Numerical Simulation of Coal Gasification with CO\textsubscript{2} Capture Based on Two-Dimensional Fluidized Bed Model

M. M. Zhao, D. N. Saulov, M. J. Cleary, and A. Y. Klimenko

Abstract—Numerical model of a fluidized bed gasifier with in-situ CO\textsubscript{2} capture is presented. The model is implemented using the software package MFIX. Simplified chemical reactions are used to describe evaporation and devolatilization processes, while the carbonation reaction is modelled by the grain model. Initial and steady state stages of the gasification process are simulated. The simulation results demonstrate that a substantial increase in hydrogen content in product gas can be achieved by the addition of the CO\textsubscript{2} sorbent material. The simulation results are in agreement with the experimental data reported in the literature.

Index Terms—Coal gasification, CO\textsubscript{2} capture, numerical simulation.

Nomenclature:
- \( R_{ml} \): Formation rate of species
- \( \vec{V} \): Velocity vector
- \( \vec{I} \): Momentum exchange
- \( \vec{S} \): Stress tensor
- \( \varepsilon \): Volume fraction
- \( \rho_m \): Density of phase m
- \( X \): Conversion of solid reactant
- \( Y \): Mass fraction
- \( P \): Partial pressure, atm
- \( T \): Temperature, K
- \( k \): Prefactor for chemical reaction rate
- \( E \): Activation energy, kJ/mol
- \( R \): Gas constant, kJ/mol/K
- \( C \): Solid reactant density, mol/cm\textsuperscript{3}
- \( \Delta H \): Heat of reaction, kJ/mol

Subscript:
- \( g \): Gas phase
- \( s \): Solid phase
- \( m \): Index of phase
- \( l \): Index of \( l \)\textsuperscript{th} species in phase m
- \( \alpha \): Index of reactions

Superscript:
- \( 0 \): Initial value
- \( * \): Equilibrium conditions

I. INTRODUCTION
Coal gasification with in-situ CO\textsubscript{2} capture is a promising clean energy technology for production of high quality hydrogen. The technology provides a potential solution for the increasing demand in environmental friendly fuel. Many studies, see for example, Refs [1]-[3], have been carried out in the recent years in order to obtain better understanding of the gasification process, which involves chemical reactions with complicated mechanisms.

Jose et al. reviewed studies on coal gasification by steam with in-situ CO\textsubscript{2} capture in fluidizing bed at low/medium temperature (600-800\textdegree{}C) [1] and also carried out experimental research of coal gasification by pure steam at 600-800 \textdegree{}C in which synthesis gas with an H\textsubscript{2} content as high as 80\% in molar fraction [2]. Lin et al investigated coal gasification by steam with continuously supplies of Coal/CaO mixtures under total pressure from 0.1to 6.0 MPa at 923 K [3]. The experimental results indicated that H\textsubscript{2} production enhanced with the pressure increase and production gas contained < 3\% CO and CO\textsubscript{2}.

One of the most important issues in the coal gasification process is the removal of CO\textsubscript{2} from the product gas. Various approaches, such as pre- and post-combustion capture as well as in-situ capture were viewed by Wall [4]. Many sorbent materials for post-combustion and in-situ capture have also been studied. It has been demonstrated [1], [5] that calcium based sorbents are the most promising materials during the gasification process with in-situ CO\textsubscript{2} capture.

In this process, CO\textsubscript{2} is captured by the carbonation reaction with the sorbent. After that, reacted sorbent is separated from the syngas and transferred to calcination reactor for regeneration. In the calcination reactor, the sequestration-ready stream of CO\textsubscript{2} is generated.

The following three major reactions can be identified in the gasification process:

Steam gasification:
- \( C + H_2O \rightarrow CO + H_2 \)
- \( \Delta H = 131.3 \text{ kJ/mol} \)

Water gas shift reaction:
- \( CO + H_2O \rightarrow CO_2 + H_2 \)
- \( \Delta H = - 41.2 \text{ kJ/mol} \)

Carbonation reaction:
- \( CaO + CO_2 \rightarrow CaCO_3 \)
- \( \Delta H = - 178.9 \text{ kJ/mol} \)

The regeneration process is characterised by the calcination reaction:
- \( CaCO_3 \rightarrow CaO + CO_2 \)
- \( \Delta H = 178.9 \text{ kJ/mol} \)

Accurate simulation of coal gasification with in-situ CO\textsubscript{2} capture process is desirable for predicting the syngas quality in industrial processes and for assisting in design of new gasifiers. Such simulation involves modelling of a reacting multiphase flow. In this study, the special software called
Multiphase Flow with Inter-phase Exchanges (MFIX) [6] is used for multiphase flow simulation. A comprehensive review of this code, which has been developed in National Energy Technology Laboratory (NETL), is presented in Ref. [7, 8], where several test cases are demonstrated. The feasibility of MFIX to simulate chemically reactive fluidized bed processes, which involve combined effects of highly-loaded, gas-particle hydrodynamics, heat transfer and complicated chemical reactions, has been demonstrated [7]. Syamlal et al. [8] numerically studied fluidised bed coal gasification using MFIX on a high performance computer. The authors presented their computational results in comparison with the experimental data and demonstrated the capabilities of MFIX in designing of a coal gasifier.

In this paper, two-dimensional, an axy-symmetrical fluidized bed model (implemented in MFIX) is used for a preliminary numerical study of a coal gasifier with in situ CO2 capture. The heat release of chemical reaction is not taken into account and the gasifier is treated as an isothermal system.

II. GAS-SOLID HYDRODYNAMICS

The coal gasification reactor contains a reacting mixture of coal and sorbent flowing with the gas. In the continuum modelling simulation approach [5] used in this paper, the coal and sorbent particles are represented as granular phases, which collocates with the gas phase to form an interpenetrating continua multiphase mixture. The multiphase model consists of the mass, momentum, energy, and species-mass balance equations for each phases. These equations are given below.

Conservation of species:
\[
\frac{\partial}{\partial t}(\varepsilon_m \rho_m) + \nabla \cdot (\varepsilon_m \rho_m \vec{V}_m) = \sum_{l=1}^{Nm} R_{ml}
\]

Conservation of mass:
\[
\frac{\partial}{\partial t}(\varepsilon_m \rho_m Y_m) + \nabla \cdot (\varepsilon_m \rho_m Y_m \vec{V}_m) = R_{ml}
\]

Conservation of momentum (gas phase \(m=g\)):
\[
\frac{\partial}{\partial t}(\varepsilon_g \rho_g \vec{V}_g) + \nabla \cdot (\varepsilon_g \rho_g \vec{V}_g \vec{V}_g) = \vec{V} \cdot \vec{S}_g + \varepsilon_g \rho_g \vec{g} - \sum_{m=1}^{M} \vec{I}_{gm}
\]

Conservation of momentum (solids phase \(m=s\)):
\[
\frac{\partial}{\partial t}(\varepsilon_m \rho_m \vec{V}_m) + \nabla \cdot (\varepsilon_m \rho_m \vec{V}_m \vec{V}_m) = \vec{V} \cdot \vec{S}_m + \varepsilon_m \rho_m \vec{g} + \vec{I}_{gm} - \sum_{l=1, l \neq m}^{M} \vec{I}_{lm}
\]

The set of equations above are closed with constitutive relations as described in [9].

III. CHEMICAL REACTION

In this study, we model gasification of the coal used in the experimental work by Hui et. al [10]. The results of proximate and ultimate analyses of this coal are given in Table I. Following [11], coal is considered as a mixture of char, ash and volatile materials (VM), which is assumed to consist of CH4, C2H6, CO, CO2, H2, H2O. Note that small amounts of NH3 (0.49%) and H2S (0.26%) were neglected. The normalised composition of the coal is given in Table II.

Table I: Properties of Shenhu coal.

<table>
<thead>
<tr>
<th>Component</th>
<th>Proximate Analysis (wt%)</th>
<th>Ultimate Analysis (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>74.62</td>
<td>C</td>
</tr>
<tr>
<td>H</td>
<td>4.65</td>
<td>H</td>
</tr>
<tr>
<td>O</td>
<td>12.7</td>
<td>O</td>
</tr>
<tr>
<td>N</td>
<td>1.02</td>
<td>N</td>
</tr>
<tr>
<td>S</td>
<td>0.62</td>
<td>S</td>
</tr>
<tr>
<td>Ash</td>
<td>6.39</td>
<td>Ash</td>
</tr>
</tbody>
</table>

Table II: Component mass fraction of coal pyrolysis (wt%).

<table>
<thead>
<tr>
<th>Component</th>
<th>69.06</th>
<th>7.16</th>
<th>1.21</th>
<th>1.94</th>
<th>0.91</th>
<th>1.05</th>
<th>12.24</th>
<th>6.43</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C2H6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H2O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ash</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Both heterogeneous and homogenous chemical reactions are considered in this study. Following [12], we treat evaporation as an additional chemical reaction. This reaction is considered to be of first order and the reaction rate is expressed in the conventional Arrhenius form. Furthermore, Binner et al. [13] demonstrated that the pyrolysis rates for dry and wet coal are similar; while Wen et al. [14] pointed out that the evaporation rate has the same order of magnitude as that of devolatilisation. In this study, the following one-step global reaction model is used to describe evaporation and devolatilization processes, while the reaction rate is given in the Arrhenius form:

\[
\text{VM} \rightarrow \text{CH}_4 + \text{C}_2\text{H}_6 + \text{CO} + \text{CO}_2 + \text{H}_2\text{O} + \text{CH}_4 + \text{H}_2 (1)
\]

The following three heterogeneous and one homogenous reactions are used to describe the gasification of char. Steam gasification:

\[
\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 (2)
\]

\[
P_{\text{H}_2\text{O}} = \frac{P_{\text{CO}} \times P_{\text{H}_2}}{\exp(17.29 - 16326/T)}
\]

CO2 gasification:

\[
\text{C} + \text{CO}_2 \rightarrow 2\text{CO} (3)
\]

\[
P_{\text{CO}_2} = \frac{P_{\text{CO}} \times P_{\text{CO}}}{\exp(20.92 - 20282/T)}
\]

Methanation:

\[
\text{C} + 2\text{H}_2 \rightarrow \text{CH}_4 (4)
\]

\[
P_{\text{H}_2} = \sqrt{\frac{P_{\text{CH}_4}}{\exp(-13.43 + 10999/T)}}
\]

Water gas shift reaction:

\[
\text{H}_2\text{O} + \text{CO} \rightarrow \text{CO}_2 + \text{H}_2 (5)
\]
To describe the capture of CO\textsubscript{2} by CaO, the grain model [14] is used. Note that product layer diffusion and particle diffusion resistances are not taken into account in the present model. According to the grain model [15], conversion of a solid reactant is proportional to the active grain radius. That is, \((1 - \varepsilon) \propto r^2\). At the same time, the surface area of the active grain is proportional to the squared radius of the grain \((S \propto r^2)\). Thus, the surface area of active CaO grains can be expressed as:

\[
S = S_0 \times (1 - X)^{2/3}
\]

where \(S_0\) denotes the initial specific area of CaO particle. Then, the rate of the carbonation reaction

\[
\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3
\]

is given by

\[
R_6 = k_6 \times \exp\left(-\frac{E_a}{RT_g}\right) \times S \times C_{\text{CaO}}
\]

The values of pre-exponential factors \(k_6\) and activation energies \(E_a\) for the reactions A-E are summarised in Table III.

### TABLE III: Reaction Rate Constants

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(k_6)</th>
<th>(E_a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A\textsuperscript{[14]}</td>
<td>(1.1 \times 10^5)</td>
<td>21200</td>
</tr>
<tr>
<td>B\textsuperscript{[14]}</td>
<td>3000</td>
<td>41200</td>
</tr>
<tr>
<td>C\textsuperscript{[14]}</td>
<td>3000</td>
<td>41200</td>
</tr>
<tr>
<td>D\textsuperscript{[14]}</td>
<td>(1.67 \times 10^{-3})</td>
<td>29</td>
</tr>
</tbody>
</table>

Since devolatilization of coal takes place in a relatively short time (an order of seconds) compared with the residence time of reacting char in the reactor (an order of minutes to hours) [14], char will be accumulated until the system reach equilibrium state, in which the mass consuming rate of coal is equal to feeding mass rate of coal. In this model, a certain amount of char is assumed to be distributed uniformly over the bed. In order to determine the feeding rate of coal, the conversion of char as a function of time is required. The conversion of char and VM vs time under the simulated conditions are shown in Fig. 1 and 2. The conversion of VM reaches the value of 0.9 in 10 seconds, while that of char reaches the value of 0.5 in approximately 3000 seconds. This indicates that the reaction rate of char is significantly lower. The initial and steady states of coal gasification with and without CO\textsubscript{2} capture were simulated under specified operational conditions, which are given in Table IV.

### TABLE IV: SIMULATION PARAMETERS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal density</td>
<td>1.3 g/cm\textsuperscript{3}</td>
</tr>
<tr>
<td>CaO density</td>
<td>2.3 g/cm\textsuperscript{3}</td>
</tr>
<tr>
<td>Feeding Coal mass rate</td>
<td>0.1 g/s</td>
</tr>
<tr>
<td>Reactor radius</td>
<td>8 cm</td>
</tr>
<tr>
<td>Feeding H\textsubscript{2}O/Coal molar ratio</td>
<td>10</td>
</tr>
<tr>
<td>CaO particle diameter</td>
<td>0.3 mm</td>
</tr>
<tr>
<td>Feeding CaO/Coal molar ratio</td>
<td>1.2</td>
</tr>
<tr>
<td>Reactor height</td>
<td>80 cm</td>
</tr>
<tr>
<td>Temperature</td>
<td>900 K</td>
</tr>
<tr>
<td>Static bed height</td>
<td>50 cm</td>
</tr>
<tr>
<td>Gas pressure</td>
<td>10 atm</td>
</tr>
</tbody>
</table>

IV. SIMULATION METHOD AND RESULTS

The assumptions and limitations made in the presented model are listed below.

1) Coal is assumed to consist of Char, Ash and Volatile Matter (kept its profile in gasification).
2) CaO particles are assumed to maintain their fixed internal pore structure during chemical reactions.
3) Evaporation and devolatilization are treated using the one-step chemical reaction.
4) The carbonation reaction is described using the grain model. The other gas-solid reactions are treated as volumetric reaction.
5) The energy equation is not solved in this model. The reactor and the incoming streams gas and solids are assumed to be at the same temperature of 900K.
6) Initial bed (with excess of CaO with 50% conversion) is assumed to be at the fluidization condition.

A cylindrical vessel of 8cm in diameter and 80cm in height is non-uniformly meshed with 3600 cells. The mixture of coal and steam were injected into the reactor from the bottom via pseudo central tube, while a second stream of fluidizing gas, nitrogen and steam mixture, entered the annular region surrounding the tube. The product syngas exits the reactor from the top. The initial bed (50cm in height) is assumed to be at the fluidization condition with the void fraction \(\varepsilon_0 = 0.5\).
In the simulation of initial stage (the first 500s of reaction), the mixture of coal and sorbent was fed into the empty reactor. As shown in Fig.3, the composition of product gas was similar to that of VM, excluding CO₂. During the initial stage, coal devolatilization is the dominating reaction, since only a small amount of char was fed into the reactor. Fig. 3 also shows that the molar fractions of H₂ and CO increase slightly in time, while that of CH₄ and C₂H₆ decrease slowly.

The results of the steady state simulation without CO₂ capture are presented in Fig.4 and 5. Fig. 4 shows the outlet composition of product gas, while Fig.5 depicts the distribution of gas species inside the reactor. Similar results of the steady state simulation with CO₂ capture are given in Fig. 6 and 7, respectively.

Comparison of Fig. 4 and 6 shows that the addition of CO₂ sorbent material results in a substantial improvement in product gas quality. That is, the fractions of H₂ and CH₄ are increased by approximately 25% and 4%, respectively. As demonstrated by Fig. 5 and 7, CO₂ is effectively captured by the sorbent material, since the carbonation reaction is faster than gasification reactions [16]. The obtained product gas composition is in agreement with the experimental data reported in the literature [2].
The model demonstrates that a substantial increase in the carbonation reaction.

V. CONCLUSION

A numerical model of a fluidized bed gasifier is presented. The model demonstrates that a substantial increase in the product gas quality can be achieved by the in-situ CO$_2$ capture using CaO-based materials. The model predictions are in agreement with the experimental data reported in the literature.

Further research will be undertaken to take into account heat balance and to employ a more sophisticated model for the carbonation reaction.

REFERENCES


