$$

## 4. RESULTS AND DISCUSSION

**4.1. Parameter Estimation.** Twenty-four sets of collected industrial data were used for the kinetic parameter estimation of the above regenerator model. The differential equations were solved using the Runge–Kutta method, and the kinetic parameters were optimized using the least-square method, which uses the sum of squares of the differences between the calculated and actual values as the objective function in eq 41.<sup>27</sup>

$$f = \sum_i^n (F_{i,cal} - F_{i,epx})^2 \quad (41)$$

The obtained kinetic parameters are shown in Table 3. The obtained reaction activation energies are close to the literature

**Table 3. Kinetic Parameters of Coke Combustion**

Parameters	Value
$k_{C_0}$ , 1/(Pa·h)	$3.853 \times 10^4$
$k_{H_0}$ , 1/(Pa·h)	$1.093 \times 10^8$
$E_C$ , J/mol	$1.620 \times 10^5$
$E_H$ , J/mol	$1.574 \times 10^5$

values which are reasonable. There was no significant difference of activation energy between the two reactions, but the effect of reaction temperature on coke combustion was obvious. The pre-exponential factor of the hydrogen combustion reaction is much larger than that of the carbon combustion reaction, and the combustion rate of hydrogen is faster than that of carbon on the catalyst.

Based on the above kinetic parameters, the calculated values and the experimental results were fitted well except for several sets of data. The main reasons of the fitting errors include the following: sometimes the recycling fluidization in the regenerator is not ideal as expected thus affecting the temperature of the recycling catalyst stream and the obtained value of catalyst flow rate between the SMTO reactor and regenerator is relatively rough.

**4.2. Model Verification.** The model verification was carried out with the remaining three sets of industrial data of different conditions, which were collected on different dates. Using the obtained SMTO industrial regenerator model, the calculated and actual values of the mass fraction of residual carbon on the regenerated catalyst as well as the temperature and flue gas composition of the regenerator outlet are listed in Table 4 and 5.

The results of the model verification show that the verification results are good, and the relative errors are mostly less than 5%, indicating that the established model is reliable.

**4.3. Axial Trend.** In this paper, the coke burning drum adopts the fast fluidized bed model, while the dense phase zone of the second dense bed adopts the CSTR model. Combining with the coke combustion kinetics, mass balance equations, and energy balance equations, the axial trend of temperature, pressure, gas phase composition, and coke fraction on catalyst in the regenerator can be calculated strictly.

The operating conditions adopted for simulation are the following: the coke content of spent catalyst is 2.86 wt %; the coke content of regenerated catalyst is 0.06 wt %; the flow rate of spent catalyst is 143.2 t/h, and the temperature is 474.6 °C; the flow rate of recycling catalyst through external catalyst cooler is 211.3 t/h, and the temperature is 489.8 °C; the flow rate of recycling regenerated catalyst is 298.1 t/h, and the temperature is 683.6 °C; the regenerator inlet air flow rate 52149.7 N m<sup>3</sup>/h, and the temperature is 133.9 °C; the regenerator inlet hot nitrogen flow rate 43.4 N m<sup>3</sup>/h, and the temperature is 38.3 °C; and the inlet pressure of coke burning drum is 171500 Pa.

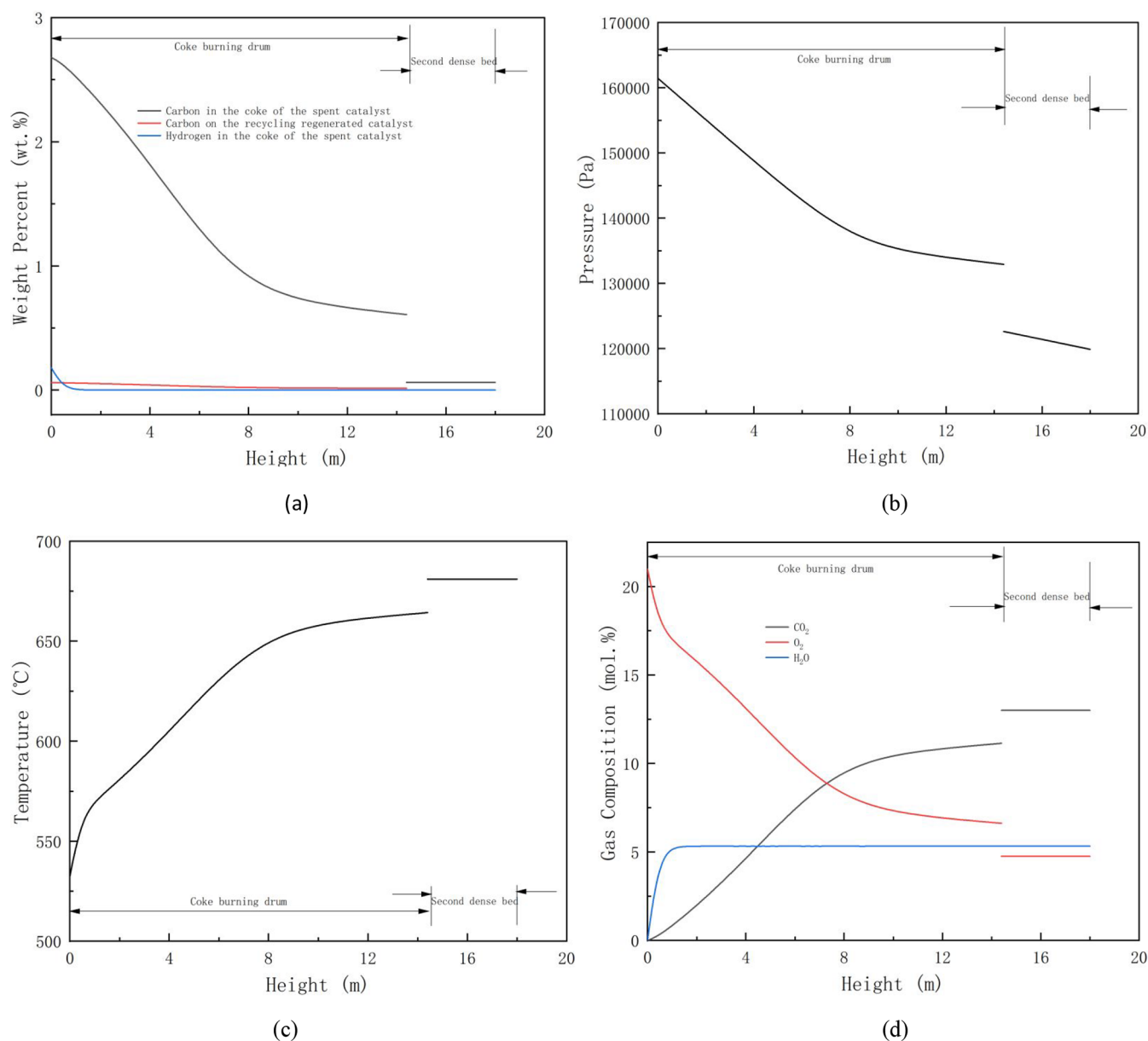
Figure 3 shows the axial trend of important variables within the regenerator, where (a) is the profile of carbon and hydrogen content of the coke, (b) is the pressure profile, (c) is the temperature profile, and (d) is the gas composition profile.

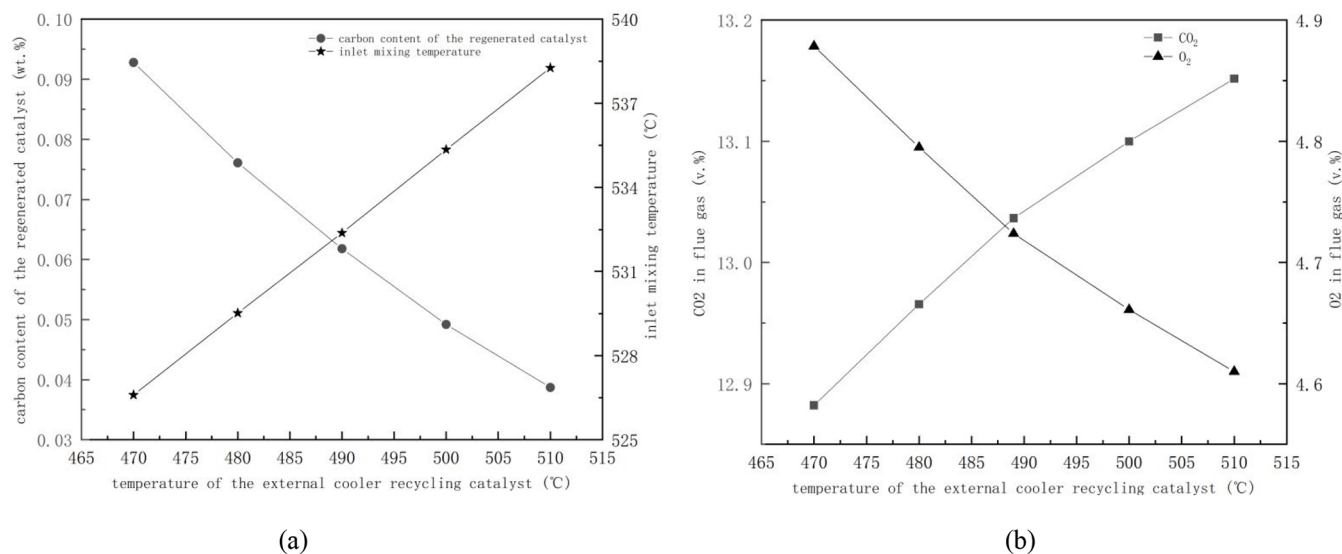
**Table 4. Comparison of Calculated and Experiment Values of Residue Carbon on Regenerated Catalyst and Temperature**

	residual carbon on regenerated catalyst, wt. %				outlet temperature of second dense bed, °C			
	measured value	calculated value	absolute error, %	relative error, %	measured value	calculated value	absolute error, °C	relative error, %
condition I	0.05	0.0497	0.0003	0.60	662.2	666.5	4.30	0.65
condition II	0.06	0.0619	0.0019	3.17	684.0	681.1	2.90	0.45
condition III	0.10	0.1180	0.0180	18.00	682.7	669.1	13.60	1.99

**Table 5. Comparison of Calculated and Experiment Values of Flue Gas Composition**

	CO <sub>2</sub> in flue gas, v %				O <sub>2</sub> in flue gas, v %			
	measured value	calculated value	absolute error %	relative error %	measured value	calculated value	absolute error, %	relative error, %
condition I	10.17	9.97	0.20	2.00	8.46	8.25	0.21	2.50
condition II	13.31	13.00	0.31	2.33	4.89	4.76	0.13	2.66
condition III	12.69	11.97	0.72	5.67	5.69	5.95	0.26	4.57

**Figure 3.** Axial trend of important variables within the regenerator: (a) the carbon and hydrogen content of the coke, (b) the pressure, (c) the temperature, and (d) the gas composition.



**Figure 4.** Effect of temperature of recycling catalyst through external catalyst cooler: (a) the variation of carbon content and inlet mixing temperature and (b) the variation of CO<sub>2</sub> and O<sub>2</sub> in the flue gas with the temperature.

Because the combustion reaction rate of carbon is related to the carbon content, the carbon in the coke of the spent catalyst burns at a fast rate and the carbon on the recycling regenerated catalyst burns at a slow rate. Most of the carbon combustion reaction takes place in the coke burning drum, the carbon in the coke of the spent catalyst decreases quickly from the bottom inlet of the coke burning drum, the carbon of the recycling regenerated catalyst decrease slowly, the temperature rises quickly, the oxygen concentration decreases quickly, and carbon dioxide concentration increases quickly. Almost all the hydrogen in the coke is burned off in the coke burning drum, so the concentration of water vapor increases rapidly then remains constant. Because the simulation of dense phase zone of the second dense bed adopts the CSTR model, the semiregenerated catalyst from the outlet of the coke burning drum continues the carbon combustion in the dense phase zone of the second dense bed, which makes the coke fraction of catalyst and the oxygen concentration decrease to a uniform value further as well as the temperature and the carbon dioxide concentration increase to a uniform value further.

Above the inlet of the coke burning drum, the voidage increases rapidly, so the bed density decreases rapidly and the pressure also decreases rapidly with the increase of the height of the coke burning drum. With the increase of the height of the second dense bed, the pressure decreases further.

**4.4. Effect of Operating Conditions.** The factors that influence the carbon content of the regenerated catalyst and flue gas composition after coke combustion are mainly temperature, pressure, air flow rate, inventory, and coke content of the spent catalyst. Among them, temperature, pressure, and air flow rate are the operating conditions of the coke regeneration process, while the coke content on the spent catalyst is determined by the SMTO reaction conditions. This paper predicts the change of carbon fraction of catalyst and flue gas composition by changing one of the influencing factors while all other factors were kept constant.

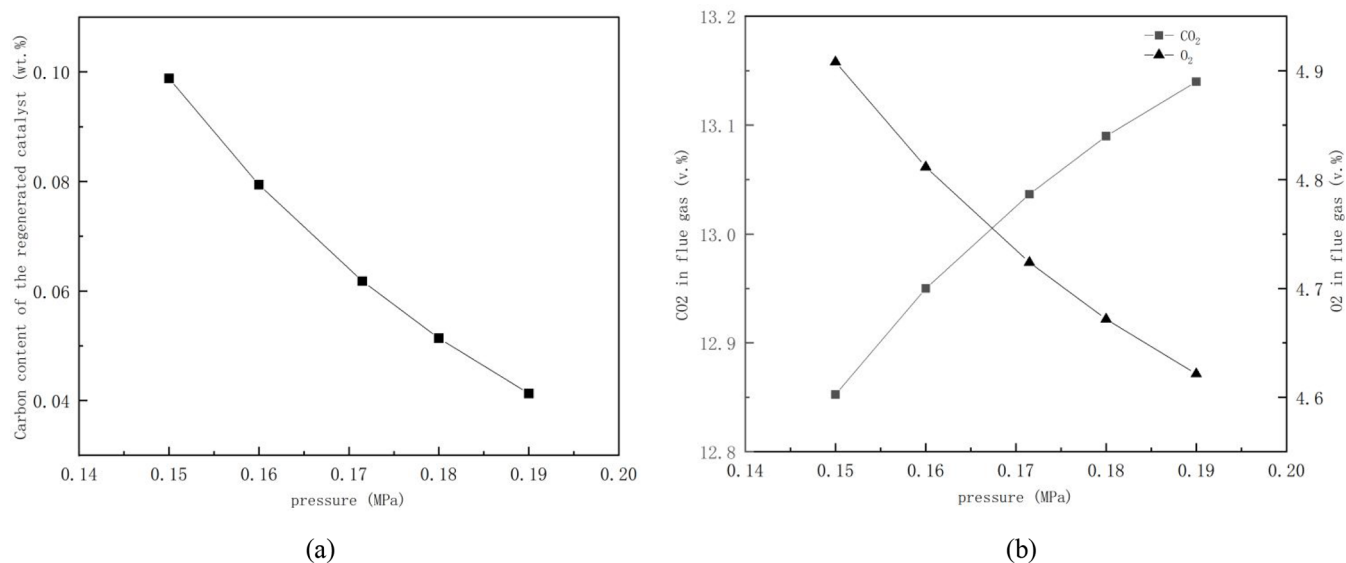
Since the carbon content of the regenerated catalyst is unknown, which is equal to the carbon content of the recycling catalyst streams to the regenerator, it is necessary to give an initial value to perform iterative calculations until the carbon content of the regenerated catalyst is decided.

The operating conditions adopted for prediction are the following: the coke content of the spent catalyst is 2.86 wt %; the flow rate of spent catalyst is 143.2 t/h, and the temperature is 474.6 °C; the flow rate of recycling catalyst through external catalyst cooler is 211.3 t/h, and the temperature is 489.8 °C; the flow rate of recycling regenerated catalyst is 298.1 t/h, and the temperature is 683.6 °C; the regenerator inlet air flow rate is 52149.7 N m<sup>3</sup>/h and the temperature is 133.9 °C; the regenerator inlet hot nitrogen flow rate is 43.4 N m<sup>3</sup>/h, and the temperature is 38.3 °C; and the inlet pressure of coke burning drum is 171500 Pa.

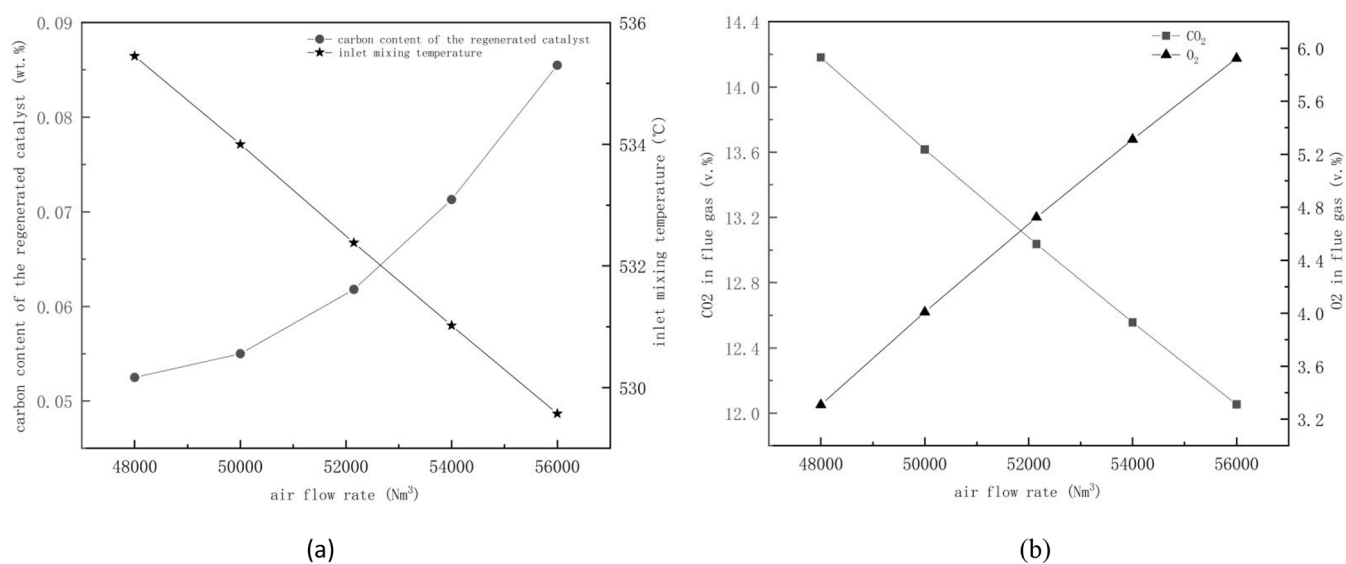
**4.4.1. Effect of Temperature.** By changing only the temperature of the recycling catalyst through external catalyst cooler (470–510 °C) and keeping other conditions constant, the predicted results of carbon content of the regenerated catalyst and flue gas composition were determined and are shown in Figure 4.

As the temperature of recycling catalyst through external catalyst cooler increases, the carbon content of the regenerated catalyst gradually decreases, the content of CO<sub>2</sub> in the flue gas increases, and the content of O<sub>2</sub> decreases. The inlet mixing temperature is 526.6 °C and the carbon content of the regenerated catalyst is 0.093 wt % at a recycling catalyst through the external catalyst cooler temperature of 470 °C, and the inlet temperature is 538.4 °C and the carbon content of the regenerated catalyst is 0.039 wt % at a recycling catalyst through the external catalyst cooler temperature of 510 °C. From the kinetic point of view, when the other conditions remain unchanged, as the temperature of the recycling catalyst through the external catalyst cooler increases, the inlet temperature increases, the regeneration temperature increases, and the reaction rate of carbon combustion becomes larger. So the carbon burned off in the carbon combustion process increases, the O<sub>2</sub> consumed increases, the carbon content on the regenerated catalyst decreases, and the CO<sub>2</sub> generated increases. The increase in the temperature of the recycling catalyst through the external catalyst cooler is beneficial to burning off the coke on the catalyst.

**4.4.2. Effect of Pressure.** By changing only the inlet pressure of the coke burning drum (0.15–0.19 MPa) and keeping other conditions constant, the predicted results of carbon content on



**Figure 5.** Effect of pressure: (a) the variation of carbon content and (b) the variation of CO<sub>2</sub> and O<sub>2</sub> in the flue gas.



**Figure 6.** Effect of air flow rate: (a) the variation of carbon content and inlet mixing temperature and (b) the variation of CO<sub>2</sub> and O<sub>2</sub> in the flue gas.

the regenerated catalyst and flue gas composition were determined and are shown in Figure 5.

As the pressure increases, the carbon content of the regenerated catalyst gradually decreases, the content of CO<sub>2</sub> in the flue gas increases, and the content of O<sub>2</sub> decreases. When the pressure is 0.15 MPa, the carbon content of the regenerated catalyst is 0.099 wt %, and when the pressure increases to 0.19 MPa, the carbon content of the regenerated catalyst decreases to 0.041 wt %. As the operating pressure increases, the partial pressure of oxygen also increases accordingly, which accelerates the reaction rate of carbon combustion and reduces the carbon content on the regenerated catalyst. Increasing the pressure is beneficial to burning off the coke on the catalyst.

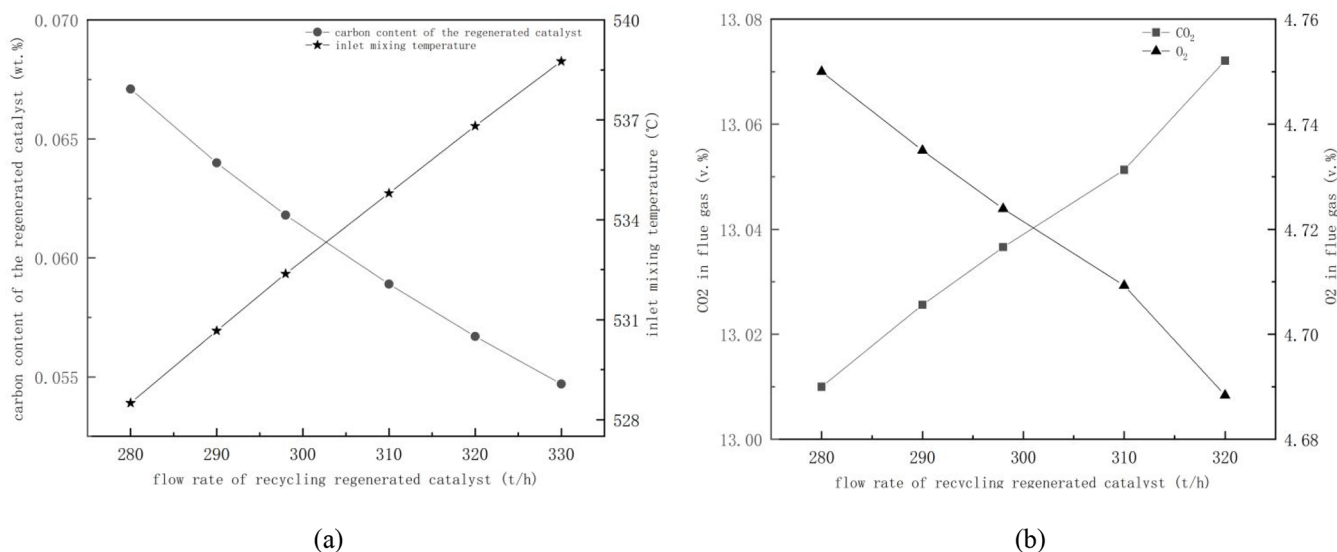
**4.4.3. Effect of Air Flow Rate.** By changing only the inlet air flow rate of the coke burning drum ( $4.8 \times 10^4$  to  $5.6 \times 10^4$  N m<sup>3</sup>/h) and keeping other conditions constant, the predicted

results of carbon content of the regenerated catalyst and flue gas composition were determined and are shown in Figure 6.

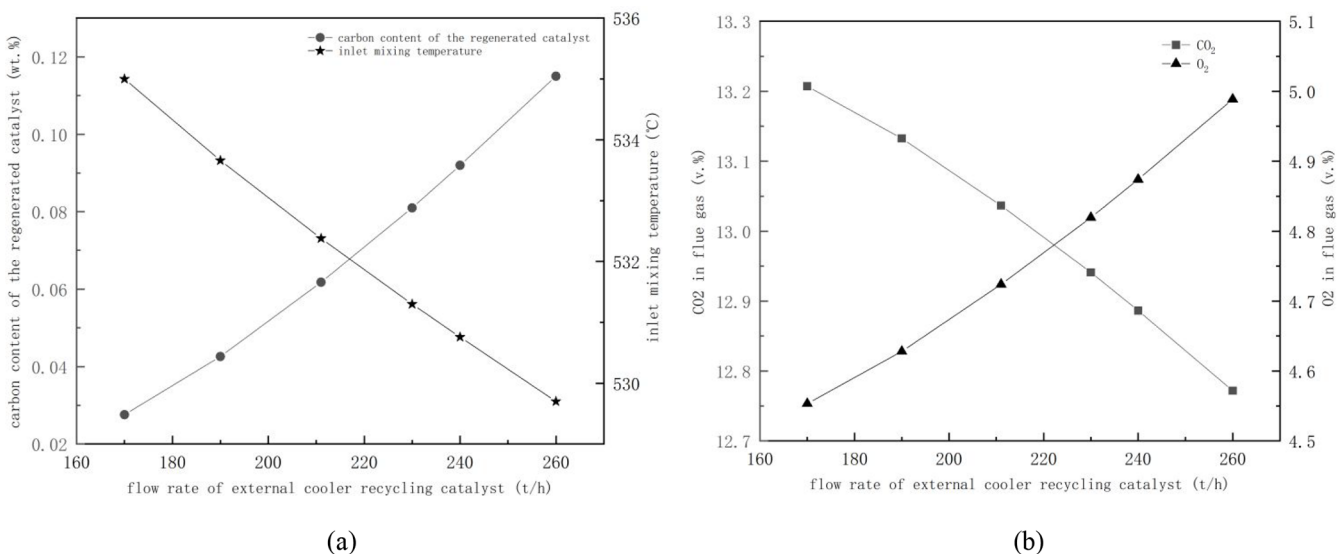
As the air flow rate becomes larger, the carbon content of the regenerated catalyst increases continuously, the content of CO<sub>2</sub> in the flue gas decreases, and the content of O<sub>2</sub> increases. When the air flow rate is  $4.8 \times 10^4$  N m<sup>3</sup>/h, the carbon content of the regenerated catalyst is 0.053 wt %, and when the air flow rate increases to  $5.6 \times 10^4$  N m<sup>3</sup>/h, the carbon content of the regenerated catalyst increases to 0.086 wt %. With the increase of air flow rate, the inlet mixing temperature decreases, and the reaction rate becomes smaller; on the other hand, the voidage increases, the solids concentration decreases, residence time is reduced, the amount of carbon combustion becomes less, and the carbon content on the regenerated catalyst becomes larger. Increasing the air flow rate is not conducive to the combustion of coke.

**4.4.4. Effect of the Flow Rate of Recycling Regenerated Catalyst.** By changing only the flow rate of recycling





**Figure 7.** Effect of the flow rate of recycling regenerated catalyst: (a) the variation of carbon content and inlet mixing temperature and (b) the variation of CO<sub>2</sub> and O<sub>2</sub> in the flue gas.



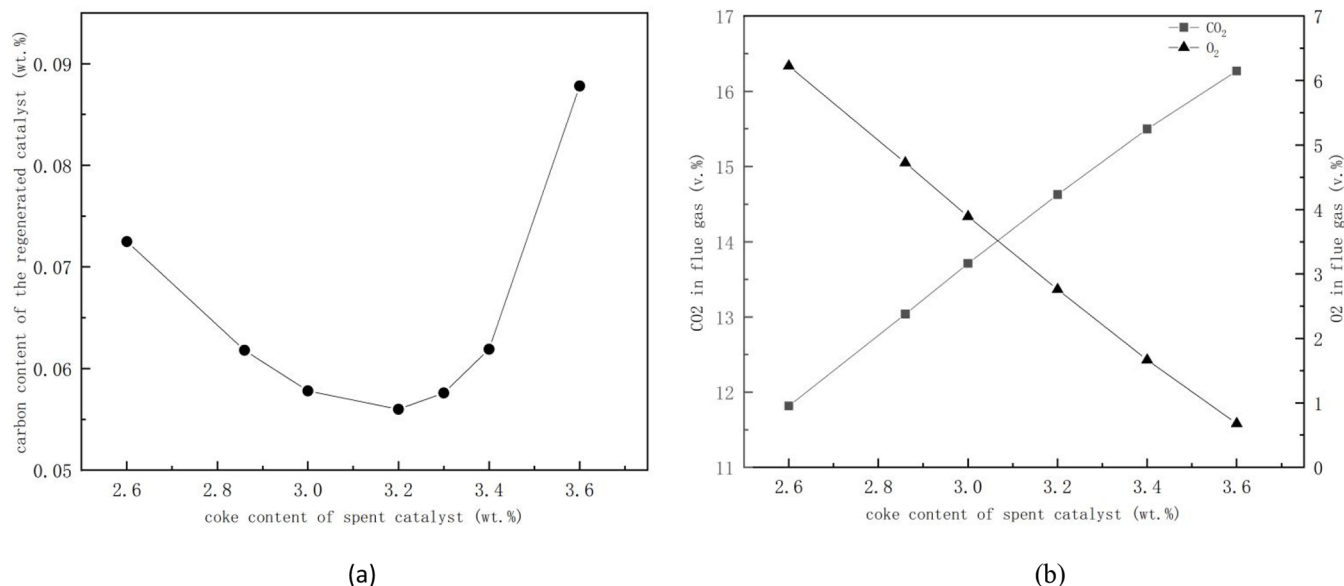
**Figure 8.** Effect of the flow rate recycling catalyst through external catalyst cooler: (a) the variation of carbon content and inlet mixing temperature and (b) the variation of CO<sub>2</sub> and O<sub>2</sub> in the flue gas.

regenerated catalyst (280–330 t/h) and keeping other conditions constant, the predicted results of carbon content of the regenerated catalyst and flue gas composition were determined and are shown in Figure 7.

As the recycling regenerated catalyst flow rate increases, the carbon content of the regenerated catalyst gradually decreases, the content of CO<sub>2</sub> in the flue gas increases, and the content of O<sub>2</sub> decreases. The carbon content of the regenerated catalyst is 0.067 wt % when the recycling regenerated catalyst flow rate is 280t/h, and the carbon content of the regenerated catalyst is 0.055 wt % when the recycle flow rate increases to 330 t/h. When the flow rate of recycling regenerated catalyst increases, the inlet mixing temperature of the coke burning drum becomes higher, so the carbon combustion reaction rate increases, and the carbon content of the regenerated catalyst decreases. Increasing the flow rate of recycling regenerated catalyst is beneficial to burning off the carbon on the catalyst.

**4.4.5. Effect of the Flow Rate of Recycling Catalyst through External Catalyst Cooler.** By changing only the flow rate of recycling catalyst through external catalyst cooler (170–260 t/h) and keeping other conditions constant, the predicted results of carbon content of the regenerated catalyst and flue gas composition are shown in Figure 8.

As the recycling catalyst through external catalyst cooler flow rate increases, the carbon content of the regenerated catalyst decreases, the content of CO<sub>2</sub> in the flue gas decreases, and the content of O<sub>2</sub> increases. The carbon content of the regenerated catalyst is 0.028 wt % when the recycling catalyst through external catalyst cooler flow rate is 170 t/h, and the carbon content of the regenerated catalyst is 0.115 wt % when the flow rate is increased to 260 t/h. When the flow rate of recycling catalyst through the external catalyst cooler increases, the inlet mixing temperature becomes lower, the carbon combustion reaction rate decreases, and the carbon content of the regenerated catalyst increases. Increasing the flow rate of



**Figure 9.** Effect of the coke content of spent catalyst: (a) the variation of carbon content and (b) the variation of CO<sub>2</sub> and O<sub>2</sub> in the flue gas.

recycling catalyst through the external catalyst cooler is not conducive to the combustion of carbon.

**4.4.6. Effect of the Coke Content of Spent Catalyst.** By changing only the coke content of spent catalyst (2.60–3.60 wt %) and keeping other conditions constant, the predicted results of carbon content of the regenerated catalyst and flue gas composition were determined and are shown in Figure 9.

The residual coke content of the regenerated catalyst is influenced by the coke content of the spent catalyst which is in the range of 2.60 wt % to 3.60 wt %. When the coke content on the spent catalyst increases to 3.2 wt %, the reaction rate becomes larger and the residue coke content on the regenerated catalyst decreases. When the coke content of the spent catalyst is higher than 3.2 wt %, the residue coke content of the regenerated catalyst increases as the coke content of spent catalyst increases. As the coke content of spent catalyst increases, the carbon burned off in the carbon combustion process increases, the more CO<sub>2</sub> is generated, and the more O<sub>2</sub> is consumed. The content of CO<sub>2</sub> in the flue gas increases, and the content of O<sub>2</sub> decreases.

As the discussion above, the established mathematical model can be used to predict the effect of different operating conditions. According to the actual production requirements, we can find suitable operating conditions for the industrial SMTO regenerator.

## 5. CONCLUSIONS

Based on the data from an industrial SMTO unit, a fluidized bed mathematical model for its regenerator was established, including the coke burning drum model and the second dense bed model.

- (1) The kinetic parameters of the coke combustion reaction were determined from industrial data.
- (2) The calculated values of the model fit well with the actual values.
- (3) For the developed regenerator model, the effects of operating conditions on the catalyst regeneration are discussed. The model can provide quantitative reference for optimizing the operation of SMTO industrial regenerator.

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### Notes

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## NOTATION

$A$  = cross-sectional area of the coke burning drum, m<sup>2</sup>

$A_1$  = cross-sectional area of the second dense bed, m<sup>2</sup>

$Ar$  = Archimedes number

$C_{p,cat}$  = specific heat capacity of the catalyst, kJ/(kg·K)

$C_{p,i}$  = specific heat capacity of the gas, kJ/(kmol·K)

$d_p$  = catalyst particle size, μm

$E_C$  = activation energies of the coke burning reaction, J/mol

$E_H$  = activation energies of the hydrogen burning reaction, J/mol

$F_{CO_2}$  = molar flow rate of carbon dioxide, kmol/h

$F_{H_2O}$  = molar flow rate of water vapor, kmol/h

$F_{i,cal}$  = calculated values of important variables

$F_{i,epx}$  = actual values of important variables

$F_{N_2}$  = molar flow rate of nitrogen, kmol/h

$F_{O_2}$  = molar flow rate of oxygen, kmol/h  
 $Fr$  = Fred number.  
 $f_s$  = total catalyst flow rate, kg/h  
 $f_{s1}$  = flow rate of the spent catalyst, kg/h  
 $f_{s2}$  = flow rate of recycling regenerated catalyst directly from the second dense bed, kg/h  
 $f_{s3}$  = flow rate of recycling catalyst through external catalyst cooler, kg/h  
 $g$  = gravitational constant, 9.8 kg/N  
 $G_S$  = catalyst mass flow rate per unit cross-sectional area, kg/(m<sup>2</sup> · s)  
 $h1$  = bed height of the second dense bed, m  
 $k_C$  = reaction rate constants for carbon combustion, 1/(Pa · h)  
 $k_{C,0}$  = pre-exponential factor for carbon combustion, 1/(Pa · h)  
 $k_H$  = reaction rate constants for hydrogen combustion, 1/(Pa · h)  
 $k_{H,0}$  = pre-exponential factor for hydrogen combustion, 1/(Pa · h)  
 $n$  = number of sets of industrial data used to estimate the kinetic parameters  
 $P$  = is the pressure, Pa  
 $P_{O_2}$  = partial pressure of oxygen, Pa  
 $R$  = gas constant, 8.314 J/(mol K)  
 $T$  = reaction temperature, K  
 $u_g$  = superficial gas velocity, m/s  
 $u_s$  = superficial solid velocity, m/s  
 $u_t$  = terminal velocity of the particles, m/s  
 $w_C$  = mass fraction of carbon on the catalyst, kgC/kgcat  
 $w_{C0}$  = average mass fraction of carbon in the catalyst at the outlet of the coke burning drum, kgC/kgcat  
 $w_{C1}$  = mass fraction of carbon on the spent catalyst, kgC/kgcat  
 $w_{C2}$  = mass fraction of carbon on the recycling regenerated catalyst, kgC/kgcat  
 $w_H$  = is the mass fraction of hydrogen on the catalyst, kgH/kgcat  
 $Z$  = height of the bed, starting from the top of the fast fluidized bed, m  
 $Z_0$  = characteristic height, m  
 $Z_i$  = height of the inflection point between the dilute and dense two phases, m  
 $\gamma$  = decay constant  
 $\epsilon$  = voidage at  $Z$  in the fast fluidized bed  
 $\epsilon_1$  = voidage of the second dense bed  
 $\epsilon_d$  = voidage at the bottom of the fast fluidized bed  
 $\epsilon_e$  = voidage at the top of the fast fluidized bed  
 $\rho_g$  = gas density, respectively, kg/m<sup>3</sup>  
 $\rho_s$  = solid density, kg/m<sup>3</sup>  
 $\Delta H_{CO_2}$  = enthalpy of formation of carbon dioxide vapor, J/mol  
 $\Delta H_{H_2O}$  = enthalpy of formation of water vapor, J/mol

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