Computational Study on Coal Direct Chemical Looping Combustion

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Abstract- Present work deals with the CFD modeling of a complete coal direct chemical looping pilot plant which uses sub- bituminous coal as a fuel and alumina supported iron (III) oxide as an oxygen carrier. A 2D CFD model, of the complete pilot plant incorporating both reactors (fuel reactor and air reactor) and their inter-connecting parts, is solved using Fluent. The model is run with 11 homogeneous reactions taking place inside the inter-connected system of reactors, for sub-bituminous coal.

The simulated results for sub-bituminous coal shows good agreement with the pilot plant data. The fuel conversion on coal basis and CO_2 purity in fuel reactor exhaust are 89.81% & 88.98% respectively while these figures for the pilot plant are 97% and 99.6% respectively.

Keywords – Chemical looping combustion, Oxygen carrier, sub-bituminous coal (SBC)

I. INTRODUCTION

Exponential rising trend of energy consumption compounded with deteriorating quality of fossil fuel is forcing scientists to search solutions for the problems related to energy crises of the 21st century. It appears that renewable energy sources like solar, wind and geothermal are unlikely to meet the energy demand in foreseeable future. Nuclear energy due to its constraint on its spent fuel management and susceptibility to catastrophic hazards makes it implausible to play a vital role in meeting future energy demands. This makes the fossil fuels as the most imminent source of energy in near future. [1]- [2]

The carbon emission from fossil fuel estimated by IPCC [3] has posed considerable challenge for researchers and scientists in the past decade. For obvious reasons, the applications of clean technologies such as chemical looping combustion, fuel cells and similar technologies are becoming an attractive proposition in foreseeable future. Research [4-5], in these fields, is gaining momentum to tackle above discussed planetary issues and to provide clean and efficient technology to meet the present and future energy demands so that the abundant reserves of coal to provide energy for 200+ years is utilized properly. In addition to it, the cost of coal is much cheaper than other fossil fuels, and its pricing is also regionally controlled which acts as one of its economic drivers.

Traditional technologies that generate electricity from fossil fuel via combustion or gasification process generate flue gas from which separation of carbon dioxide is costly and technically cumbersome. The chemical looping technology, where carbon dioxide is available as a directly sequestration ready stream, offers significant cost effectiveness. In the last decade, chemical looping process has gained momentum and has been targeted mainly towards efficient carbon capturing, hydrogen and power generation, etc. Researchers [6] have worked with different segments of this process. They have adopted experimental as well as simulation based approaches to study this process with a variety of gaseous and solid fuels and nearly more than 700 different type of oxygen carrier have been tested so far.

Z. Deng et al. [7] carried out CFD based simulation study on reaction kinetics of chemical looping combustion using FLUENT for fuel reactor only and demonstrated the effect of particle diameter, gas flow rate and bed temperature on fuel conversion. H. Kruggel-Emden et al. [8] conducted an interconnected multiphase CFD simulation study of chemical looping combustion using methane as fuel and Mn_3O_4 supported on Mg-ZrO_2 as oxygen carrier using bubbling fluidized bed for fuel reactor and riser as air reactor separately. In the absence of actual interaction study, they considered time dependent mass exchanges between these two reactors through inlet and outlet boundary conditions only. X. Wang et al. [9] developed a three dimensional CFD model for circulating fluidized bed fuel

reactor only using solid coal as fuel and ilmenite as an oxygen carrier. In addition to it, they have evaluated the effect of operating variables on the fuel conversion in the fuel reactor.

Though a considerable work has been carried out in the field of chemical looping, there appears to be substantive gap related to CFD based study of the complete coal direct chemical looping process which incorporates the flow through fuel reactor, air reactor and their inter-connecting parts simultaneously to incorporate interaction between various parts of the process necessary for its development. To bridge the above gap, the present CFD simulation is carried out for a 25 kW_{th} complete pilot plant developed at Ohio State University, USA and discussed by H.R. Kim et al. [10]. They have also reported the design criteria and operating condition of the pilot plant wherein sub-bituminous coal (SBC) has been used with iron (III) oxide supported on alumina as an oxygen carrier. They also considered eleven reactions that are taking place inside the fuel reactor and air reactor and their inter-connecting parts. For comparison purpose the present simulation also takes eleven reactions reported by H.R. Kim et al. [10].

II. PROCESS DESCRIPTION

In the chemical looping combustion process, carbonaceous fuel such as coal reacts with a metal oxide (an oxygen carrier) in a fuel reactor reducing the metal oxide to metal. The above reaction yields rich carbon dioxide and steam as products from which carbon dioxide is readily separable by condensing steam. The reduced metal in the fuel reactor is oxidized again by air in an air reactor for its regeneration to metal oxide. The metal oxide is then recycled back to the fuel reactor for reuse. The cyclic process is shown in Fig. 1. Chemical looping combustion process using gaseous fuel has been developed in the last decade however; abundance of solid fuel like coal and biomass as carbonaceous fuel for chemical looping combustion is providing the necessary thrust for its recent and future development.

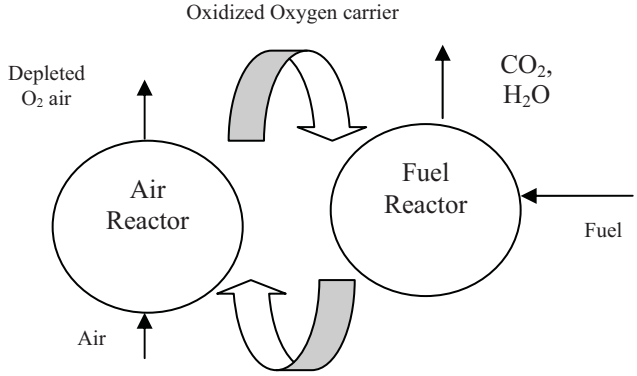


Figure 1. Chemical looping process

III. PROBLEM DESCRIPTION

The geometrical as well as operating parameters of a 25 kW_{th} pilot plant developed by Ohio State University, USA and described by [9] has been considered for the present CFD simulation. The pilot plant parameters and its geometry are shown in Fig. 2 with different dimension of sections taken from thesis [11] and reported in Table 1 SBC is used as a fuel in the pilot plant with iron (III) oxide as an oxygen carrier. Table 2 provides the details of proximate and ultimate analysis of SBC having average particle size of 89.8 μm. Oxygen carrier having an average particle size of 120 μm and density of 4724 kg/m^3 and containing 40-60% reactive metal oxide is used for the present study.

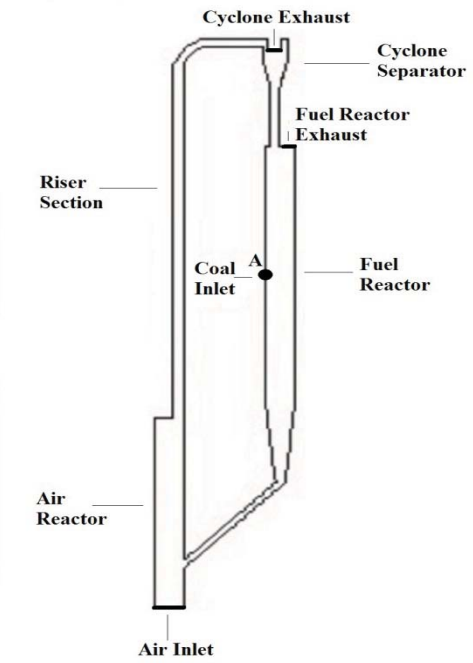


Figure 2. Pilot Plant of present study

Table -1 Geometry Parameters

Fuel Reactor Height	**3.37m**
Fuel Reactor Diameter	**0.34m**
Air Reactor Height	**1.88m**
Air Reactor Diameter	**0.33m**
Tube Diameter	**0.11m**
Riser Height	**4.68m**
Cyclone Separator Height	**0.62m**
Cyclone Separator Diameter	**0.28m**

Table -2 Properties of fuel

	Proximate Analysis		**Ultimate Analysis**
Ash	**11.38%**	**Carbon**	**65.5%**
Volatile Matter	**39.57%**	**Hydrogen**	**4.41%**
Fixed Carbon	**49.05%**	**Nitrogen**	**0.78%**
Moisture	**10.53%**	**Sulfur**	**0.77%**
Net Energy Value	**29,391 kJ/kg**	**Oxygen**	**17.16%**

IV. MODEL DEVELOPMENT

A 2-D CFD model for inter-connected fuel and air reactor is developed using commercial computational software Fluent 6.3.2 and mesh for the above geometrical layout has been developed using GAMBIT 2.3.16. The mixture (fuel and oxygen carrier) containing solid particles in the range of 90-120 μm along with amount of gases injected in the system as well as created from the reactions which amounts to about 76% by volume are assumed to flow as a fluid inside both the reactors and their inter-connecting parts. This assumption has been used for the development of a simplified CFD model. The 11 reactions discussed in [10] as given in Table 6, are considered in the modeling of the present CFD study. Before a complicated two phase CFD model is selected for the analysis for the present problem, it is thought logical to use the least complicated model, the Species-Transport model with volumetric reaction for the present study. The good agreement between the model predictions and that of pilot plant results shows that the assumed model is worth investigating. Following governing equations are solved on commercial available software Fluent 6.3.2 for the present model:

The equation for mass conservation/continuity equation can be written as:

$$\frac{\partial p}{\partial t} + \nabla.(\rho \vec{v}) = S_m \quad (1)$$

In an inertial frame, the momentum conservation equation is described as below Eq. 2:

$$\frac{\partial(\rho \vec{v})}{\partial t} + \nabla.(\rho \vec{v}\vec{v}) = -\nabla p + \nabla.(\bar{\bar{\tau}}) + \rho \vec{g} + \vec{F} \quad (2)$$

The conservation of Energy is defined by the following Eq. 3:

$$\frac{\partial(\rho E)}{\partial t} + \nabla.(\vec{v}(\rho E + p)) = \nabla.\left(k_{eff} \nabla T - \sum_j h_j \vec{J}_j + (\bar{\bar{\tau}}_{eff}.\vec{v}) \right) + S_h \quad (3)$$

Species Transport Equations:

The local mass fraction of each species (Y_i) through the solution of a convection-diffusion equation for the i^{th} species is solved. It takes the following general form:

$$\frac{\partial}{\partial t}(\rho Y_i) + \nabla.(\rho \vec{v} Y_i) = -\nabla.\vec{J}_i + R_i + S_i \quad (4)$$

In the present model, dilute approximation is assumed, under which it is defined as follows:

$$\vec{J}_i = -\rho D_{i,m} \nabla Y_i \quad (5)$$

The net source of chemical species i^{th} due to reaction is computed as the sum of the Arrhenius reaction sources over the N_R reactions that the species participate in:

$$R_i = M_{w,i} \sum_{r=1}^{N_R} \hat{R}_{i,r} \quad (6)$$

Consider the r^{th} reaction written in general form as follows in Eq. 7 which is valid for both reversible and non reversible reactions. For non-reversible reactions the backward rate constant is omitted.

$$\sum_{i=1}^{N} v'_{i,r} M_i \underset{k_{b,r}}{\overset{k_{f,r}}{\rightleftharpoons}} \sum_{i=1}^{N} v''_{i,r} M_i \quad (7)$$

For a non-reversible reaction, the molar rate of creation/destruction of specie 'i' in reaction r is given by

$$\hat{R}_{i,r} = \Gamma(v''_{i,r} - v'_{i,r}) \left(k_{f,r} \prod_{j=1}^{N} [C_{j,r}]^{(\eta'_{j,r} + \eta''_{j,r})} \right) \quad (8)$$

For a reversible reaction, the molar rate of creation/destruction of species i in reaction r, is given by,

$$\hat{R}_{i,r} = \Gamma(v''_{i,r} - v'_{i,r}) \left(k_{f,r} \prod_{j=1}^{N} [C_{j,r}]^{\eta'_{j,r}} - k_{b,r} \prod_{j=1}^{N} [C_{j,r}]^{v''_{j,r}} \right) \quad (10)$$

The forward rate constant $k_{f,r}$ for reaction r, is computed using the Arrhenius expression

$$k_{f,r} = A_r T^{\beta_r} e^{-E_R/RT} \quad (11)$$

Reactions Kinetics:

The present study is carried out for sub-bituminous coal. There are 11 possible reactions, those proposed by [10], that can take place inside the two reactors and their inter-connecting parts. In Table 6, 11 reactions proposed by [10] are described with their kinetics.

Table -3 Reactions proposed by [9] for coal direct chemical looping process

Reaction no.	Reaction	E_R (J/kmol)	Pre-exponential factor	β_k
1	$C_{6.154}H_{4.931}N_{0.063}S_{0.027}O_{1.211} \rightarrow 4.59675C + 1.13275\,CH_4 + 0.063\,NO_2 + 0.027\,SO_2 + 0.42CO_2 + 0.191H_2O$	1.14×10^8	111.3	1
2	$2Fe_2O_3 + C \rightarrow 4FeO + CO_2$	3.0124×10^8	8.2	1
3	$4Fe_2O_3 + CH_4 \rightarrow 8FeO + 2H_2O + CO_2$	1.352×10^8	9.8	0.5
4	$Fe_2O_3 + CO \rightarrow 2FeO + CO_2$	8.07×10^7	0.1	0.5
5	$Fe_2O_3 + H_2 \rightarrow 2FeO + H_2O$	6.5×10^7	0.062	0.5
6	$FeO + CO \rightarrow Fe + CO_2$	1.205×10^7	7.44	0.5
7	$FeO + H_2 \rightarrow Fe + H_2O$	2.151×10^7	9.5	0.5
8	$C + CO_2 \rightarrow 2CO$	2.11×10^8	0.8593	0.5
9	$C + H_2O \rightarrow CO + H_2$	2.31×10^8	8.593	0.5
10	$2Fe + 1.5O_2 \rightarrow Fe_2O_3$	2.025×10^7	6.3	0.5
11	$2FeO + 0.5\,O_2 \rightarrow Fe_2O_3$	2.55×10^7	0.0019	0.5

Standard k-ε turbulence model:

The standard k-ε turbulence model described by Launder and Spalding in 1974 is used for the present study.

Eq. 12 is described for turbulent kinetic energy k

$$\frac{\partial(\rho k)}{\partial t} + \frac{\partial(\rho k u_i)}{\partial x_i} = \frac{\partial}{\partial x_i}\left[\left(\mu + \frac{\mu_t}{\sigma_k}\right)\frac{\partial k}{\partial x_j}\right] + G_k + G_b - \rho\varepsilon - Y_M + S_k \quad (12)$$

And Eq. 13 is described for the rate of dissipation ε with $C_{1\varepsilon}$, $C_{2\varepsilon}$, $C_{3\varepsilon}$ are the constants ($C_{1\varepsilon}$ = 1.44, $C_{2\varepsilon}$ =1.92)

$$\frac{\partial(\rho\varepsilon)}{\partial t} + \frac{\partial(\rho\varepsilon u_i)}{\partial x_i} = \frac{\partial}{\partial x_i}\left[\left(\mu + \frac{\mu_t}{\sigma_k}\right)\frac{\partial \varepsilon}{\partial x_j}\right] + C_{1\varepsilon}\frac{\varepsilon}{k}(G_k + C_{3\varepsilon}G_b) - C_{2\varepsilon}\rho\frac{\varepsilon^2}{k} + S_\varepsilon \quad (13)$$

V. SOLUTION TECHNIQUE

Solution technique based on finite volume is adopted for the present study. The plant dimensions are taken from the mechanical drawing of the pilot plant described in [10-11]. The boundary conditions for air inlet and coal inlet are defined as velocity inlet and mass flow inlet and for fuel reactor exhaust and cyclone exhaust it is defined as pressure outlets with no slip condition at wall boundary. Unsteady state simulations are carried out for present study with a time step of 0.001s. The optimum grid size evaluated from grid independency test for the present problem is 0.01(m).

Table -4 Computational and Simulation Parameters for the study

Parameter	Value
Operating Pressure	10 atm
Air inlet velocity	0.005 m/s
Fuel flow rate	1.3 kg/h
Air and Fuel inlet temperature	320 K
Carrier CO_2 gas flow rate	10 LPM
Model Parameters	
Solver	Unsteady state, 2nd order implicit
Discretization Scheme	2nd order upwind
Pressure-Velocity coupling	SIMPLE
Convergence criterion	10^{-5}
Time step	0.001 s
Iteration per time step	30

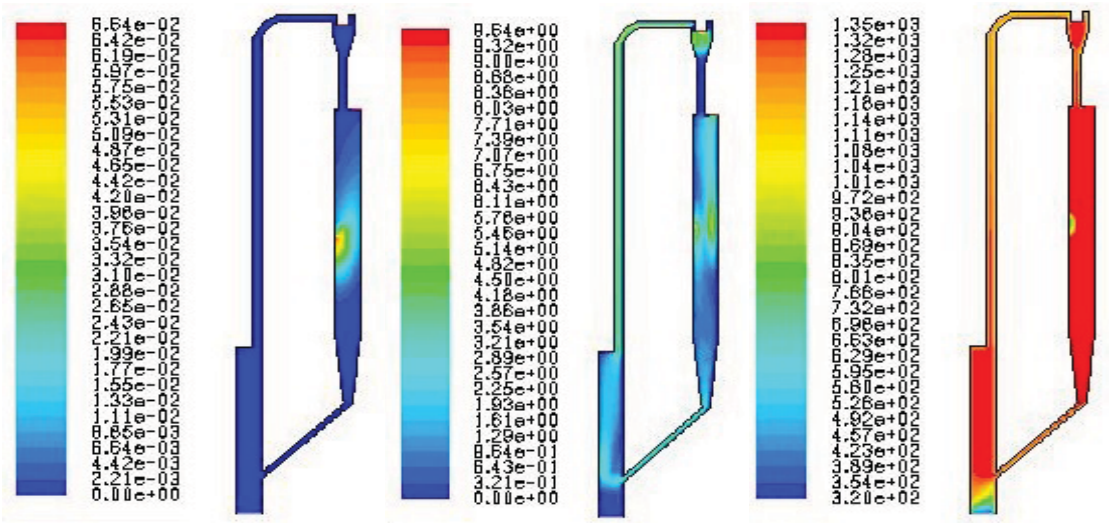
VI. RESULTS

In Table 5, mass weighted average rate of reactions discussed in Table 3 are computed from the CFD model for SBC. From Table 5 it could be seen that, reaction Nos. 1, 6, 10 and 6 are prevailing in fuel reactor, inter-connecting parts, air reactor and riser section of the process respectively.

Table -5 Mass weighted average rate of reactions for SBC in different section of the pilot plant

Reaction number	Mass weighted average Rate of Reaction in Fuel reactor (kmol/m^3-s)	Mass weighted average Rate of Reaction in inter-connecting pipe (kmol/m^3-s)	Mass weighted average Rate of Reaction in Air reactor (kmol/m^3-s)	Mass weighted average Rate of Reaction in riser section (kmol/m^3-s)
1	1.3×10^{-4}	2.8×10^{-7}	0	0
2	1.25×10^{-5}	4.94×10^{-7}	0	0
3	3.37×10^{-7}	0	0	0
4	3.04×10^{-7}	2.58×10^{-7}	0	0
5	3.22×10^{-14}	4.54×10^{-14}	0	0
6	0	5.38×10^{-3}	5.01×10^{-5}	1.87×10^{-6}
7	0	2.00×10^{-10}	1.47×10^{-11}	3.13×10^{-14}
8	3.31×10^{-5}	1.43×10^{-3}	0	0
9	2.91×10^{-10}	0	0	0
10	0	0	5.52×10^{-5}	5.34×10^{-7}
11	0	0	5.65×10^{-8}	5.91×10^{-9}

Fig.3 (a, b & c) shows the contour of reaction 1, velocity and temperature profiles respectively for the system while Fig. 4, shows the molar concentration of important species. The presence of very low quantity of nitrogen and oxygen in fuel reactor meets the objective of chemical looping process which prohibits, to a large extent, mixing of nitrogen with carbon dioxide to avoid energy expenditure to separate these from fuel reactor exhaust gases. The presence of slight amount of carbon and carbon monoxide in the air reactor is due to seepage of left over carbon and carbon monoxide from the fuel reactor via inter-connecting pipe.



(a) (b) (c)

Figure 3. (a) Contour of rate of reaction 1 (b) Velocity profile (c) Temperature profile

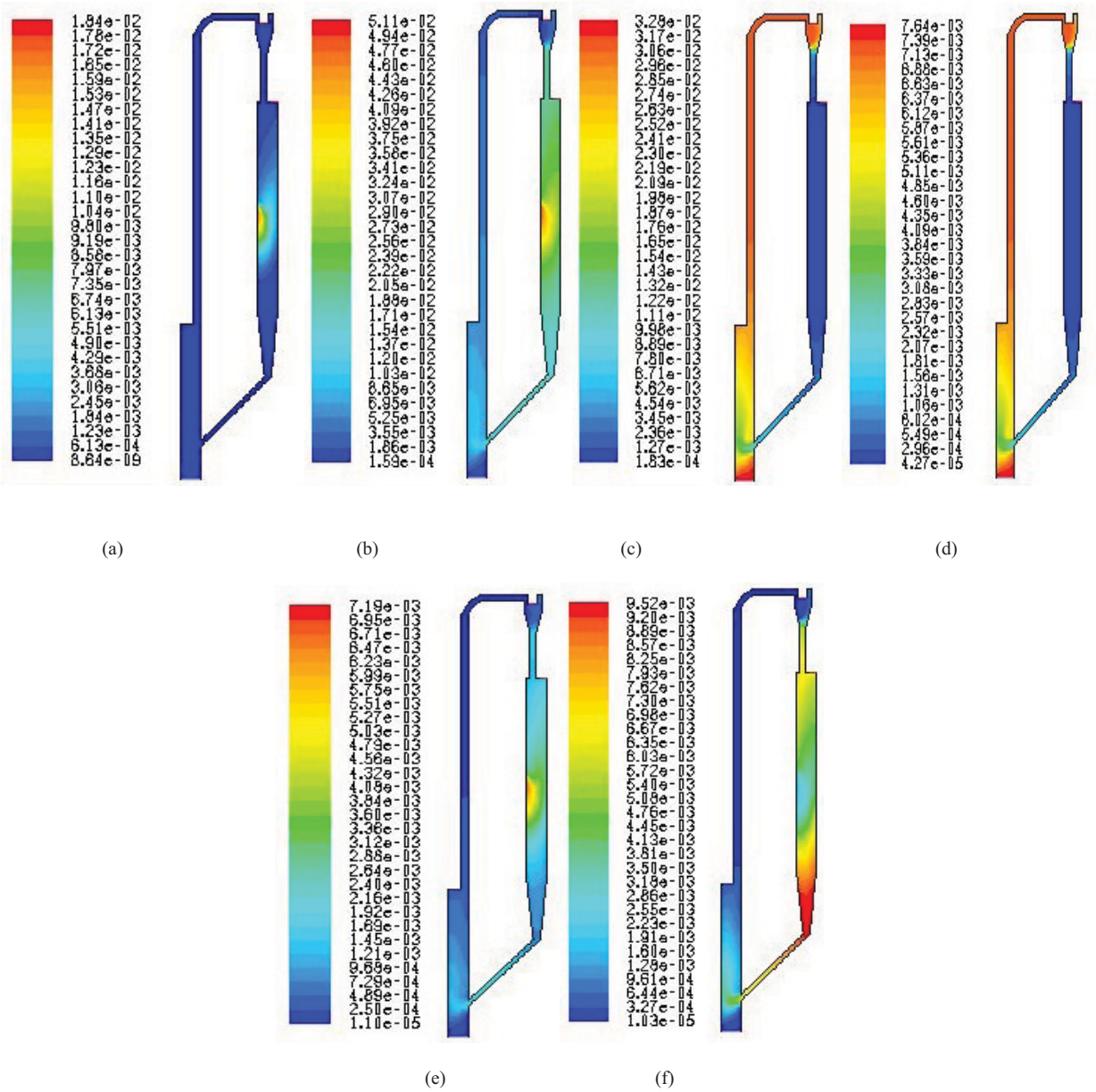


Figure 4. Molar Concentration contour of (a) SBC (b) iron (III) oxide (c) Nitrogen (d) Oxygen (e) carbon dioxide (f) carbon monoxide

The mass average velocity for fuel reactor outlet is 3.044 m/s and the molar concentration of SBC with time along the pathline trajectory is shown in Fig 5. Table 6, shows the comparison between the model predictions with that of pilot plant results and reveals that model predictions are within an error band of +7% to +11%.

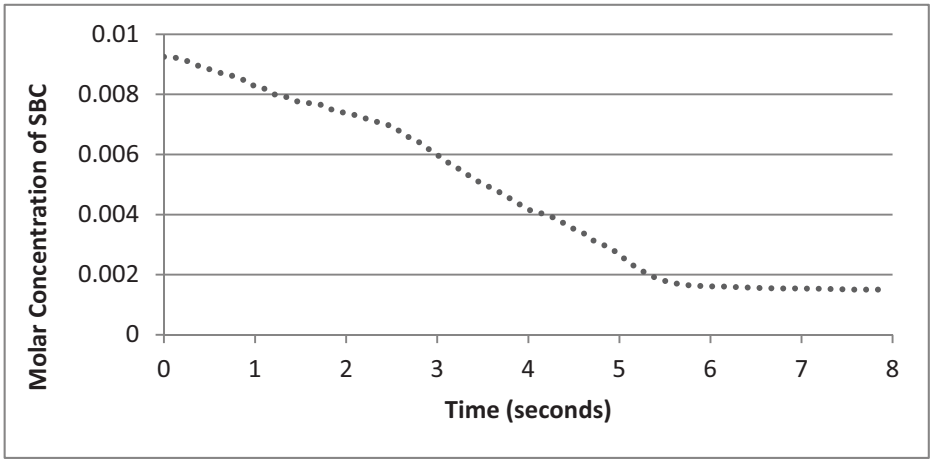


Figure 5. Variation of molar concentration of SBC with time along the pathline trajectory

Table -6 Verification of present CFD model for SBC

Parameters	Model Prediction	Pilot Plant data	Error
Fuel conversion (on dry ash free basis)	89.81%	97%	7.41%
Fuel Reactor Exhaust mole fraction on dry and nitrogen free basis			
CO_2	88.98%	99.6%	10.66%
CO	0.067%	0.08%	16.25%
CH_4	0.219%	0.25%	12.4%
Cyclone Exhaust mole fraction			
O_2	16.82%	18.5%	9.08%
CO_2	0.12%	0.1%	-20%
CH_4	0.023%	0.02%	-15%

VII.CONCLUSION

Results of the present simplified CFD model taking into account 11 reactions are in good agreement with the results of pilot plant developed at Ohio State University, USA. The simulated fuel conversions for SBC show an error equal to 7.41% when compared with reported values for pilot plant. It indicates that the present simplified CFD model can be used for coal direct chemical looping process simulation if the above error limits can be tolerated. Further the simulation predicts that the coal devolatilization reactions, oxidation reaction of iron are dominant reactions taking place in the fuel and air reactors.

VIII.NOMENCLATURE

A_r	Pre- exponential factor
β_r	Temperature coefficient
$C_{j,r}$	Molar concentration of species j in reaction r
$D_{i,m}$	Diffusion coefficient of i^{th} specie in the mixture
ε	Rate of dissipation
E_R	Activation energy of reaction
$\vec{F}$	External body forces and also contain user-defined terms
$\gamma_{j,r}$	Third body efficiency of the j^{th} species in the r^{th} reaction
g_i	Gravitational vector in i^{th} direction
G_b	Generation of turbulence kinetic energy due to buoyancy
G_k	Generation of turbulence kinetic energy due to mean velocity gradients
I	Unit tensor
$\vec{J}_i$	Diffusion flux of the i^{th} soecues
k	Turbulence kinetic energy
$k_{f,r}$	Forward rate constant for reaction r
μ	Molecular viscosity
M_i	Symbol denoting species i
$\eta'_{j,r}$	Rate exponent for reactant species j in reaction r
$\eta''_{j,r}$	Rate exponent of product species j in reaction r
N	Number of chemical species in the system

P	**Static pressure**
ρg	**Gravitational body force**
R	**Universal gas constant**
R_i	**Net rate of production of species i by chemical reaction**
$\bar{R}_{if}$	**Arrhenius molar rate of creation/destruction of species i^{th} in reaction r**
σ_ε	**Turbulent Prandtl number for ε**
σ_k	**Turbulent Prandtl number for k**
S_ε, S_k	**Unser defined source terms**
$\bar{\bar{\tau}}$	**Stress tensor**
$v'_{i,r}$	**Stoichiometric coefficient for reactant I in reaction r**
$v''_{i,r}$	**Stoichiometric coefficient for product i in reaction r**
Y_j	**Mass fraction of species j**
Y_M	**Contribution of the fluctuating dilation in compressible turbulence to overall dissipation rate**

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