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# A Comprehensive Model of Trace Element Distribution in Solid and Gas Phases from Waste Wood Combustion in 250-kW Pilot-scale Entrained Flow Combustion Unit

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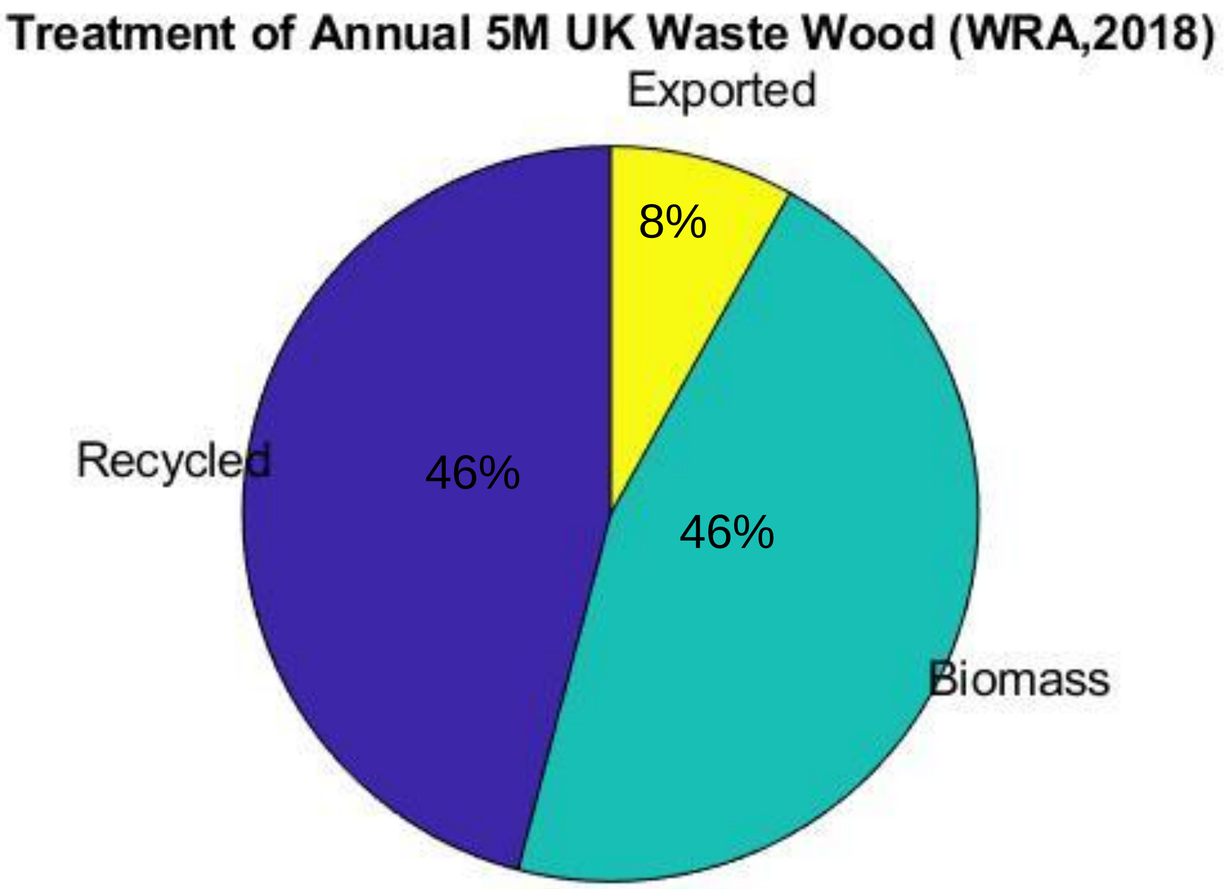
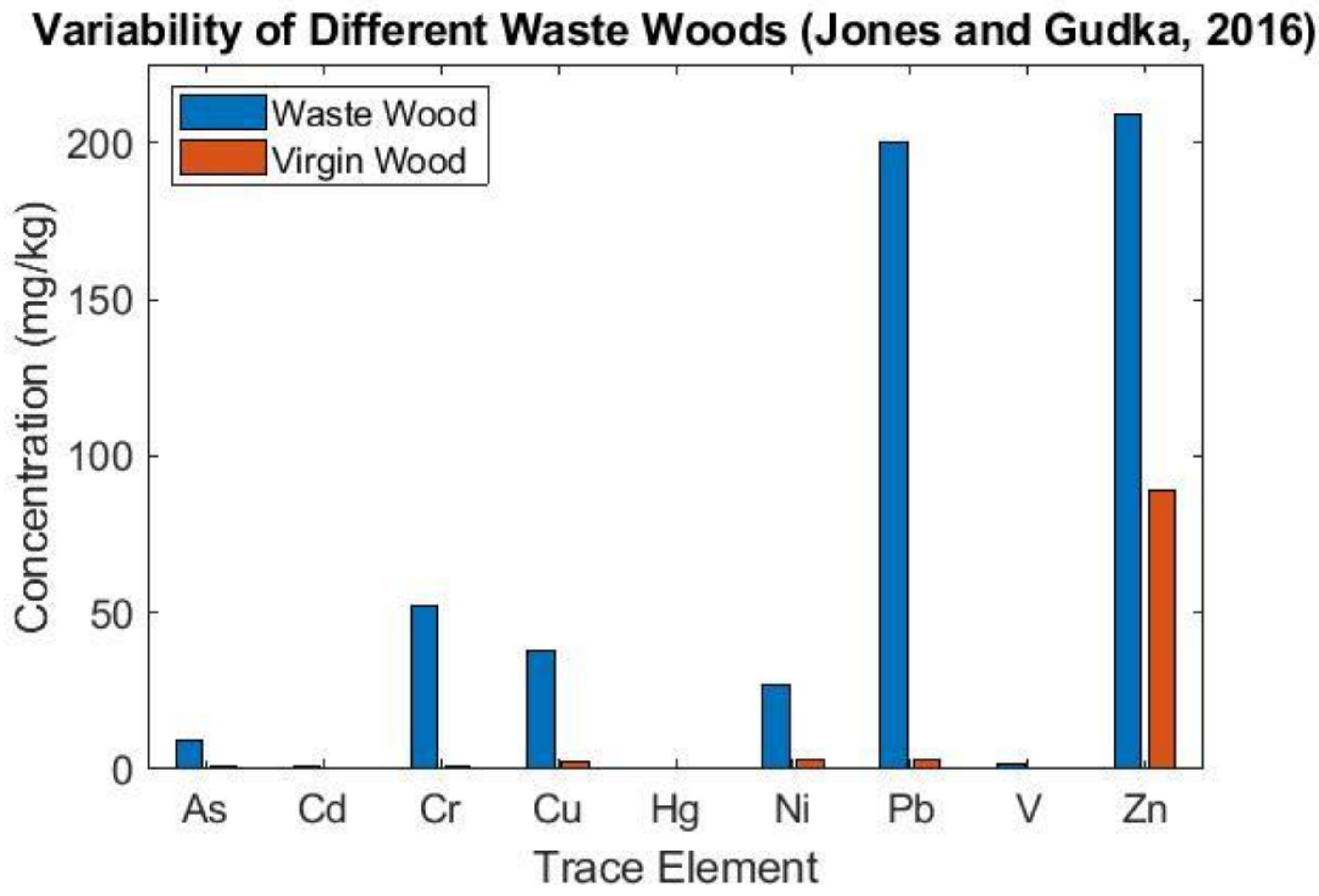
**Content**


Treatment of Annual 5M UK Waste Wood (WRA,2018)
Exported
8%
Recycled
46%
46%
Biomass


Variability of Different Waste Woods (Jones and Gudka, 2016)
Waste Wood
Virgin Wood
Concentration (mg/kg)
0
50
100
150
200
As
Cd
Cr
Cu
Hg
Ni
Pb
V
Zn
Trace Element

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## Background

**Waste Wood Trace Element Origin**

Fossil Fuel Emission
Element: Hg and Cd

Chromated Copper Arsenate
Element: Cr, Cu, and As

Siccative and Coating
Element: Co

Vanadium Carbide Coating
Element: V

Plating and Coating
Element: Ni

Paint
Element: Cr and Pb

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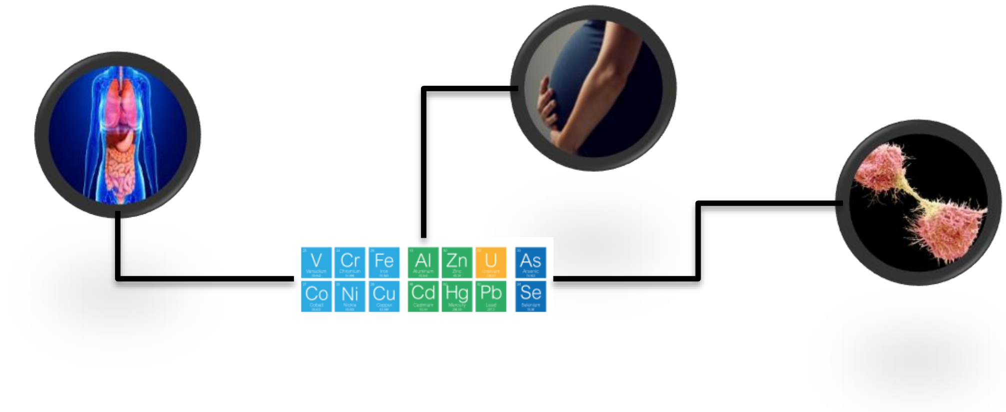
## Background
**Trace Element Health Impact**




### As

- Lung Cancer
- Nausea
- Skin Irritation

### Cd

- Respiratory Irritation
- Kidney Failure
- Bone Deformities
- Osteoporosis
- Renal Dysfunction
- Liver Fibrosis
- Oxidative Stress

### Cr

- Cell Growth Failure
- Cell Apoptosis

### Pb

- Ca Deficiency
- Neurotoxicity
- Cognitive Failure
- Reproductive Failure
- Parkinson’s Disease

### Hg

- Neurotoxicity
- Neural Inflammation
- Oxidative Stress

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## Directive 2010/75/EU

| Element and Its Compound | Emission Limit (mg/Nm3) |
|---|---|
| Cd | Total: 0.05 |
| Tl | |
| Hg | 0.05 |
| Sb | Total: 0.5 |
| As | |
| Pb | |
| Cr | |
| Co | |
| Cu | |
| Mn | |
| Ni | |
| V | |

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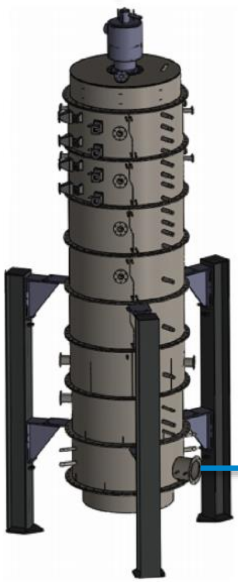
1. To predict the distribution of trace elements within emissions resulting from waste wood combustion and the formation of liquid/eutectics at biomass particle surface
2. To create a comprehensive tool to calculate the occurrence of trace and ash-forming elements from combustion of various waste wood types
3. To assess this information in order to optimise the conditions and minimise the trace element emissions and ash deposition in association with particle surface liquid formation

# Combustion Experiment

## 250kW PACT Facility Burner

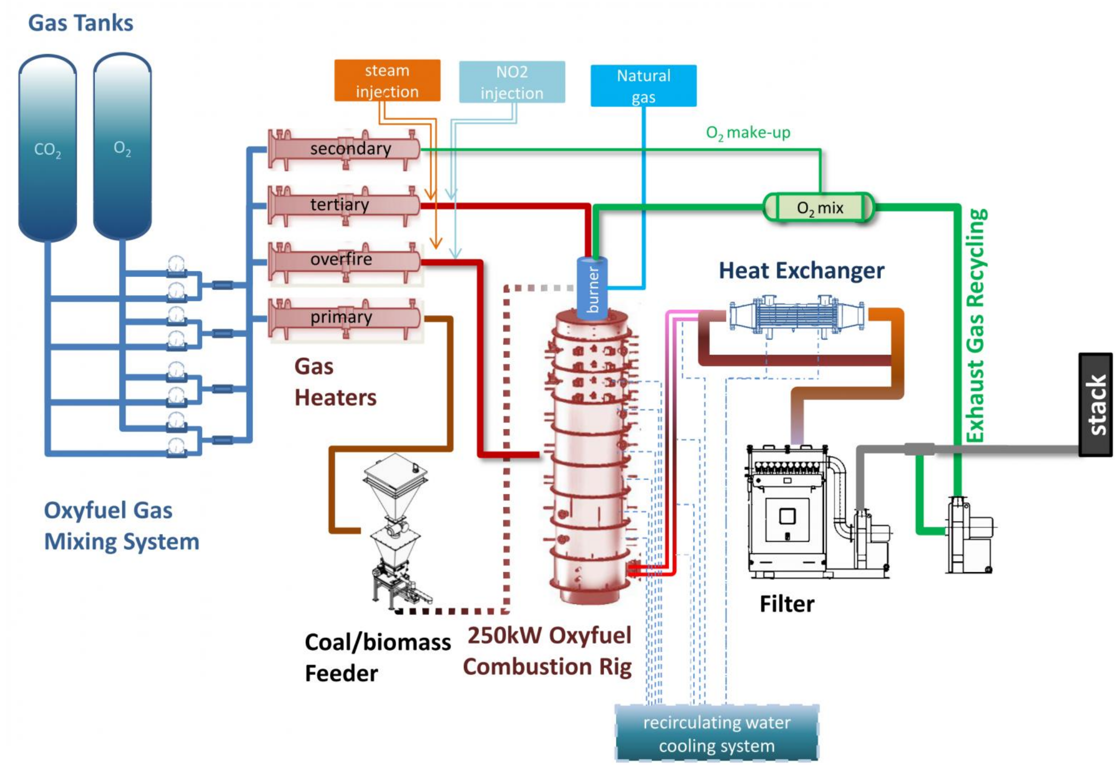
Waste Wood
+
Air



Trace Element

Ash + Trace Element

250kW Oxyfuel Combustion Plant for Coal/Biomass



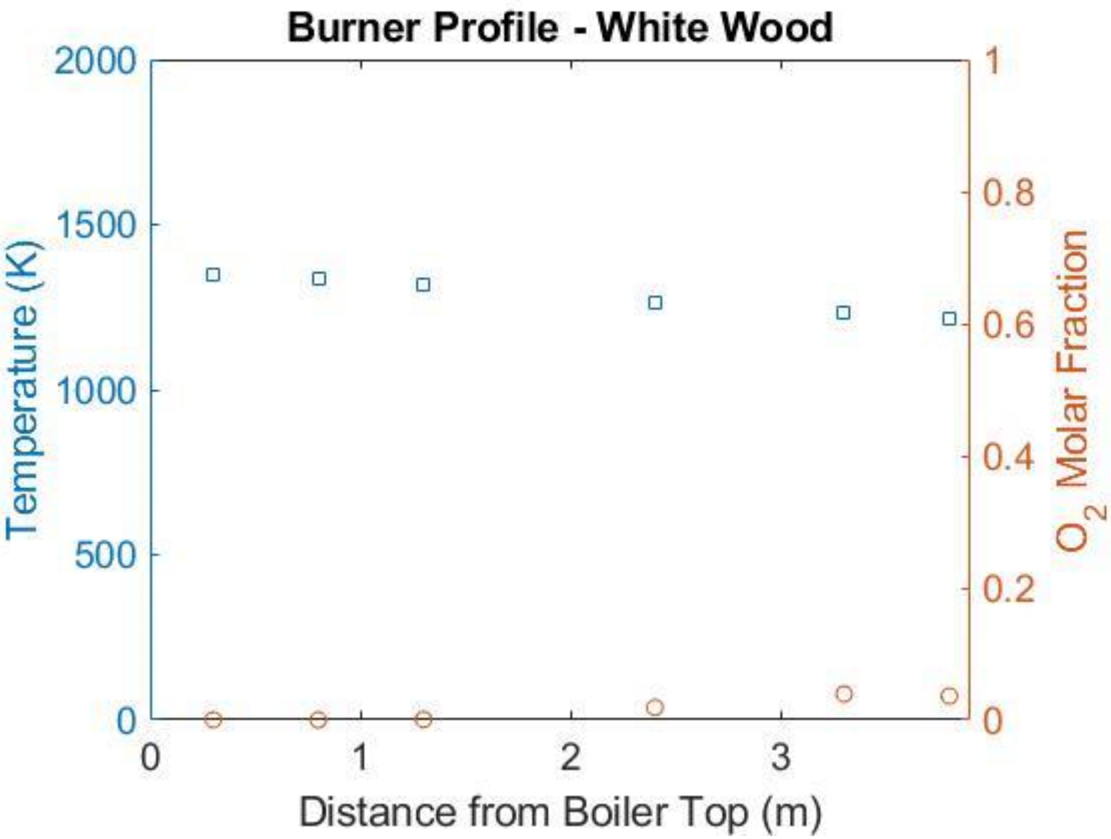
## Combustion Experiment

**White Wood Combustion**

Boiler – 250-kW PACT Facility
Type – Entrained Flow without Bottom Bed
Location – Sheffield, England
Biomass – US White Wood Pellet
Biomass Flow Rate – 39.8 kg/h
Gas – Air
Gas Flow Rate – 2.789 mol/s

Proximate Analysis (Mass Fraction)
Moisture – 6.69%
Volatiles – 78.1%
Fixed Carbon – 14.51%
Ash – 0.7%

Ultimate Analysis (Mass Fraction)
N – 0.15%
C – 48.44%
H – 6.34%
S – less than 0.02%
Cl – less than 0.01%
O – 37.69%
GHV – 19.41 (kJ/kg)



- Release Rate
  - $\frac{d[X]}{dt} = Ae^{\left(\frac{-E_A}{RT}\right)}[X]$
- Reaction Rate
  - $aX + bY \rightarrow Product$
  - $\frac{d[X]}{dt} = -Ae^{\left(\frac{-E_A}{RT}\right)}[X]^a[Y]^b$
- Transfer Rate (for both temperature and concentration)
  - $\frac{\partial[X]}{\partial t} = \frac{D_{eff\,p}}{r}\frac{\partial}{\partial r}\left(r\frac{\partial[X]}{\partial r}\right) + D_{eff\,p}\frac{\partial^2[X]}{\partial z^2} + \frac{1}{r}\frac{\eta_p}{\mu_p}\frac{\partial}{\partial r}\left(r[X]\frac{\partial p}{\partial r}\right) + \frac{\eta_p}{\mu_p}\frac{\partial}{\partial z}\left([X]\frac{\partial p}{\partial z}\right)$
  - $\frac{\partial T}{\partial t} = \frac{\alpha}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) + \alpha\frac{\partial^2 T}{\partial z^2}$
- Total Rate (for both temperature and concentration)
  - $\frac{\partial[X]}{\partial t}_{total} = \frac{\partial[X]}{\partial t}_{release} + \frac{\partial[X]}{\partial t}_{reaction} + \frac{\partial[X]}{\partial t}_{transfer}$
  - $\frac{\partial T}{\partial t}_{total} = \frac{\partial T}{\partial t}_{release} + \frac{\partial T}{\partial t}_{reaction} + \frac{\partial T}{\partial t}_{transfer}$

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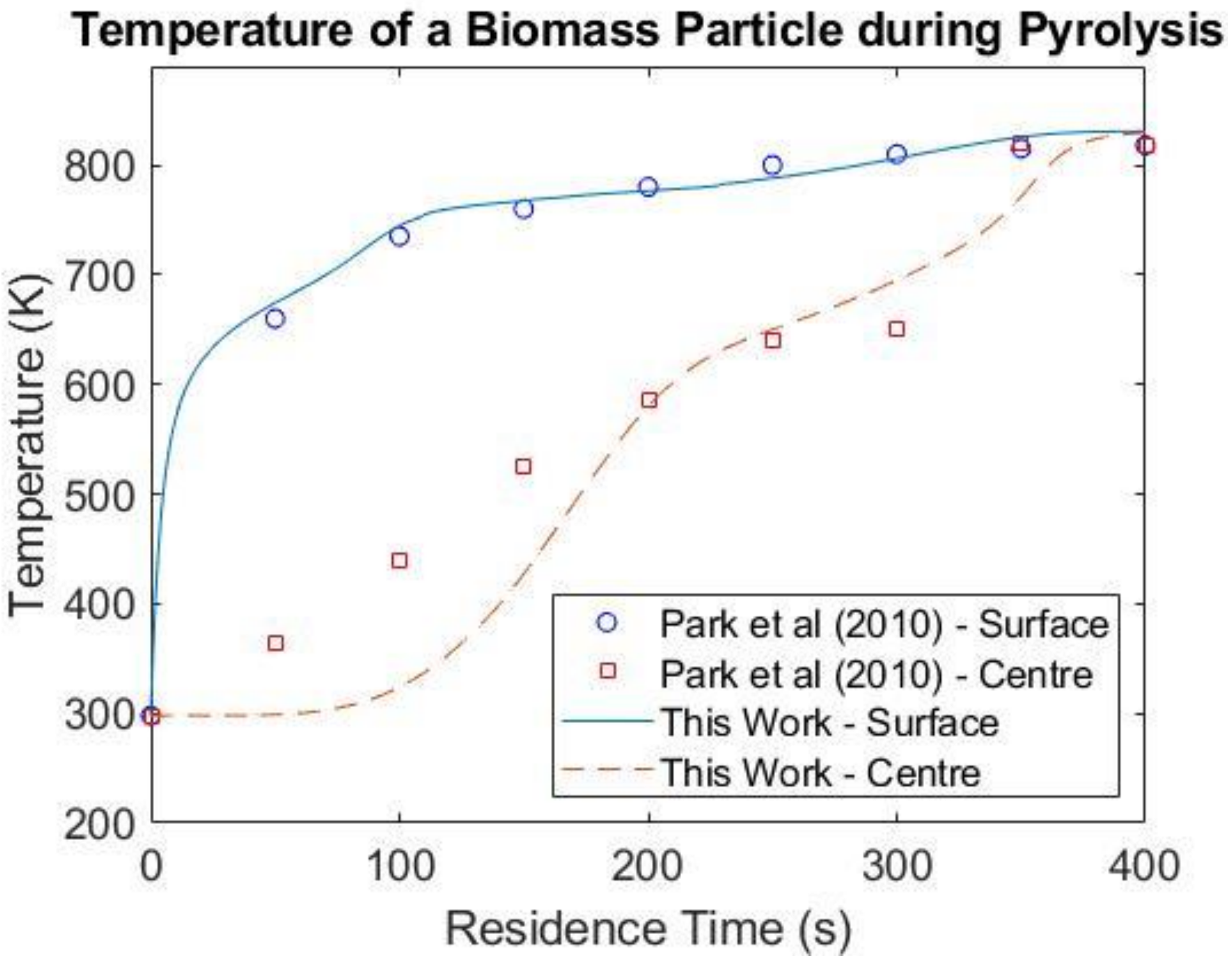
# Combustion Model

**Single Particle Model**

| Reaction | Kinetic Formula | Pre-exponential Factor, A | Activation Energy, $E_A$ | Reference |
|---|---|---|---|---|
| $CH_4 + 1.5O_2 \rightarrow CO + H_2O$ | $r_{CH_{4(g)\_p}} = -Ae^{\left(-\frac{E_A}{RT}\right)} \left(\frac{[CH_{4(g)\_p}]}{\varepsilon}\right)^{0.7} \left(\frac{[O_{2(g)\_p}]}{\varepsilon}\right)^{0.8} \varepsilon$ | $1.5849(10^{10})$ | 202,505.6 | (Dryer & Glassman, 1973) |
| $CO + 0.5O_2 \rightarrow CO_2$ | $r_{CO_{(g)\_p}} = -Ae^{\left(-\frac{E_A}{RT}\right)} \left(\frac{[CO_{(g)\_p}]}{\varepsilon}\right) \left(\frac{[O_{2(g)\_p}]}{\varepsilon}\right)^{0.25} \left(\frac{[H_2O_{(g)\_p}]}{\varepsilon}\right)^{0.5} \varepsilon$ | $1.2589(10^{10})$ | 179,912 | (Dryer & Glassman, 1973) |
| $H_2 + 0.5O_2 \rightarrow H2O$ | $r_{H_{2(g)\_p}} = -Ae^{\left(-\frac{E_A}{RT}\right)} \left(\frac{[H_{2(g)\_p}]}{\varepsilon}\right)^{0.25} \left(\frac{[O_{2(g)\_p}]}{\varepsilon}\right)^{1.5} \varepsilon$ | $3.8239(10^{13})T^{-1}$ | 167,360 | (W. P. Jones & Lindstedt, 1988) |
| $CO + H_2O = CO_2 + H_2$ | $r_{CO_{(g)\_p}} = -Ae^{\left(-\frac{E_A}{RT}\right)} \left(\frac{[CO_{(g)\_p}]}{\varepsilon}\right) \left(\frac{[H_2O_{(g)\_p}]}{\varepsilon}\right) \varepsilon$ | $2.75(10^{6})$ | 83,680 | (W. P. Jones & Lindstedt, 1988) |
| $CH_4 + H_2O = CO + 3H_2$ | $r_{CH_{4(g)\_p}} = -Ae^{\left(-\frac{E_A}{RT}\right)} \left(\frac{[CH_{4(g)\_p}]}{\varepsilon}\right) \left(\frac{[H_2O_{(g)\_p}]}{\varepsilon}\right) \varepsilon$ | $3(10^{5})$ | 125,520 | (W. P. Jones & Lindstedt, 1988) |
| $Char + 0.5O_2 \rightarrow CO$ | $r_{O_{2(g)\_p}} = -Ae^{\left(-\frac{E_A}{RT}\right)} p_{O_{2(g)p}}{}^{0.53} \rho_{char}{}^{0.47} \frac{1000}{MW_C}$ | $5.3(10^{5})$ | 125,000 | (Janse et al, 1998) |
| $Char + CO_2 \rightarrow 2CO$ | $r_{CO_{2(g)p}} = -Ae^{\left(-\frac{E_A}{RT}\right)} p_{CO_{2(g)p}}{}^{0.8} \rho_{char}{}^{\frac{2}{3}} \frac{1000}{MW_C}$ | $9.1(10^{6})T^{-0.8}$ | 166,000 | (Aarsen et al, 1985) |
| $Char + H_2O \rightarrow CO + H_2$ | $r_{H_2O_{(g)p}} = -Ae^{\left(-\frac{E_A}{RT}\right)} p_{H_2O_{(g)p}}{}^{0.41} \rho_{char} \frac{1000}{MW_C}$ | $5.3(10^{5})$ | 179,000 | (Kojima et al, 1993) |

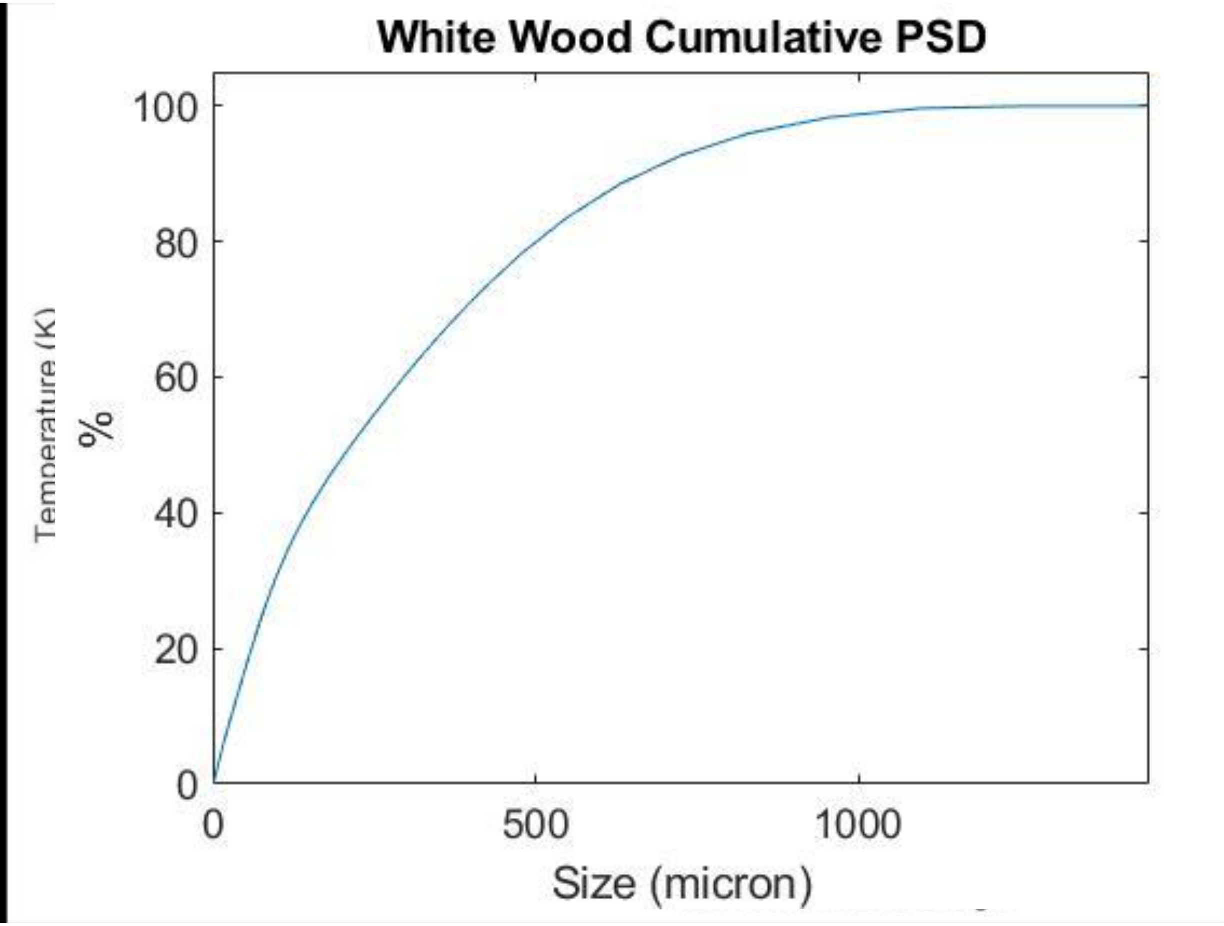
## Combustion Model
**Model Validation**




Park DK, Kim SD, Lee SH, Lee JG. Co-pyrolysis characteristics of sawdust and coal blend in TGA and a fixed bed reactor. Bioresource technology. 2010 Aug 1;101(15):6151-6.
Mason PE, Darvell LI, Jones JM, Pourkashanian M, Williams A. Single particle flame-combustion studies on solid biomass fuels. Fuel. 2015 Jul 1;151:21-30.

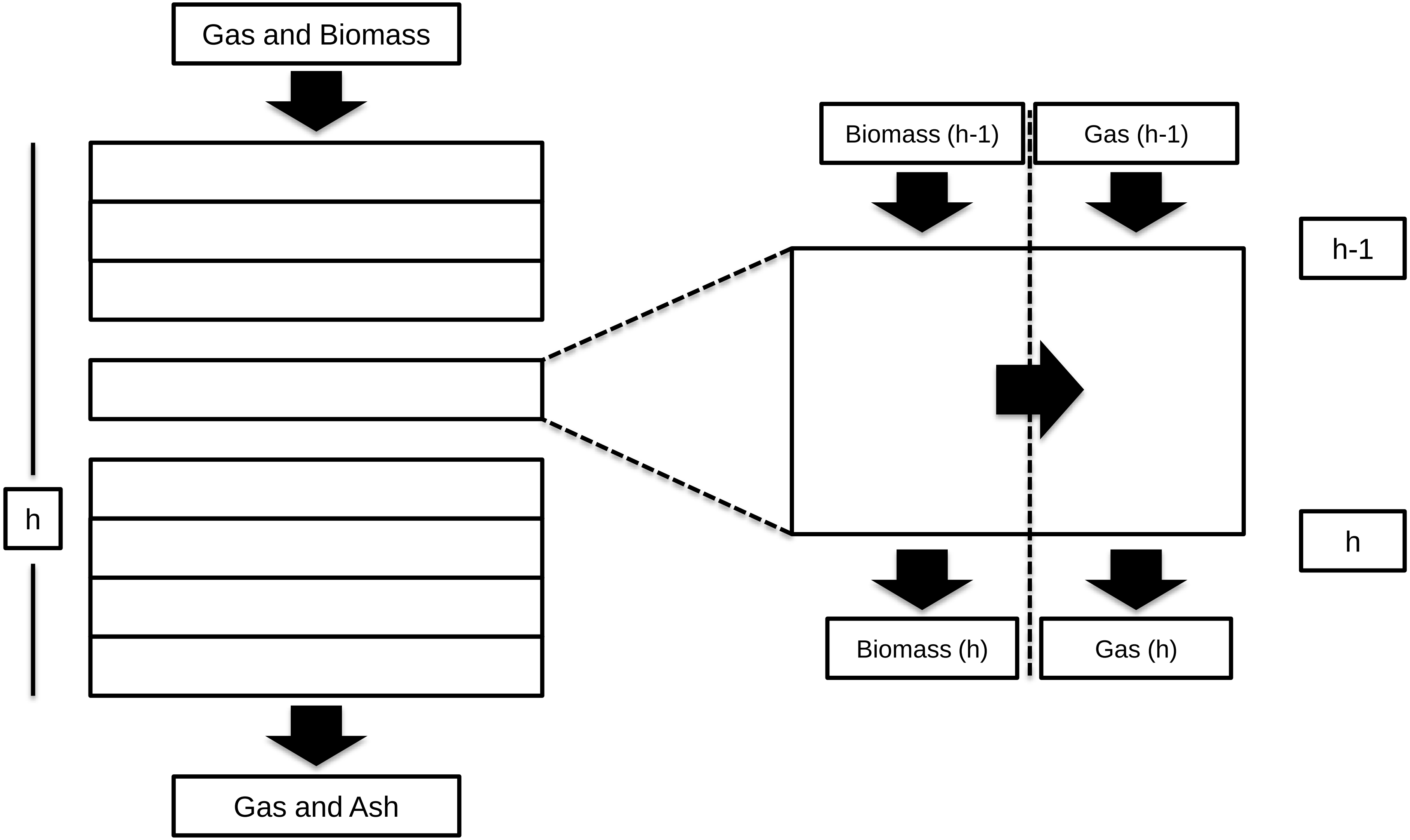
# Combustion Model

**Discretised Model – Temperature Uniformity**



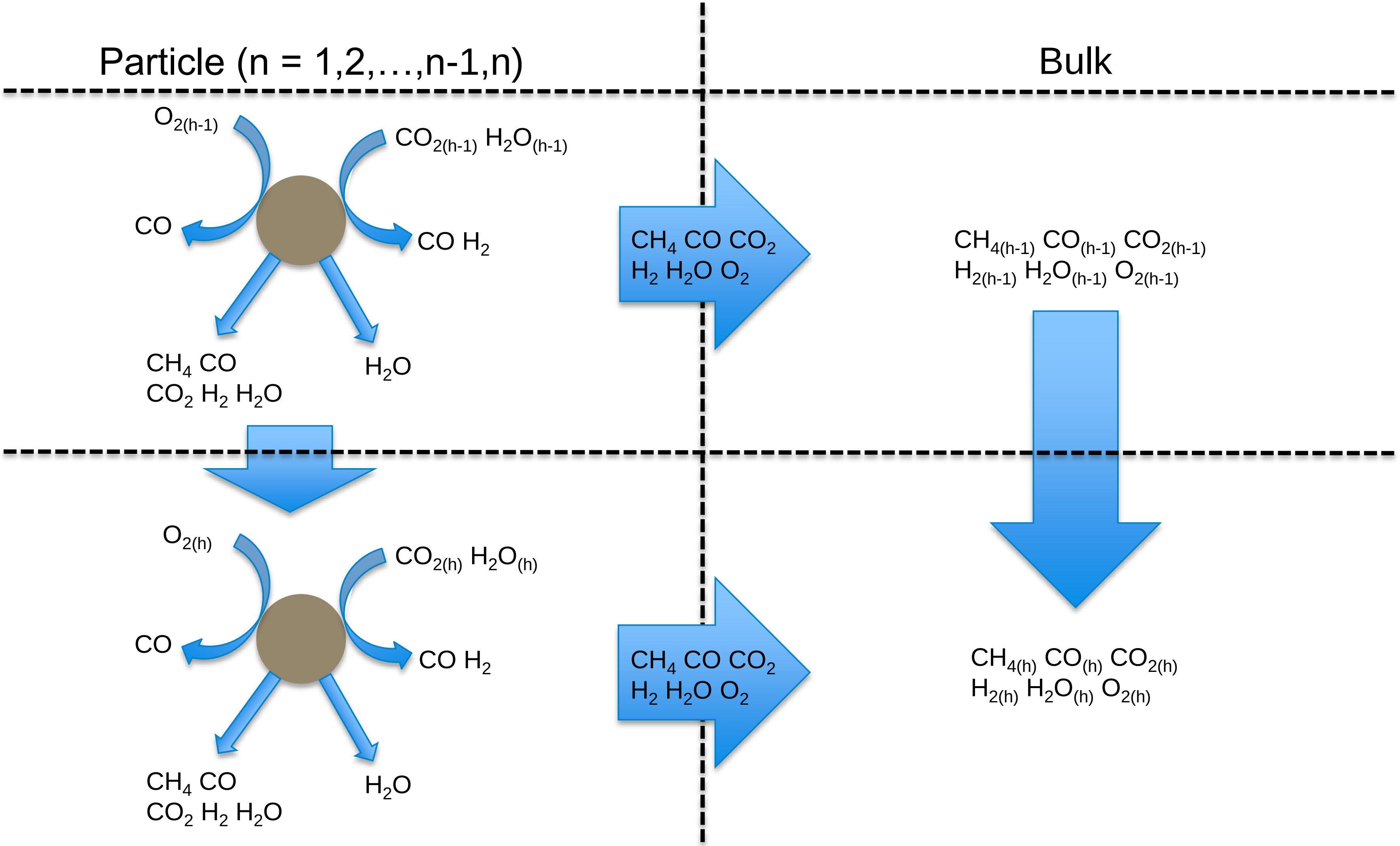
## Combustion Model

**Model Hierarchy**



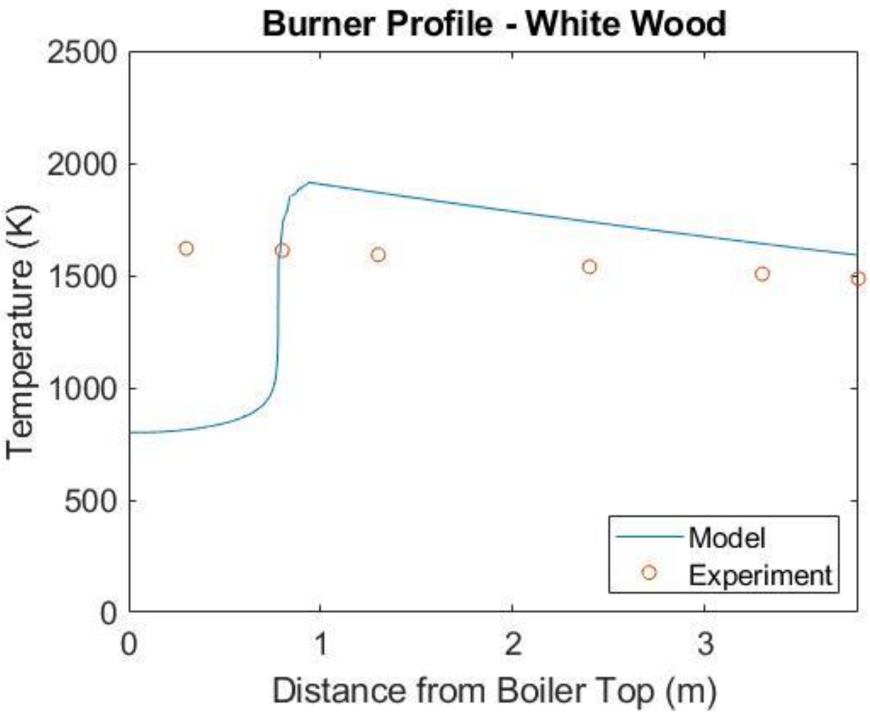
## Combustion Model

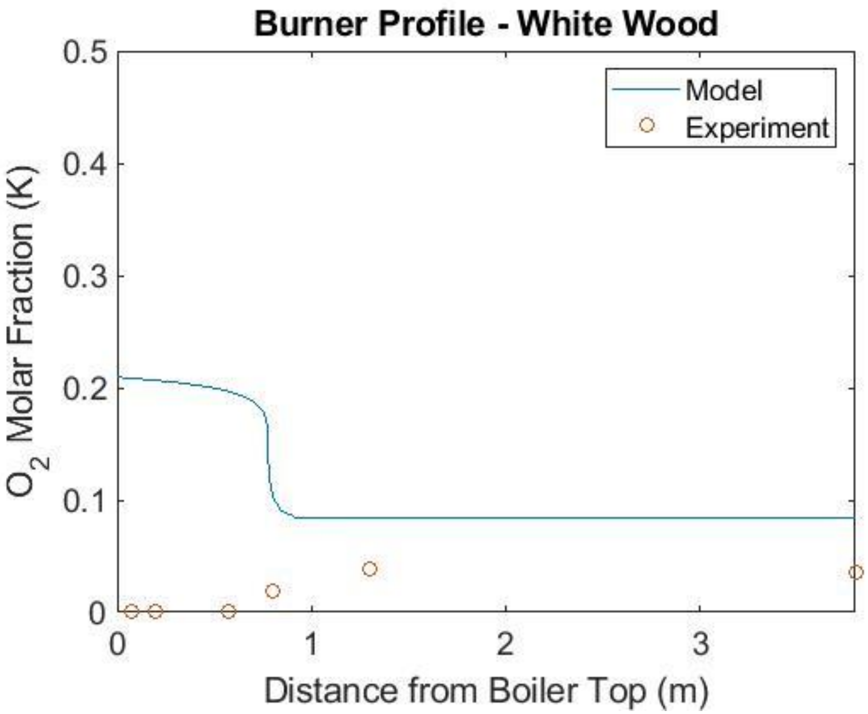
**Model Hierarchy**



**Combustion Model**

**White Wood Combustion Validation**

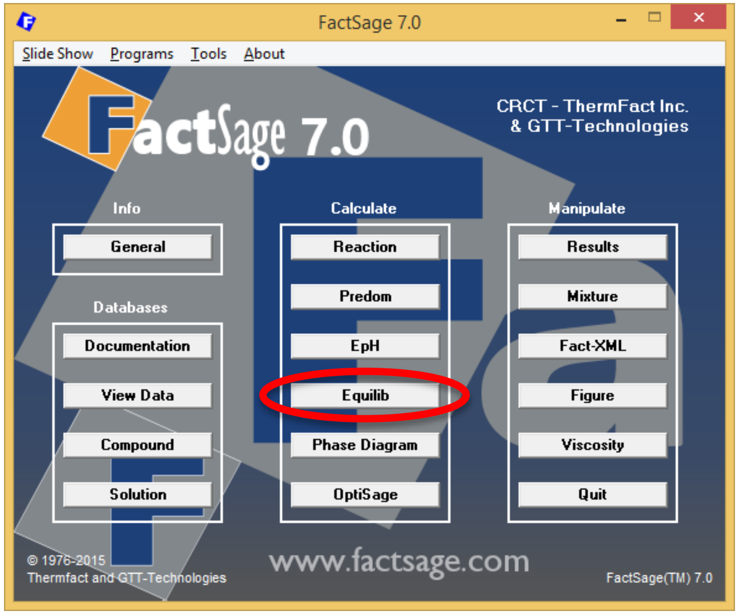


Trace element and ash-forming element phases and amounts are calculated based on minimisation of Gibb's energy.

1. Lack of available reaction kinetic data
2. Reduce calculation complexity of multi-elements

Equilibrium phase and mass are calculated using Equilib module in FactSage™.




$$G = \sum_{\substack{ideal\\gas}} n_i\left(g_i{}^o + RT\ln P_i\right) + \sum_{\substack{pure\\condensed\\phase}} n_i\, g_i{}^o + \sum_{solution\ 1} n_i\left(g_i{}^o + RT\ln X_i + RT\ln\gamma_i\right)$$

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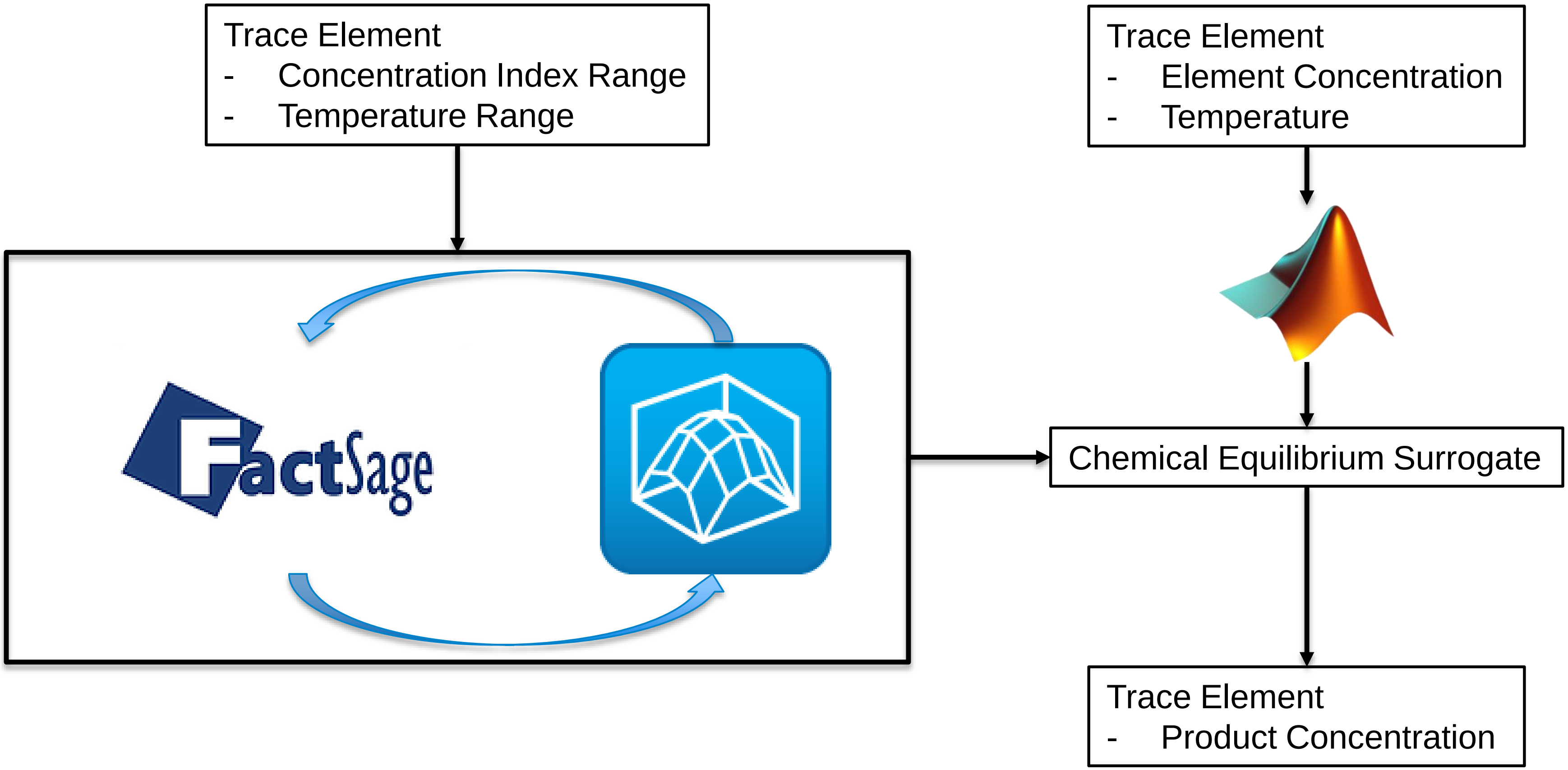
## Chemical Equilibrium Model

**Chemical Equilibrium Surrogate**



## Chemical Equilibrium Model
**Elemental Balance**

Old ($CH_4$, $CO$, $CO_2$, $H_2$, $H_2O$, $O_2$, $N_2$), Old Ash-forming Compound, Old Trace Compound

↓

Old (C, H, O, N) and Old (S, Cl, Al, Ca, Fe, K, Mg, Mn, Na, P, Si, Ti, As, Cd, Cr, Cu, Pb, Hg, Ni, V, Zn)

↓

Chemical Equilibrium Surrogate

↓

Equilibrium Product

- New Trace Compound
- New Ash-forming Compound
- New C = (C in $CH_4$, $CO$, and $CO_2$) – (C in New Trace Compound and New Ash-forming Compound)
- New H = (H in $CH_4$, $H_2$, and $H_2O$) – (H in New Trace Compound and New Ash-forming Compound)
- New O = (O in $CO$, $CO_2$, $H_2O$, and $O_2$) – (O in New Trace Compound and New Ash-forming Compound)
- New N = (N in $N_2$) – (N in New Trace Compound and New Ash-forming Compound)

↓

Equilibrium Product

$CH_4 + CO + CO_2$ = New C

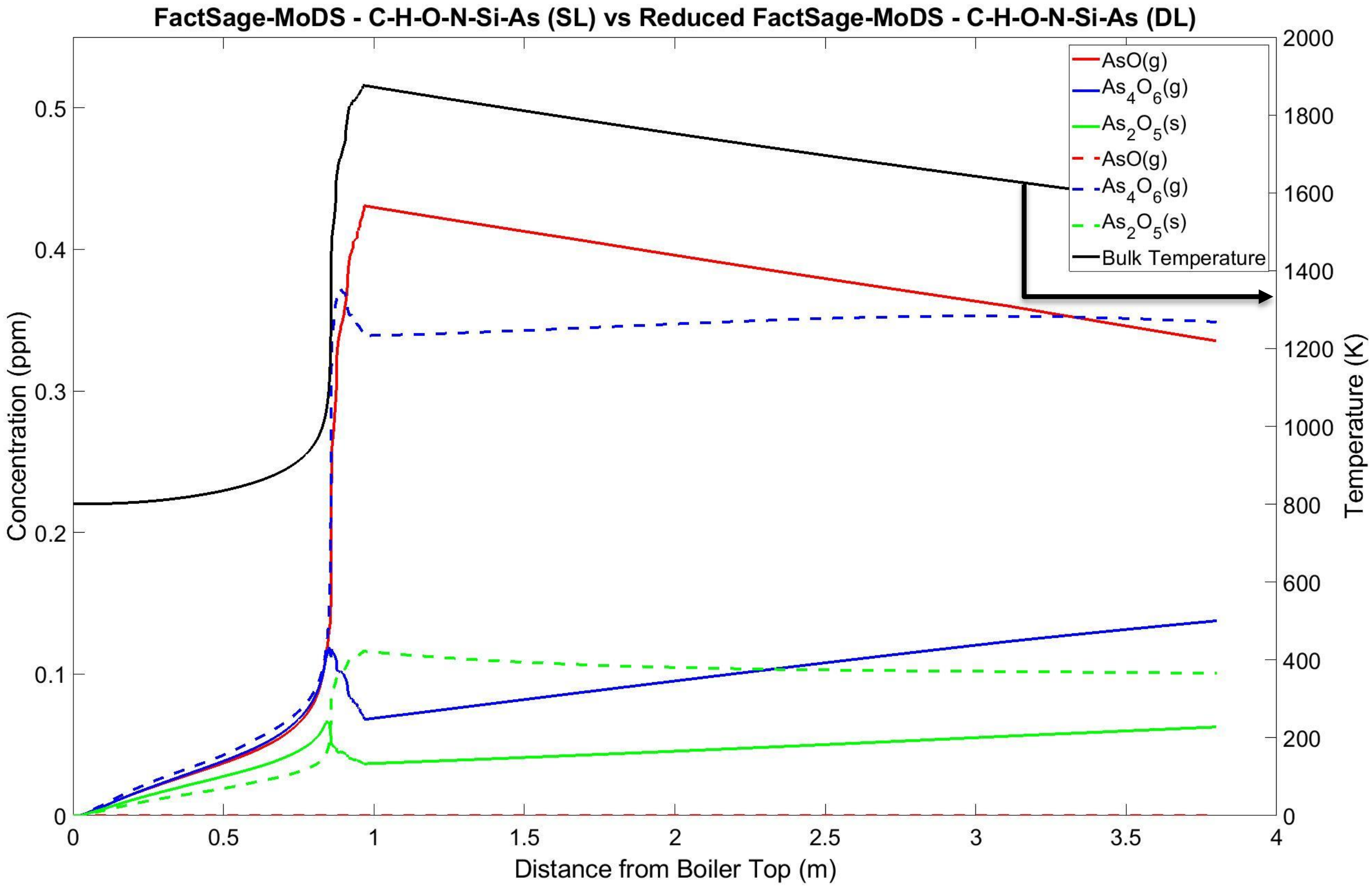
$4CH_4 + 2H_2 + 2H_2O$ = New H

$CO + 2CO_2 + H_2O + 2O_2$ = New O

$2N_2$ = New N

# Chemical Equilibrium Model

**Reduced Chemical Equilibrium**



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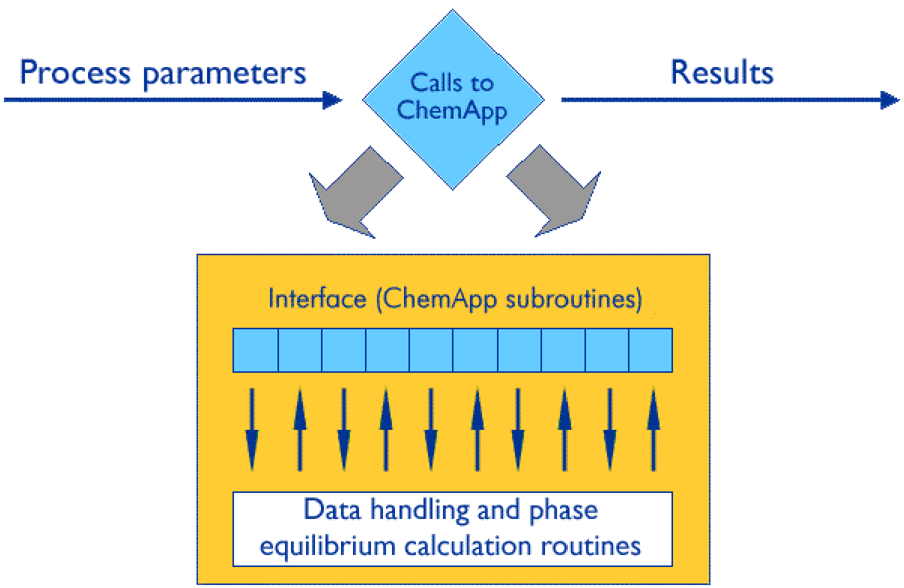
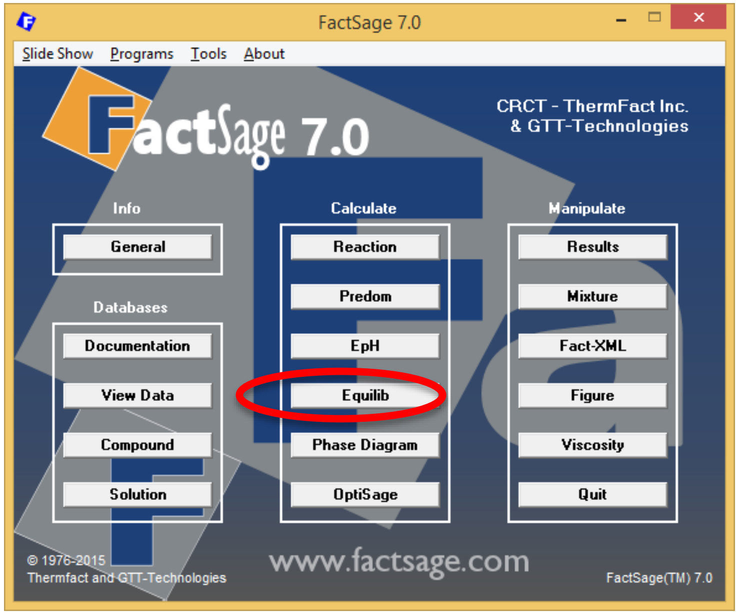
# Chemical Equilibrium Model

**Minimisation of Gibb's Energy**

## ChemApp




## FactSage




$$G = \sum_{\substack{ideal\\gas}} n_i\left(g_i{}^o + RT\ln P_i\right) + \sum_{\substack{pure\\condensed\\phase}} n_i\, g_i{}^o + \sum_{solution\ 1} n_i\left(g_i{}^o + RT\ln X_i + RT\ln \gamma_i\right)$$

# Chemical Equilibrium Model

**Chemical Equilibrium Library**


Transparent Data File (.cst)

Visual Studio

- Dynamic Link Library (.dll)
- ChemApp Interface (.c)
- Transparent Data File (.cst)
- Binary Data File (.bin) for Fortran

Trace Element
- Element Concentration
- Temperature

Mex File

Trace Element
- Product Concentration

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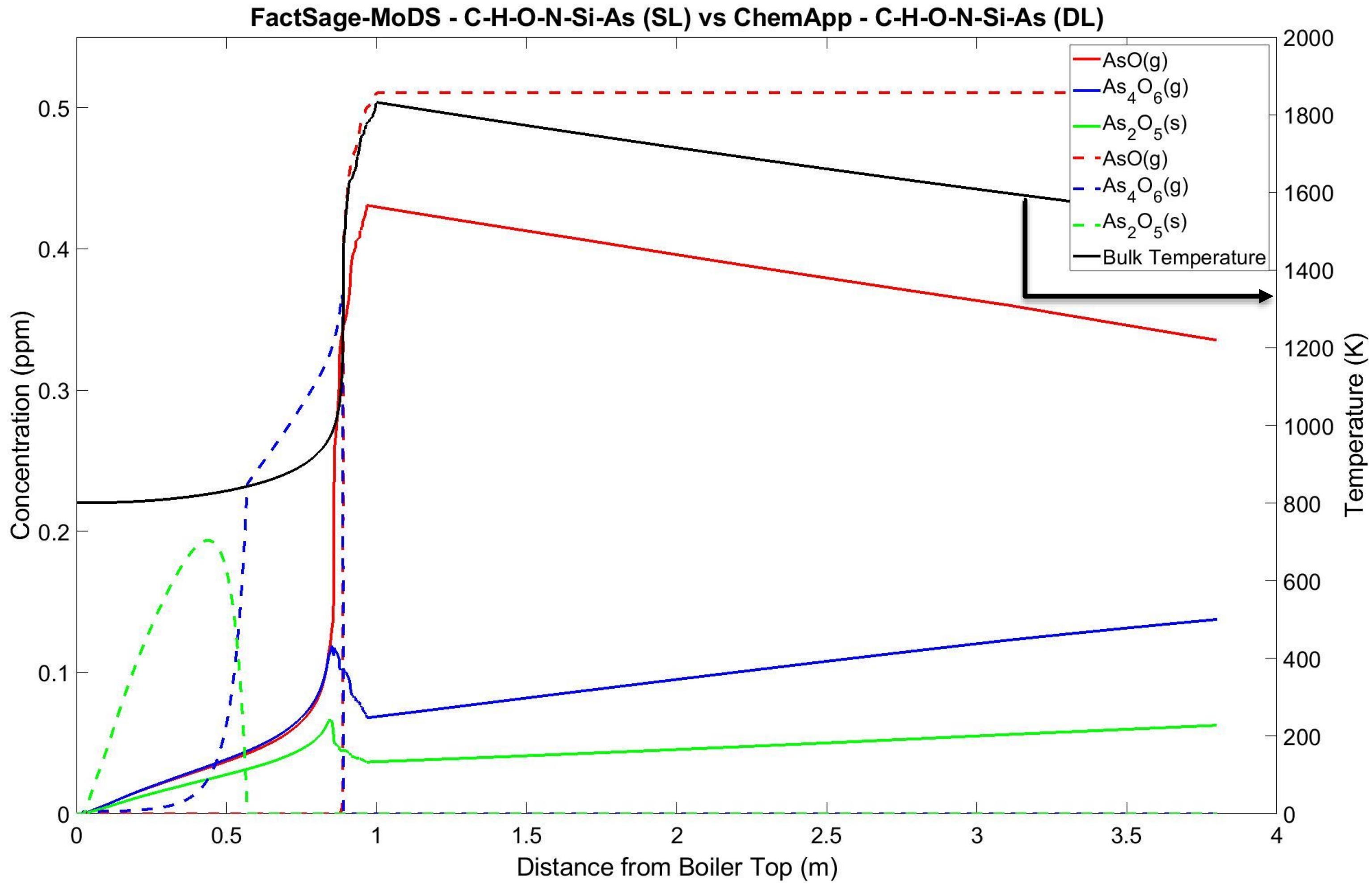
## Chemical Equilibrium Model

**ChemApp and FactSage-MoDS Comparison**



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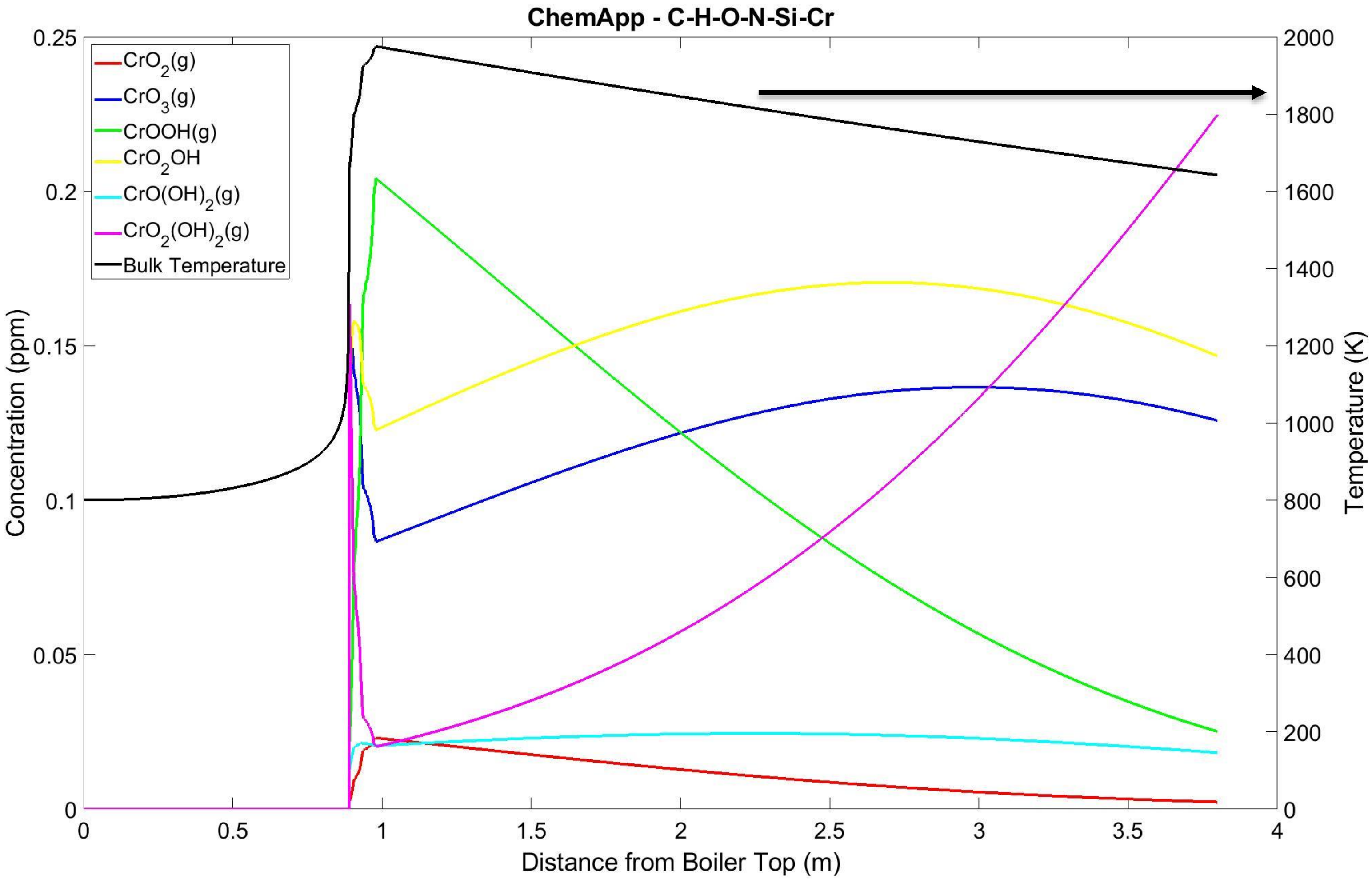
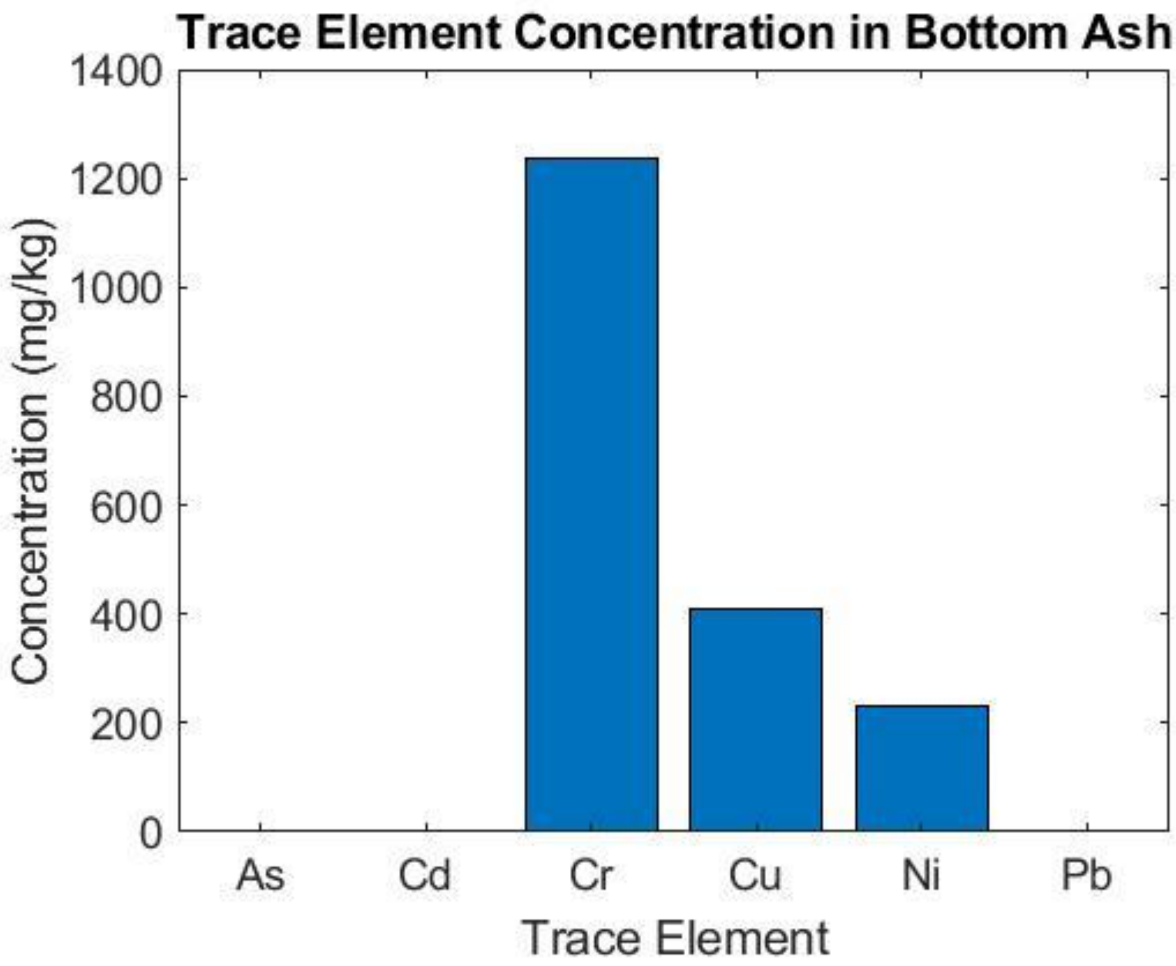
# Chemical Equilibrium Model

**ChemApp with Various Trace Elements**



## Chemical Equilibrium Model

**Trace Element Residue in Bottom Ash**



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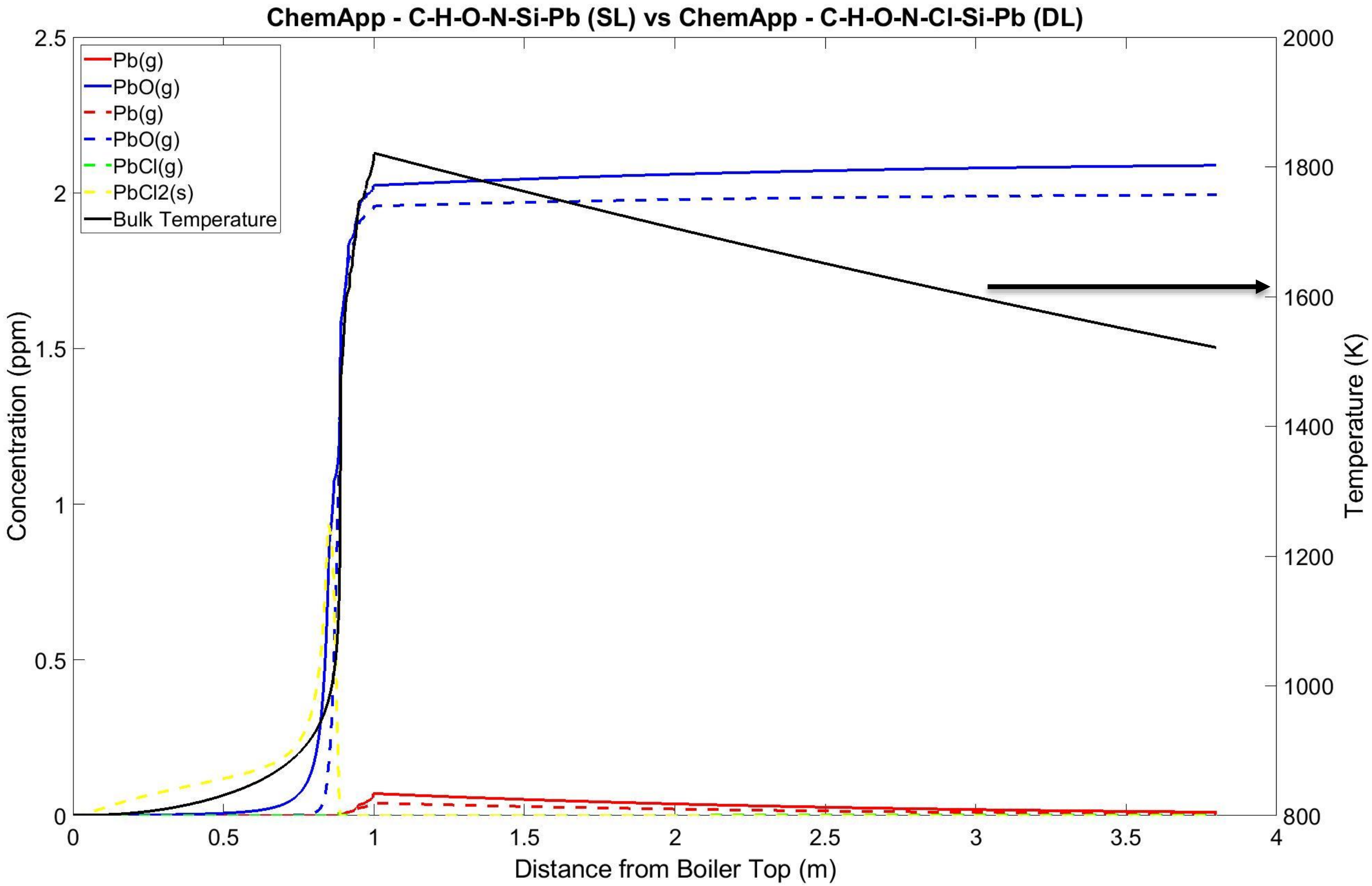
# Chemical Equilibrium Model

Chlorine Inclusion



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Conclusions
1. The burner model results describe the O2 concentration and temperature profile reasonably well despite different trend at burner top
2. Chemical equilibrium with Gibb's free energy minimisation has been successfully implemented in the model to estimate the concentration of trace element released during biomass combustion

Future Work
1. Model combustion incorporating important elements, e.g. Cl, S, Ash-forming elements, to observe their influence to trace element volatility and liquid/eutectics formation at particle surface in association with ash deposition initial build-up
2. Model trace element relative enrichment factor and compare it with that from ash digestion