Numerical Simulation of Coal Gasification with CO_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_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_2 sorbent material. The simulation results are in agreement with the experimental data reported in the literature.**

***Index Terms*—Coal gasification, CO_2 capture, numerical simulation.**

Nomenclature:

R_{ml}	Formation rate of species
$\vec{V}$	Velocity vector
$\vec{I}$	Momentum exchange
$\bar{\bar{S}}$	Stress tensor
ε	Volume fraction
ρ_m	Density of phase m
X	Conversion of solid reactant
Y	Mass fraction
P	Partial pressure, atm
T	Temperature, K
k	Prefaotor for chemical reaction rate
E	Activation energy, kJ/mol
R	Gas constant, kJ/mol/K
C	Solid reactant density, mol/cm^3
ΔH	Heat of reaction, kJ/mol

Subscript:

g	Gas phase
s	Solid phase
m	Index of phase
l	Index of lth species in phase m
α	Index of reactions

Superscript:

0	Initial value
$*$	Equilibrium conditions

I. INTRODUCTION

Coal gasification with in-situ CO_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_2 capture in fluidizing bed at low/medium temperature (600-800℃) [1] and also carried out experimental research of coal gasification by pure steam at 600-800 ℃ in which synthesis gas with an H_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_2 production enhanced with the pressure increase and production gas contained < 3% CO and CO_2.

One of the most important issues in the coal gasification process is the removal of CO_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_2 capture.

In this process, CO_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_2 is generated.

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

Steam gasification:

$$C + H_2O \rightarrow CO + H_2 \qquad \Delta H = 131.3 \text{ kJ/mol}$$

Water gas shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H = -41.2 \text{ kJ/mol}$$

Carbonation reaction:

$$CaO + CO_2 \rightarrow CaCO_3 \qquad \Delta H = -178.9 \text{ kJ/mol}$$

The regeneration process is characterised by the calcination reaction:

$$CaCO_3 \rightarrow CaO + CO_2 \qquad \Delta H = 178.9 \text{ kJ/mol}$$

Accurate simulation of coal gasification with in-situ CO_2 capture process is desirable for predicting the syngas quality in industrial processes and for assisting in design of new gasifers. Such simulation involves modelling of a reacting multiphase flow. In this study, the special software called

Manuscript received October 25, 2012; revised December 6, 2012.

This work is partially supported by the Australian Research Council.

M. M. Zhao and D. N. Saulov are with School of Mechanical and Mining Engineering, The University of Queensland, Brisbane 4072, Australia(e-mail: mengmeng.zhao@uq.edu.au, d.saulov@uq.edu.au).

M. J. Cleary is with School of Aersopace, Mechanical and Mechatronic Engineering, The University of Sydney, NSW 2006, Australia(e-mail: m.cleary@sydney.edu.au)

A. Y. Klimenko is with School of Mechanical and Mining Engineering, The University of Queensland, Brisbane 4072, Australia(e-mail: a.klimenko@uq.edu.au).

DOI: 10.7763/IJCEA.2012.V3.245

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 heavily-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 gasifer.

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 CO_2 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:

$$\frac{\partial}{\partial t}(\varepsilon_m \rho_m Y_{ml}) + \nabla \cdot (\varepsilon_m \rho_m Y_{ml} \vec{V}_m) = R_{ml}$$

Conservation of momentum (*gas phase* $m=g$):

$$\begin{aligned}\frac{\partial}{\partial t}(\varepsilon_g \rho_g \vec{V}_g) + \nabla \cdot (\varepsilon_g \rho_g \vec{V}_g \vec{V}_g) \\ = \nabla \cdot \bar{\bar{S}}_g + \varepsilon_g \rho_g \vec{g} - \sum_{m=1}^{M} \vec{I}_{gm}\end{aligned}$$

Conservation of momentum (*solids phase* $m=s$):

$$\begin{aligned}\frac{\partial}{\partial t}(\varepsilon_m \rho_m \vec{V}_m) + \nabla \cdot (\varepsilon_m \rho_m \vec{V}_m \vec{V}_m) \\ = \nabla \cdot \bar{\bar{S}}_m + \varepsilon_m \rho_m \vec{g} + \vec{I}_{gm} - \sum_{l=1, l \neq m}^{M} \vec{I}_{ml}\end{aligned}$$

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 CH_4, C_2H_6, CO, CO_2, H_2, H_2O. Note that small amounts of NH3 (0.49%) and H_2S (0.26%) were neglected. The normalised composition of the coal is given in Table II.

TABLE I: PROPERTIES OF SHENHUA COAL

Proximate analysis (wt%)		Ultimate analysis (wt%)	
Fixed carbon	52.26	C	74.62
Moisture	8.7	H	4.65
Volatile matter	32.65	O	12.7
Ash	6.39	N	1.02
		S	0.62
		Ash	6.39

TABLE II: COMPONENT MASS FRACTION OF COAL PYROLYSIS (WT%)

Char	CH4	C2H6	CO	CO2	H2	H2O	Ash
69.06	7.16	1.21	1.94	0.91	1.05	12.24	6.43

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:

$$VM \rightarrow CH_4+C_2H_6+CO+CO_2+H_2O+CH_4+H_2 \tag{1}$$

$$R_1 = k_1 \times exp(-E_1/RT) \times Y_{vm}$$

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

Steam gasification:

$$C+H_2O \rightarrow CO+H_2 \tag{2}$$

$$R_2 = k_2 \times exp(-E_2/RT) \times C_c \times (P_{H2O} - P_{H2O}^*)$$

$$P_{H2O}^* = \frac{P_{CO} \times P_{H2}}{exp(17.29 - 16326/T)}$$

CO_2 gasification:

$$C+CO_2 \rightarrow 2CO \tag{3}$$

$$R_3 = k_3 \times exp(-E_3/RT) \times C_c \times (P_{CO2} - P_{CO2}^*)$$

$$P_{CO2}^* = \frac{P_{CO} \times P_{CO}}{exp(20.92 - 20282/T)}$$

Methanation:

$$C + 2H_2 \rightarrow CH_4 \tag{4}$$

$$R_4 = exp(-7.087 - 8078/T) \times C_c \times (P_{H2} - P_{H2}^*)$$

$$P_{H2}^* = \sqrt{\frac{P_{CH4}}{exp(-13.43 + 10999/T)}}$$

Water gas shift reaction:

$$H_2O+CO \rightarrow CO_2+H_2 \tag{5}$$

$$R_5 = 1.956 \times 10^3 \times a \times P^{(0.5-P/250)} \times exp\left(-27760/RT_g\right) \times (Y_{CO}Y_{H2O} - Y_{CO2}\,Y_{H2}/b)$$

$$a = \varepsilon \times (1-\varepsilon) \times \rho^0_{Ash} \times exp(-8.91 + 5553/T_g)$$

$$b = exp(-3.63 + 3.955/T_g)$$

To describe the capture of CO_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, $(1-X) \propto r^3$. 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

$$CaO + CO_2 \rightarrow CaCO_3 \tag{6}$$

is given by

$$R_6 = k_6 \times exp\left(-E_6/RT_g\right) \times S \times C_{CaO}$$

The values of pre-exponential factors k_α and activation energies E_α for the reactions A-E are summarised in Table III.

TABLE III: REACTION RATE CONSTANTS

reaction	k_α	E_α
A[14]	1.1×10^5	*21200*
B[14]	*3000*	*41200*
C[14]	*3000*	*41200*
F[16]	1.67×10^{-3}	*29*

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 $\varepsilon_0 = 0.5$.

TABLE IV: SIMULATION PARAMETERS

Coal density	1.3 g/cm3	Reactor radius	8 cm
CaO density	2.3 g/cm3	Feeding Coal mass rate	0.1 g/s
Coal particle diameter	0.38 mm	Feeding H_2O/Coal mass ratio	10
CaO particle diameter	0.3 mm	Feeding CaO/Coal molar ratio	1.2
Reactor height	80 cm	Temperature	900 K
Static bed height	50 cm	Gas pressure	10 atm

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_2 capture were simulated under specified operational conditions, which are given in Table IV.

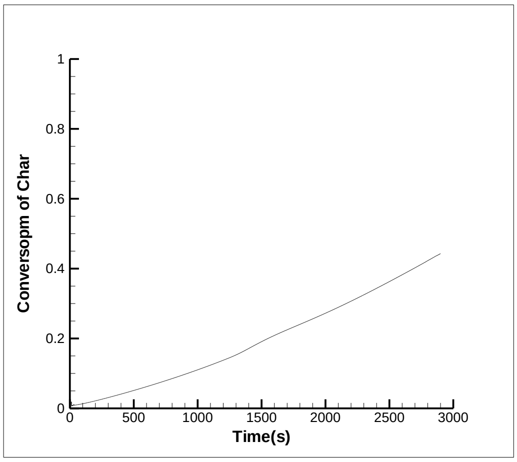


Fig. 1. The conversion of char as function of time

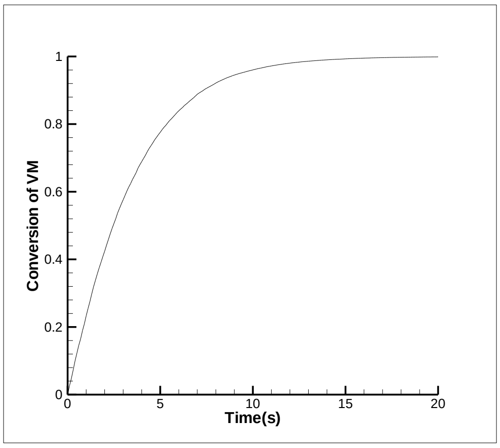


Fig. 2. The conversion of VM as function of time

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 CO_2. 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 H_2 and CO increase slightly in time, while that of CH_4 and C_2H_6 decrease slowly.

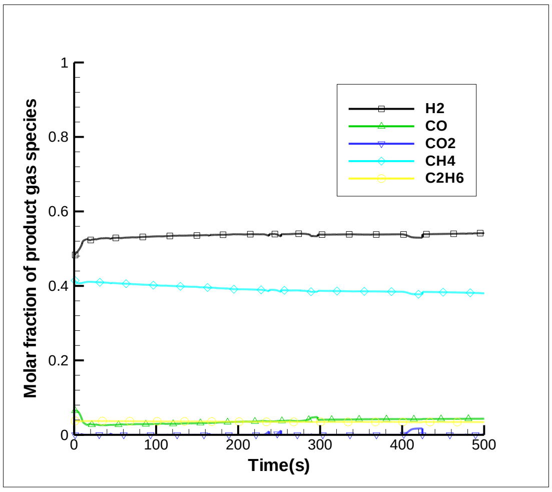


Fig. 3. The outlet molar fractions of gas species (dry basis and N_2 free, initial stage with CO_2 capture)

The results of the steady state simulation without CO_2 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 CO_2 capture are given in Fig. 6 and 7, respectively.

Comparison of Fig. 4 and 6 shows that the addition of CO_2 sorbent material results in a substantial improvement in product gas quality. That is, the fractions of H_2 and CH_4 are increased by approximately 25% and 4%, respectively. As demonstrated by Fig. 5 and 7, CO_2 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].

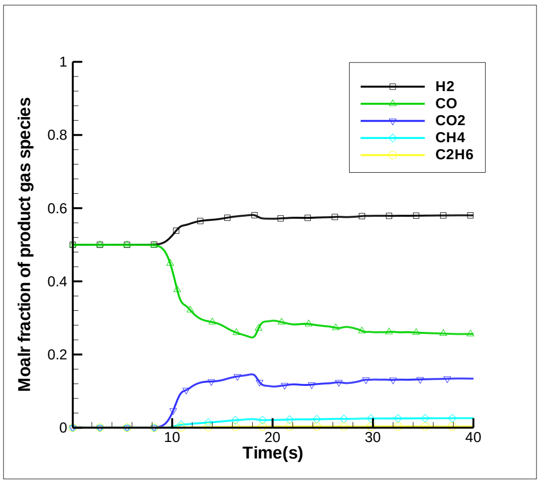


Fig. 4. The outlet molar fractions of gas species (dry basis and N_2 free, steady state without CO_2 capture)

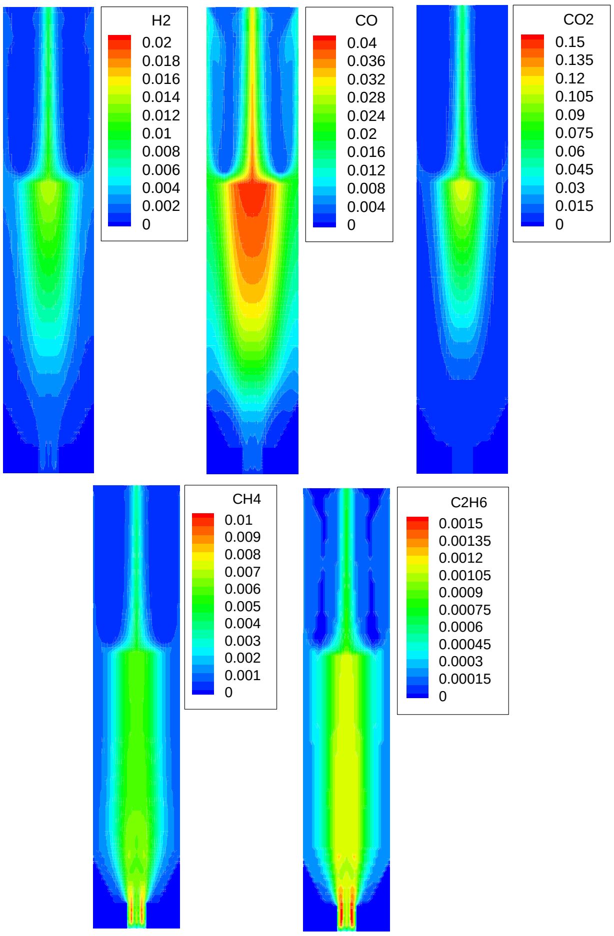


Fig. 5. The mass fraction contours of gas species at steady state (without CO_2 capture)

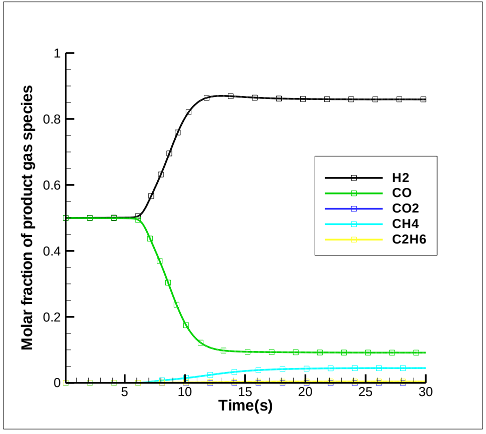
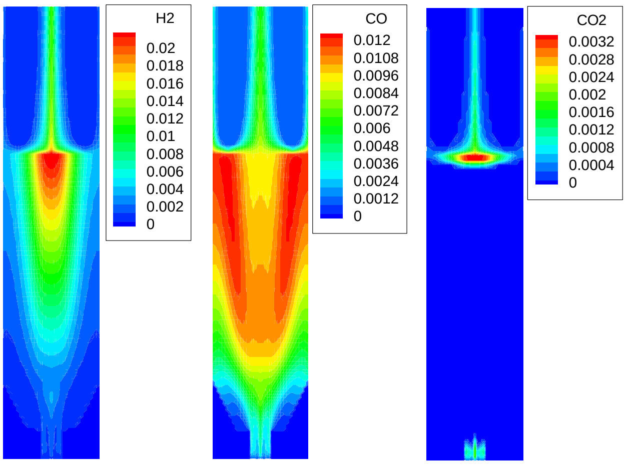


Fig. 6. The outlet molar fractions of gas species (dry basis and N_2 free, steady state with CO_2 capture)



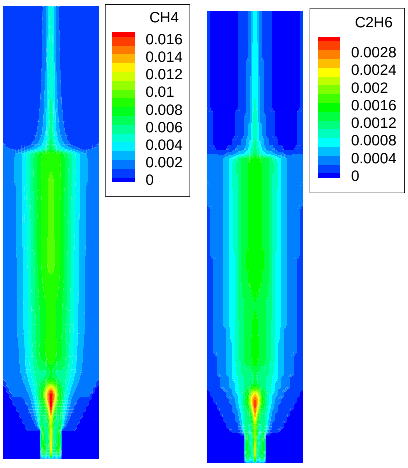


Fig. 7. The mass fraction contours of gas species at steady state (with CO_2 capture)

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 untaken to take into account heat balance and to employ a more sophisticated model for the carbonation reaction.

REFERENCES

[1] J. Corella, J. M. Toledo *et al.*, “Steam Gasification of Coal at Low−Medium (600−800°C) Temperature with Simultaneous CO_2 Capture in Fluidized Bed at Atmospheric Pressure: The Effect of Inorganic Species. 1. Literature Review and Comments,” *Industrial & Engineering Chemistry Research*, vol. 45, no. 18, pp. 6137-6146, 2006.

[2] J. Corella, J. M. Toledo *et al.*, “Steam Gasification of Coal at Low−Medium (600−800 °C) Temperature with Simultaneous CO2Capture in a Bubbling Fluidized Bed at Atmospheric Pressure. 2. Results and Recommendations for Scaling Up,” *Industrial & Engineering Chemistry Research*, vol. 47, no. 6, pp. 1798-1811, 2008.

[3] S. Lin, M. Harada *et al.*, “Continuous experiment regarding hydrogen production by coal/CaO reaction with steam (I) gas products,” *Fuel*, vol. 83, no. 7–8, pp. 869-874, 2004.

[4] T. F. Wall, “Combustion processes for carbon capture,” *Proceedings of the Combustion Institute*, vol. 31, no. 1, pp. 31-47, 2007.

[5] MFIX - Multiphase Flow with Interphase eXchanges. [Online]. Available: https://mfix.netl.doe.gov/

[6] B. Feng, H. An *et al.*, “Screening of CO2 Adsorbing Materials for Zero Emission Power Generation Systems,” *Energy & Fuels*, vol. 21, no. 2, pp. 426-434, 2007.

[7] T. J. O'Brien, M. Syamlal, and C. Guenther, “Computational fluid dynamics simulations of chemically reactive fluidized bed processes,” in *Proc. The 3rd International Conference on CFD in the Minerals and Process Industries*, Melbourne, Australia, December 2003, pp. 10–12.

[8] M. Syamlal, C. Guenther, A. Gel and S. Pannala, “Advanced coal gasifier designs using large-scale simulations,” *Journal of Phusics: Conference Series*, vol. 180 , 2009.

[9] M. Syamlal, W. Rogers, and T. J. O’Brien. MFIX Documentation Theory Guide. [Online]. Available: https://mfix.netl.doe.gov/

[10] H. An, T. Song *et al.*, “Coal gasification with in situ CO2 capture by the synthetic CaO sorbent in a 1 kWth dual fluidised-bed reactor,” *International Journal of Hydrogen Energy*, vol. 37, no. 19, pp. 14195-14204, 2012.

[11] D. Merrick, “Mathematical models of the thermal decomposition of coal: 1. The evolution of volatile matter,” *Fuel*, vol. 62, no. 5, pp. 534-539, 1983.

[12] J. Xu and L. Qiao, “Mathematical Modeling of Coal Gasification Processes in a Well-Stirred Reactor: Effects of Devolatilization and Moisture Content,” *Energy & Fuels*, vol. 26, no. 9, pp. 5759-5768, 2012.

[13] E. Binner, J. Facun *et al.*, “Effect of Coal Drying on the Behavior of Inorganic Species during Victorian Brown Coal Pyrolysis and Combustion,” *Energy & Fuels*, vol. 25, no. 7, pp. 2764-2771, 2011.

[14] C. Y. Wen, H. Chen, and M. Onozaki, “User’s manual for computer simulation and design of the moving bed coal gasifier,” Springfield, Virginia: National Technical Information Service, 1982.

[15] J. Szekely, J. W. Evans, and H. Y. Sohn, *Gas Solid Reactions*, Academic Press, London, 1976.

[16] P. Sun, J. R. Grace *et al.*, “Determination of intrinsic rate constants of the CaO–CO2 reaction,” *Chemical Engineering Science*, vol. 63, no. 1, pp. 47-56, 2008.