Modeling and optimization of a fast fluidized bed reactor for carbonation reactions

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Abstract—A carbonator is described as a fast fluidized bed reactor to capture CO2. The proposed mathematical model is validated by literatures and experimental data. In our approach, the bed temperature and inventory weight are used to optimize the reactor design and the water gas shift (WGS) reaction with calcium oxide improves the hydrogen production under the modified WGS kinetics. It is validated that the carbonation can break the chemical equilibrium of WGS and make the reaction go forward to reduce CO and generate a quantity of hydrogen gas.

I. INTRODUCTION

CO2 capture has been developed for many years. There are several ways to capture CO2 from combustion plant exhaust gas, like Calcium Looping or Pressure Swing Adsorption (PSA) etc. According to Susarla and MacKenzie’s economic estimation, Calcium Looping has 23.697 $/ tons CO2 of its operating cost, which is lower than PSA, 29 $/tons CO2.[1, 2] For economic efficiency, calcium looping is chosen to be a CO2 capture simulation process in this study. The process of Calcium looping is shown as Figure 1, the coal gasification plant sent the syngas with a part of CO and CO2. In order to increase the purity of syngas and separate CO2, Calcium looping uses CaO particles as sorbents to capture CO2 and become CaCO3 in carbonator at temperature 600~700°C. Next step, CaCO3 particles are sent to calciner to release CO2 and regenerate CaO sorbent at 900°C, and then go back to carbonator capture CO2 again. The calciner can also improve Water Gas shift reaction (WGS) to convert CO into CO2 which can also be captured by CaO.[3] In the other hand, the syngas can be CO and CO2 free discharged from the carbonator outlet. In contrast, the outlet gas from calciner contains high concentration CO2 which can be stored in high pressure tank underground. According to Abanades’ design, both carbonators and calciner are built as fluidized bed reactors; calciner is built 10 cm in diameter, 6.5m in height, and calciner is built 10 cm in diameter and 6m in height.[4] From the result of Abanades work, the calciner can regenerate nearly 100% CaO. However, the carbonator can only operate stably until 30 minutes, because CaO particles are unstable in their size which will affect fluidized bed flow and can also increases complexity of simulation[4], so there are several assumptions to simplify the reactor to simulate the initial stable period:

1. The carbonator is operated isothermally.
2. The calciner can fully regenerate CaO particles and sent back to carbonator.
3. Steady state operation and there is no sorbent deactivated.
4. The CaO particles maintain 100μm in size.

II. REACTION KINETIC

A. Carbonation

Carbonation reaction can be categorized into two types: fast type and slow type, respectively. The fast type will take place on CaO surface, and then CaCO3 will form a layer which covers CaO particles. Then, the slow type occurs after CaCO3 layer has developed. In the slow type reaction, CO2 will diffuse through the layer then react with CaO at the inner layer of particles.[5] In the fast fluidized bed, for the short retention time, the fast type reaction dominates the carbonation rate. Sun et al. announced that the fast type carbonation reaction rate can be expressed as power law below[6]:

\[
\frac{dX}{dt(1-X)} = M_{CaO} k_s (P_{CO2} - P_{CO2,eq})^n S
\]

where X, the CaO conversion, is the molar fraction of CaO that reacts to CaCO3, t is retention time in 1/sec, M_{CaO} is CaO molar weight (56 g/mol), S is specific area and suggested as initial specific area 29 m2/g for limestone. The reaction constant, k_s, and the reaction order, n, will be changed by \(P_{CO2} - P_{CO2,eq}\). For \(P_{CO2} - P_{CO2,eq}\) ≤10kPa, n = 1, which indicates carbonate is a first order reaction.

\[
k_s = 1.67 \times 10^{-4} \exp\left(\frac{AE}{RT}\right) \text{ mol/m}^2\text{s kPa. (2)}
\]

For \(P_{CO2} - P_{CO2,eq}\) ≥10kPa, carbonate becomes zero order, n = 0, and

\[
k_s = 1.67 \times 10^{-3} \exp\left(\frac{AE}{RT}\right) \text{ mol/m}^2\text{s kPa. (3)}
\]

The difference between CO2 partial pressure and CO2 equilibrium partial pressure, \(P_{CO2} - P_{CO2,eq}\), provides a driving force for carbonation. According to Barker, CO2 equilibrium partial pressure can determined as follows[7]:

\[
P_{CO2,eq} = \frac{P_{CO2} \cdot P_{CO2,eq}}{P_{CO2} + P_{CO2,eq}}
\]
$$p_{CO_2,eq} = 1.01325 \cdot 10^{\left(7.079 - \frac{38000}{4.574 \cdot T}\right)}.$$  \hspace{1cm} (4)

With different temperature circumstances, $p_{CO_2,eq}$ can determine whether carbonation or calcination occurs. In Equation (4), $p_{CO_2,eq}$ increases as temperature goes up and the driving force will inverse from carbonation to calcination when $p_{CO_2,eq}$ exceeds $p_{CO_2}$, as a result, calcination will occur.

Figure 2 shows the carbonation and calcination reaction condition. Because the governing equations of fast fluidized bed reactor can be calculated only by gas concentration, $dX/dt$ should be modified as CO$_2$ concentration from Equation (1). The carbonation reaction rate equation will become

$$\frac{dC_{CO_2}}{dt} = M_{CaO} \cdot k_5 \cdot R \cdot T \cdot \rho_{bed} (C_{CO_2} - C_{CO_2,eq})^n \cdot S \cdot (1 - X) \hspace{1cm} (5)$$

Where R is the gas constant as (8.314 L kPa/mol K), T is absolute temperature in K, $C_{CO_2}$ and $C_{CO_2,eq}$ are concentration in mol/L, and $\rho_{bed}$ is the bed molar density in (mol/L).

B. Water gas shift reaction

Water Gas Reaction (WGS) is always used in coal gasification factory to produce H$_2$ and CO$_2$ by consuming CO and steam:

$$CO + H_2O \leftrightarrow H_2 + CO_2.$$ \hspace{1cm} (6)

By using CaO as CO$_2$ sorbent can reduce the CO$_2$ concentration in exhaust gas, which can break the chemical equilibrium and make WGS reaction go forward to produce more H$_2$. In addition, CaO can also enhance WGS reaction rate, however, research for kinetics between CaO and WGS is still unclear. As a result, this study has modified the kinetics from previous study and validate by experiment data from Muller’s work.[3] The WGS reaction kinetics model has been built by Xu and Froment as follows[8]:

$$R = \frac{1}{(DEN)^2} \frac{k_{WGS}}{c_{H_2}} \left( C_{CO}C_{H_2}O - C_{H_2}C_{CO_2} \right),$$ \hspace{1cm} (7)

where

$$DEN = 1 + R \cdot T \left( K_{CO}C_{CO} + K_{CH_4}C_{CH_4} + K_{H_2}C_{H_2} + K_{CO_2}C_{CO_2} \right) \cdot \frac{K_{H_2}C_{H_2}O}{c_{H_2}}.$$ \hspace{1cm} (8)

In Xu and Froment’s work, the rate constant $k_{WGS}$ is determined by the catalyst which contains 15.2% nickel, supported on magnesium spinel, and defined as:

$$k_{WGS} = 7.588 \exp \left[ -\frac{67130}{R} \left( \frac{1}{T} - \frac{1}{648} \right) \right].$$ \hspace{1cm} (9)

In this study, $k_{WGS}$ has been modified by building a Packed Bed Reactor(PBR) model and fitting the data from Muller’s experiment.[3] Using different catalyst can only affects the reaction rate instead of equilibrium constant, reaction heat or activity energy, $k_{WGS}$ can be modified as

$$k_{WGS} = 1.2841 \exp \left[ -\frac{67130}{R} \left( \frac{1}{T} - \frac{1}{648} \right) \right] \cdot (1 - X + 0.8 \cdot X).$$ \hspace{1cm} (10)

The pre-exponential factor 1.2841 is 5.9 times smaller than the original value 7.588, which indicates WGS reaction is much slower by using CaO as catalyst. $(1 - X + 0.8 \cdot X)$ shows CaCO$_3$ increasing can slow down WGS reaction and the reaction rate enhanced by CaCO$_3$ is 80% by CaO. The concentration change of each component in PBR is showed

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{Figure2.png}
\caption{The equilibrium of carbonation dependent on CO$_2$ partial pressure and temperature [4]}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{Figure3.png}
\caption{WGS reaction profile of components in PBR with time and catalyst weight.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{Figure4.png}
\caption{Mole fraction of WGS reaction components from PBR outlet and the comparison between simulation and Xu and Froment's experiment [3]}
\end{figure}
by Figure 3; the WGS reaction is not significant until the middle of PBR and is retard when CaCO₃ increasing. Figure 4 shows the comparison between PBR simulation results and experiment data.

III. FLUIDIZED BED DESIGN

A. Physical property

The Solid volume fraction can affect carbonation efficiency effectively. In fast fluidized bed, the bed will be divided into high lean region and low dense region. Werther and Wein suggest there is a constant and higher volume fraction in low dense region. Here solid volume fraction is defined as[9]:

\[ f_d = (1 - \varepsilon_b)(1 - \varepsilon_f)(1 - 0.4R_e^{-0.4} \cdot Ar^{-0.13}) \]  \hspace{1cm} (11)

where \( \varepsilon_b \) is bubble volume fraction and \( \varepsilon_f \) is minimum fluidization porosity. The dimensionless \( R_e \) and \( Ar \) are particle Reynold number and Archimedes number given by:

\[ R_e = \frac{u - u_{mf}}{\nu_f} \]  \hspace{1cm} (12)

\[ Ar = \frac{g \cdot d_p^3 \cdot \rho_s - \rho_g}{\rho_g} \]  \hspace{1cm} (13)

where \( u \) is superficial velocity in cm/s, \( u_{mf} \) denotes minimum fluidization velocity in cm/s, \( g \) is acceleration of gravity (980 cm/s²), \( d_p \) denotes average solid diameter in cm, \( \nu_f \) is kinematic viscosity in cm²/s, \( \rho_s \) and \( \rho_g \) are solid density and gas density in g/cm³. Kunii and Levenspiel show the solid volume fraction has an exponential decay through the lean high region, which is defined as follows[10]:

\[ f_t = f_e + (f_d - f_e) - \alpha h \]  \hspace{1cm} (14)

Here \( h \) indicates the bed height and decay constant \( \alpha \) is defined as 0.02/cm. \( f_e \) is solid volume fraction at infinite height:

\[ f_e = \frac{k_{elu}}{\rho_s u} \]  \hspace{1cm} (15)

Where \( k_{elu} \) is elutriation rate constant in g/s · cm³. The elutriation rate constant measures the mass flow rate of particles which flow out from a cross section area. The constant \( k_{elu} \) is suggested by Colakyan and Levenspiel:

\[ k_{elu} = 1.1 \cdot \rho_s \cdot (1 - \frac{\nu_f}{u})^2 \]  \hspace{1cm} (16)

Where \( \nu_f \) is terminal velocity in cm/s. The height of low dense region and high lean region are determined by sorbent weight in each region. Werther and Wein have defined the sorbent weight in low dense region, \( W_d \), and weight in high lean region, \( W_t \), as follows[9]:

\[ W_d = \int_0^{H_d} A \cdot \rho_s \cdot f_d \, dh, \]  \hspace{1cm} (17)

\[ W_t = \int_{H_d}^{H} A \cdot \rho_s \cdot f_t \, dh, \]  \hspace{1cm} (18)

where \( A \) is the bed cross-section area and \( H_b \) is total bed height. A given total inventory weight, \( W_{T,I} \), is the sum of \( W_d \) and \( W_t \). And bed height in low dense region, \( H_d \), can be solved by eq(17), eq(18) and the mass balance equation:

\[ W_{T,I} = W_d + W_t. \]  \hspace{1cm} (19)

The bed height in high lean region, \( H_t \), is defined as follows after \( H_d \) has been solved:

\[ H_t = H_e - H_d. \]  \hspace{1cm} (20)

B. Reaction in fast fluidized bed

Fast fluidized bed can separates the bed into lower dense region and high lean region; as a result, Kunii and Levenspiel suggest different governing equations corresponding to these two reaction regions. [10]

In low dense region, the 1st order reaction can be simplified the following equation:

\[ \frac{dC_{ad}}{dh} = (f_{core} \cdot k + \frac{1}{R_{cw}} \cdot \frac{f_{wall}}{0.1}) \cdot C_{ad}, \]  \hspace{1cm} (21)

Where \( C_{ad} \) is concentration of each component in low dense region in mol/L and \( k \) is reaction rate constant in 1/s. \( f_{core} \) indicates solid volume fraction at bed center which approximately equal \( f_e \) and \( K_{cw} \) which is gas exchange coefficient between wall and gas and is defined as 15/s. Eq(21) is suitable for 1st order Carbonation when \( (P_{CO_2} - P_{CO_2,eq}) \leq 10kPa \). However, WGS reaction is not a 1st order reaction from Eq(28), so the reaction should be solve numerically by the following balance equations of fluidized bed:

\[ \frac{dC_B}{dt} = -(f_B \cdot R_B) - K_{BC}(C_B - C_C) \]  \hspace{1cm} (25)

\[ K_{BC}(C_B - C_C) = f_C \cdot R_C + K_{CE}(C_C - C_E) \]  \hspace{1cm} (26)

\[ K_{CE}(C_C - C_E) = f_E \cdot R_E \]  \hspace{1cm} (27)

where

\[ R_j = \frac{1}{(\delta E_k)^2} \cdot \frac{k_{was}}{c_{H_2}} (C_{CO}C_j - C_{H_2}C_{CO_2}), \]  \hspace{1cm} (28)

\( R_B \), \( R_C \) and \( R_E \) are WGS reaction kinetics in bubble, cloud and emulsion phase respectively. Similarly, \( C_B \), \( C_C \) and \( C_E \) are gas concentration in those three phases. \( K_{BC} \) is mass transfer coefficient between bubble and cloud phase and
\( K_{CE} \) is mass transfer coefficient from cloud to emulsion phase. \( f_B, f_C, \) and \( f_E \) are the solid volume fraction dispersed in bubble, cloud and emulsion phase. In fast fluidized bed, the bubble phase expand so large that the cloud phase is no more exist, in addition, the mass transfer rate between cloud phase and emulsion is nearly infinite. Therefore, \( f_B = f_{core} \cdot f_C + f_E = f_{wall} \) and \( K_{CE} \approx \infty \).

In high lean region

\[
\frac{dC_{Al}}{dh} = \eta_l \cdot f_i \cdot k \cdot C_{Al}.
\]  

(22)

Where \( C_{Al} \) is component concentration in high lean region in mol/L and the term \( \eta_l \) is fluidized bed efficiency factor in high lean region and is determined:

\[
\eta_l = 1 - (1 - \eta_d)^{bh}
\]  

(23)

Where \( b \) is decay constant for fluidized bed efficiency and defined as 0.0662/cm. Similarly, \( \eta_d \) is fluidized efficiency factor in low dense region which is determined as follows:

\[
\eta_d = \frac{f_{core} + \frac{1}{k_{CE} f_{wall}}}{f_{core} + f_{wall}}.
\]  

(24)

The higher fluidized bed efficiency can make fluidized bed reactor more similar to plug flow reactor. The \( \eta_d \) remains in constant because of a constant \( f_{core} \) and \( f_{wall} \). In high lean region, solid disperses more uniform, so \( \eta_l \) will increase as height rising.

IV. RESULT

A. Comparison with experiment data

In Rodriguez’s work, the carbonator diameter is 10 cm and 650 cm in height and has been operated at 568°C to 722°C with inlet gas containing 20 vol % of CO\(_2\) and inventory weight 33 to 357 kg/m\(^3\). With superficial gas velocity 3 m/s, the CO\(_2\) capture rate is about 4 mol m\(^2\) s\(^{-1}\) and capture efficiency is stable above 70%.[11] Figure 5 shows the comparison with experiment data with different inventory weight. The efficiency tendency from simulation can match the experiment data well from inventory weight 50 to 200 kg/m\(^2\). When inventory is over 200 kg/m\(^2\), the increment of CO\(_2\) capture efficiency is predicted to become slower as sorbent increasing and reach a maximum eventually.

B. Fast fluidized bed

Solid volume fraction can affect carbonation much in fast fluidized bed. From Figure 6, solid volume fraction maintains in low dense region, which also keep a great reaction rate; the other way, in high lean region, solid volume fraction decays exponentially and makes the CO\(_2\) capture rate goes down dramatically, as a result, the decreasing of CO\(_2\) concentration become gently. As shown in Figure 7, most carbonation occurs in low dense region and CO\(_2\) concentration decrease fast, so the height of low dense region, \( H_d \), becomes an important factor for designing fast fluidized bed. One way to increase \( H_d \) is increasing inventory weight; however, the effectiveness will decrease with increasing too much sorbent from Figure 5.
C. Optimization

Inventory weight and temperature can be the two important factors to operate carbonator. Figure 8 and Figure 9 show the effect of temperature and inventory weight on CO$_2$ capture efficiency. The temperature below 550°C and over 650°C can cause carbonation rate declining; the former low temperature makes low reaction rate; the latter leads to higher P$_{CO_2,eq}$ and makes driving force (P$_{CO_2} - P_{CO_2,eq}$) which against carbonation. The CO$_2$ capture efficiency can reach a peak from 550°C to 650°C. From Figure 5, the efficiency can reach an upper limit with increasing inventory weight and the limits can vary with different temperature, this study assumes 95% of upper operation limit as constraints at each temperature and is showed as a red line in Figure 9. Carbonation is so slow at low temperature that reactor needs more inventory weight to reach operation constraints; at high temperature, although the efficiency can reach operation constraint rapidly, high temperature still leads to low efficiency because of insufficient driving force from (P$_{CO_2} - P_{CO_2,eq}$). From Figure 9, there is a greatest CO$_2$ capture efficiency located on temperature 574 °C, inventory weight 459.034 kg/m$^2$ and the CO$_2$ capture efficiency reaches 93%.

D. Prediction of coal gasification process

Because of the effect by using Calcium Looping to produce hydrogen through WGS and capture CO$_2$ in the carbonator, this study has built a fast fluidized bed simulation model combining WGS and carbonation to predict the effectiveness of Calcium looping in coal gasification. The inlet gas of Calcium looping is come from gasification product syngas. The syngas data including gas volume velocity and components is cited from the Wabash River Coal Gasification Repowering Project. [12] The operation condition of Carbonator is showed in Table 2, this study keeps the same superficial velocity 3 m/s as Rodriguez’s work and uses the CO$_2$ capture optimization point from Figure 9. The simulation results in Figure 10 shows the components change in carbonator and Table 2 indicated the outlet CO reduce 64.83% compared with inlet gas and there are 70% carbon atoms in CO and CO$_2$ is capture into limestone and hydrogen produce is almost twice than inlet raw syngas.

![Figure 8. CO$_2$ capture efficiency varies with temperature and inventory weight](image1)

![Figure 9. The contour line of CO$_2$ efficiency with temperature and inventory weight. The operation limit is given in red solid line.](image2)

![Figure 10. The changes of CO$_2$, CO and H$_2$ in carbonator](image3)

TABLE 2. OPERATION CONDITION OF CARBONATOR WITH WGS REACTION AND CARBONATION

| Superficial velocity [m/s] | 3 |
| Reactor diameter [cm] | 28.8 |
| Inventory weight [kg/m$^2$] | 459.034 |
| Temperature [°C] | 574 |
| Pressure [atm] | 1 |

TABLE 1. THE INLET AND OUTLET GAS COMPOSITION CONCENTRATION OF CARBONATOR

<table>
<thead>
<tr>
<th>Component</th>
<th>Inlet [mol/s]</th>
<th>Outlet [mol/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>0.409</td>
<td>0.0615</td>
</tr>
<tr>
<td>CO</td>
<td>1.1727</td>
<td>0.4124</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>1.1902</td>
<td>0.4299</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0.8905</td>
<td>1.6508</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0.0492</td>
<td>0.0492</td>
</tr>
</tbody>
</table>

V. CONCLUSION

CaO can enhance WGS reaction and capturing CO$_2$ to produce clean fuel gas hydrogen and reduce greenhouse gas
at the same time in the carbonator. The carbonator model built by fundamental fluidized bed design is not only helpful to predict a complicate reaction in circulating fluidized bed but to do optimization analysis. These predictions and analysis can be used to scale up the calcium looping unit in industry. In this way, there is a most efficient CO2 capturing condition at 574°C and inventory weight 459.034 kg/m² in Rodriguez’s work. This operation point is used in the simulation model combining WGS reaction and carbonation to predict hydrogen production. The result shows carbonation can break the chemical equilibrium of WGS and make the reaction go forward to reduce CO and generate a quantity of hydrogen gas. Although this model is limited by operating in steady state and isothermally, the calcium looping is still potential to be applied in gasification and gas reforming plants.

REFERENCE