# Diffusion Modeling in TGA in Context of $CO_2$ Gasification of Char

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**Abstract:** The Thermo- Gravimetric Apparatus (TGA) is often used for kinetics determination. A typical TGA experiment is performed by filling cylindrical crucible with a few milligrams of char. The gasifying agent flows across the top of the crucible at a constant concentration and temperature. With this kind of setup, gasification reaction may be limited by the reach (diffusion) of the gasification agent to the internal surfaces of the char particles. In addition to this, after some time, ash is formed between the bulk of the gas and the upper surface of char as well as the char bed consists of small particles surrounded by empty spaces, through which the gasification agent has to diffuse to reach the external surfaces of the porous char particles. Furthermore, if the endo/exothermicity of the reaction is higher, and if the external heat transfer process is not fast enough, the temperature of the external layer of the char bed may be significantly different than that of the bulk of the gas. The present modeling exercise is aimed at examining the diffusion effects on TGA gasification experiments using $CO_2$ as a gasification agent. The diffusion processes may seriously affect the observed gasification rate and must be considered when interpreting results of laboratory studies and determining the kinetic parameters. $CO_2$ gasification data (weight of char vrs time and temp) and kinetics parameters determined by single layer TGA experiments are available. (Ramesh Mandapati, 2012). Initially the simulations were run with a constant temperature of char ~ equal to temperature of bottom wall of TGA crucible (available in TGA data). This assumption was considered to be valid as the heat of reaction as well as rate of reaction of gasification are not very high and the TGA crucible is very small. To check the validity of constant temperature assumption, heat transfer enabled simulation is carried out. It was observed from the results that variation in temperature is very less. Minimum temperature attained in crucible is 0.6 K less than the initial temperature.

**Keywords:** TGA, Diffusion Modeling, Coal Gasification, Kinetics

## 1. Introduction

Coal is one of the most abundant sources of energy for power generation. Most of the coal based power plants have a combustion-based process [1]. But the conventional use of coal as energy source is affecting climate in adverse way by increasing carbon emissions [2]. To reduce these carbon emissions, some advanced clean coal technologies are considered to be the promising options worldwide e.g. Underground Coal Gasification (UCG). Product gas from UCG can be used for power generation or as synthesis gas for making other chemicals [3]. UCG process involves many reactions including combustion, steam and $CO_2$ gasification of coal/char, water gas shift reaction and combustion of product gases. These reactions may either be controlled by intrinsic kinetics or external mass transfer or diffusion through particle depending on coal type and operating conditions. $CO_2$ gasification and steam gasification of the char are two most important reactions in UCG, as they produce combustible gases [4]. For developing a process model, knowledge of the exact controlling step for a particular reaction, at the specified operating conditions, is very important.

The Thermo- Gravimetric Apparatus (TGA) is often used for kinetics determination because of the simple design and easy operation [5]. In TGA setup, gasification reaction may be limited by the reach (diffusion) of the gasification agent to the internal surfaces of the char particles. In addition to this, after some time, ash layer develops between the bulk of the gas and the surface of char as well as the char bed consists of small particles surrounded by empty spaces, through which the gasification agent has to diffuse to reach the external surfaces of the porous char particles. The diffusion processes may seriously affect the observed gasification rate and must be

considered when interpreting results of laboratory studies and determining the kinetic parameters [5,6].

In the case of UCG, the diffusion resistance to gas flow in the particle/bed of particles has an important role and it influences the overall rate of the reaction. Therefore we model these diffusion effects within bed of char particles. In the present work, $CO_2$ gasification data (weight of char vrs time and temp) and kinetic parameters determined by single layer TGA experiments[7] are used for determination of diffusion effects in full-crucible experiments.

## 2. Model Development

The present modeling exercise is for the same gasification experiments carried out with a cylindrical crucible of TGA filled with fine particles of char. The main assumptions of the model are:

1.  Continuum description of the porous solid bed.

2.  The system is two-dimensional and axisymmetrical.

3.  The char bed is composed of char and ash, and char is the only reacting species (no catalytic effect of ash). It is also assumed that the amount of ash and its bulk density remains constant during the conversion of the char bed.

4.  There is no disintegration process within the char bed structure, i.e. the height of the sample remains essentially constant.

5.  Perfect gas behavior is assumed for the gasifying agent.

6.  The flow of gas across the TGA crucible is assumed to be very fast and heat transfer to the wall of crucible is also assumed to be faster (constant temperature at all the walls and constant partial pressure of $CO_2$ at the top of TGA crucible).

7.  Diffusivity through char bed and ash layer is considered to be same.

Geometry considered for modeling is as shown in figure 1. Dimensions of the cylindrical crucible are 0.2 cm in height and radius both.

Considering all the assumptions stated above, following are the governing equations. Conservation equation for $CO_2$:

$$\frac{\partial C_{CO_2}}{\partial t} + \nabla \cdot (-D_{eff} \nabla C_{CO_2}) = R_{CO_2}$$

Where $C_{CO_2}$ is concentration $CO_2$, $D_{eff}$ is diffusivity of $CO_2$ through char and ash layer, $R_{CO_2}$ is rate of consumption of $CO_2$.
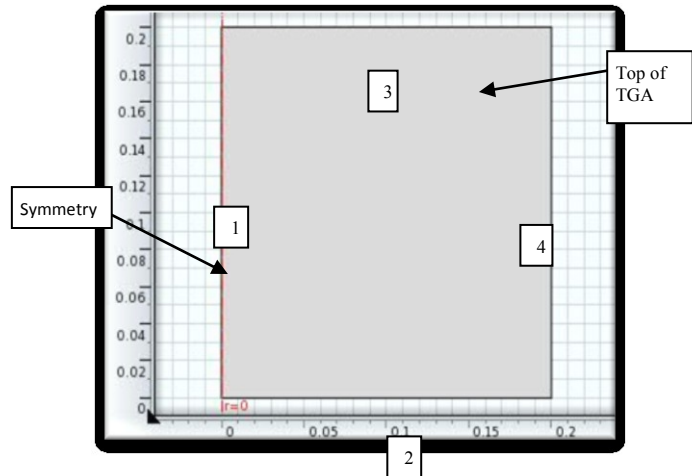


**Figure 1:** Axisymmetric geometry of TGA considered for modeling (numbers represent boundary number, used in specifying boundary conditions)

But for the $CO_2$ gasification of char, i.e. C + $CO_2$ → 2CO, the system is multicomponent, so the flux is defined as [8],

$$N_{CO_2} = -D_{eff} \nabla C_{CO_2} + x_{CO_2} \sum_{i=1}^{n} N_i$$

$$\text{and,} \quad N_{CO} = 2 N_{CO_2}$$

$$\therefore N_{CO_2} = -\frac{D_{eff}}{1 + x_{CO_2}} \nabla C_{CO_2}$$

Where $n$ is total number of components, $x_{CO_2}$ is mole fraction of $CO_2$ and $N$ denotes flux.

As a result of this, conservation equation for $CO_2$ becomes:

$$\frac{\partial C_{CO_2}}{\partial t} + \nabla \cdot \left( - \frac{D_{eff}}{1 + x_{CO_2}} \nabla C_{CO_2} \right) = R_{CO_2}$$

For char, conservation equation is as following:

$$\frac{\partial C_{char}}{\partial t} = R_{char}$$

Where $C_{char}$ is concentration of char and $R_{char}$ is rate of consumption of char which is defined by random pore model [9] (for exact expression, see table 2)

For conservation equation for energy is as following [8]:

$$\rho_{eff} \, C_{p-eff} \frac{\partial T}{\partial t} + \nabla \cdot \left( - k_{eff} \nabla T \right) = \Delta H * R_{char}$$

Where $\rho_{eff}$ is effective density, $C_{p-eff}$ is effective specific heat, $k_{eff}$ is effective thermal conductivity, $\Delta H$ is heat of reaction.

All the constant and dependent variable are defined in table 1 and 2.

**Table 1:** Constants used in TGA modeling

| Name | Expression |
|------|------------|
| R_g | 8.314[J/K/mol] |
| p_atm | 101325[Pa] |
| k0 | 1025600000/60 |
| E | 237020.00[J/mol] |
| psi | 3.479565177 |
| T_wall | (966+273.16)[K] |
| weight | 10.791[mg] |
| volume | pi*(.2^2)*.2*1e-6[m^3] |
| mol_wt | 12[g/mol] |
| w | weight/volume/mol_wt |
| ash_wt | 2.308[mg] |
| k_gas | (6.77e-2*(1239/1000)^.5)[W/m/K] |
| rho_init | (ash_wt+weight)/volume |
| delta_H | 11517[J/mol] |

| k_s | 14.46[W/m/K] |
|-----|--------------|
| por_init | .2531 |

**Table 2:** Variables used in TGA modeling

| Name | Expression |
|------|------------|
| rate | k*pco2^(.4679)*sqrt(1-psi*log(1-X))*c_c*flc2hs(c_co2,1e-4) |
| p_co2 | p_atm |
| k | k0*exp(-E/R_g/T) |
| X | max(Xdash/c_cinit,0) |
| c_cinit | weight/volume/mol_wt |
| pco2 | max(c_co2*R_g*T/101325[Pa],eps^2) |
| D_c_co | (6.2/600000)[m^2/s] |
| D_c_co2 | (6.2/600000)[m^2/s] |
| c_co2init | p_co2/R_g/T |
| Xdash | (c_cinit-c_c) |
| k_eff1 | k_s*(1-por)+k_gas*por |
| rho_eff | c_c*mol_wt+ash_wt/volume |
| Cp_eff | 1000[J/kg/K] |
| phi | rho_eff/rho_init |
| x_ash | ash_wt/(ash_wt+weight) |
| por | 1-((1-por_init)*(1-(1-x_ash)*X)) |
| K_eff | (1-eps) /((1/k_s)+ (1/(k_gas/psi_+dp*hrs))) |
| eps | por |
| dp | 100e-6[m] |
| psi_ | .1 |
| hrs | .1952*(p/(2-p))*(1239/100)^3 |
| hrv | (.1952/(1+(eps/2/(1-eps)*((1-p)/p))))*(T/100)^3 |
| p | .75 |

Following are the boundary conditions:

-   At boundary 1: Axial symmetry.
-   At boundary 2: No flux for $CO_2$, CO and char and constant temperature (T_wall)
-   At boundary 3: const conc for $CO_2$ and CO (c_co2init, 0 respectively), no flux for char, constant temp (T_wall)
-   At boundary 4: No flux for $CO_2$, CO and char and constant temperature (T_wall)

Following are the initial values:

-   Zero concentration for $CO_2$ and CO, c_cinit for char and T_wall for temperature.

## 3. Results and Discussions

These simulations are performed with known kinetics but an unknown diffusivity which becomes a fitting parameter for these simulations. Fitted value of diffusivity is 6.2 $cm^2$/min. Diffusivity is determined by fitting simulation data with experimental conversion for different diffusion coefficients. A fit of the conversion is shown in figure 2.
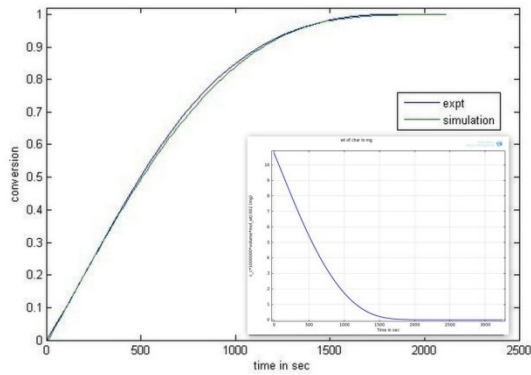


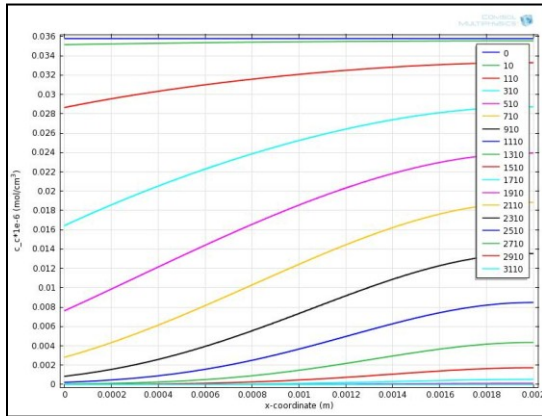**Figure 2:** Profile of char conversion: experimental and simulation, (Inset: profile of char weight)



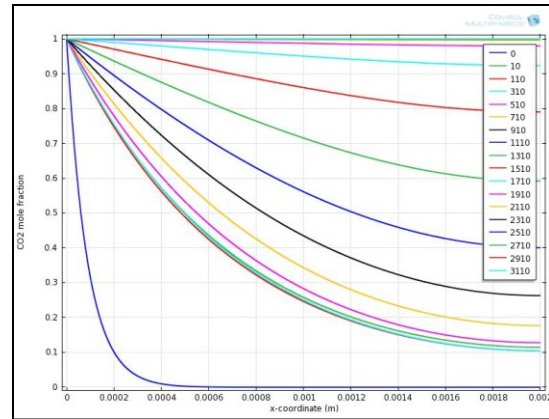**Figure 3:** Char concentration profile inside crucible at different times



**Figure 4:** $CO_2$ mole fraction profile inside crucible at different times
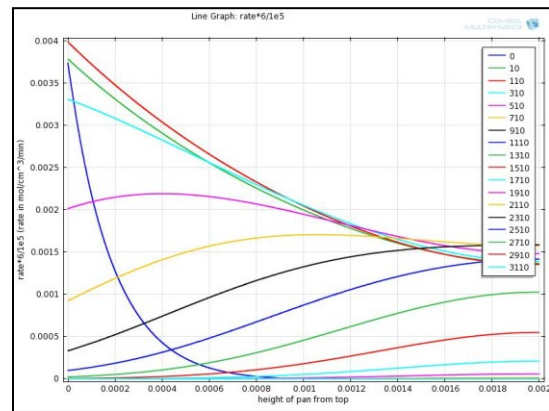


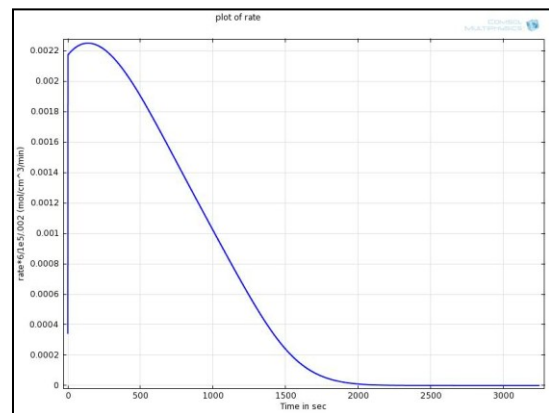**Figure 5:** Reaction rate profile at different time along height of TGA crucible



**Figure 6:** Total surface averaged reaction rate profile at different time

As $CO_2$ starts diffusing through the char bed and later through ash layer, char gasification starts. As the rate of reaction is not very high, $CO_2$ diffuses inside the crucible and starts reacting there too, while the char at top is gasifying. As a result the char concentration at all the positions inside crucible starts reducing as shown in figure 3. Profiles of $CO_2$ diffusing into the crucible, as shown in figure 4, doesn't follow a straight line, as part of it is getting consumed during diffusion. Figure 5 shows profiles of reaction rate. It can be seen that initially, rate is high near the top as $CO_2$ and char both are available in large quantities. But as the char reacts, the rate reduces near the top and same time, peak in the rate profile (figure 5) shifts towards the bottom of crucible. The surface averaged rate profile of gasification reaction shows a peak in its profile (figure 6), it is indication of the time at which $CO_2$ has reached throughout the crucible and it is readily available for reaction. As a result of this, char reacts at this highest rate and its concentration decreases, and this itself becomes a reason for decrease in rate after attaining the peak value.

Initially the simulations were run with a constant temperature of char, and it was considered to be equal to temperature of bottom wall of TGA crucible (available in TGA data). This assumption was considered to be valid as the heat of reaction as well as rate of reaction of gasification are not very high and the TGA crucible is very small.
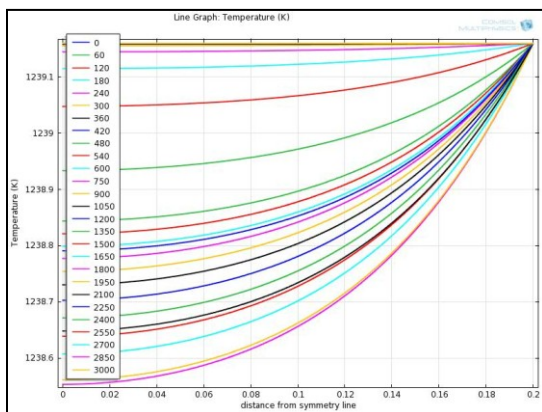


**Figure 7:** Profile of temperature of char along a horizontal line passing through centre of crucible
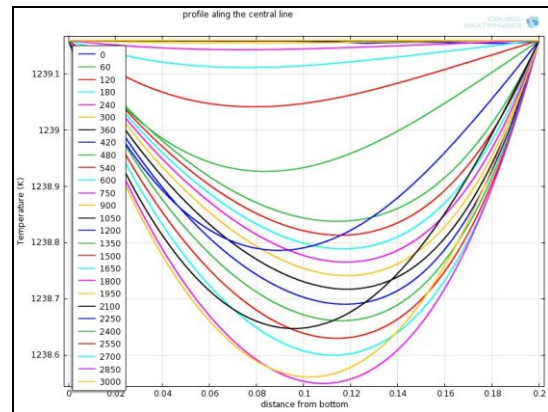


**Figure 8:** Profile of temperature of char along a vertical line passing through centre of crucible

To check the validity of constant temperature assumption, heat transfer enabled simulation is carried out. Governing equation and boundary conditions for this simulation are given initially. Figure 7 and 8 are results of HT enabled simulations. It can be observed that variation in temperature is very less. Minimum temperature attained in crucible is 0.6 K less than the initial temperature. So our assumption of constant temperature stands valid in case of $CO_2$ gasification, as it has very less effect on conversion. But the same will not be true with any highly endo/exotheric fast reaction e.g. char oxidation.

## 4. Conclusion

A one-dimensional reaction diffusion model is developed for the reaction in the bed by assuming linear change of diffusivity within the bed and this model is able to explain the bed diffusion and kinetics of monolith particles of all the coals. Thus the relevant parameters such as rate constants and diffusivities are successfully estimated for the coals of interest as regards to underground coal gasification. The kinetic model developed in the present work can be suitably incorporated in the global process model of UCG.

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