Kinetic Analysis of the Interactions between Calcium Ferrite and Coal Char for Chemical Looping Gasification Applications

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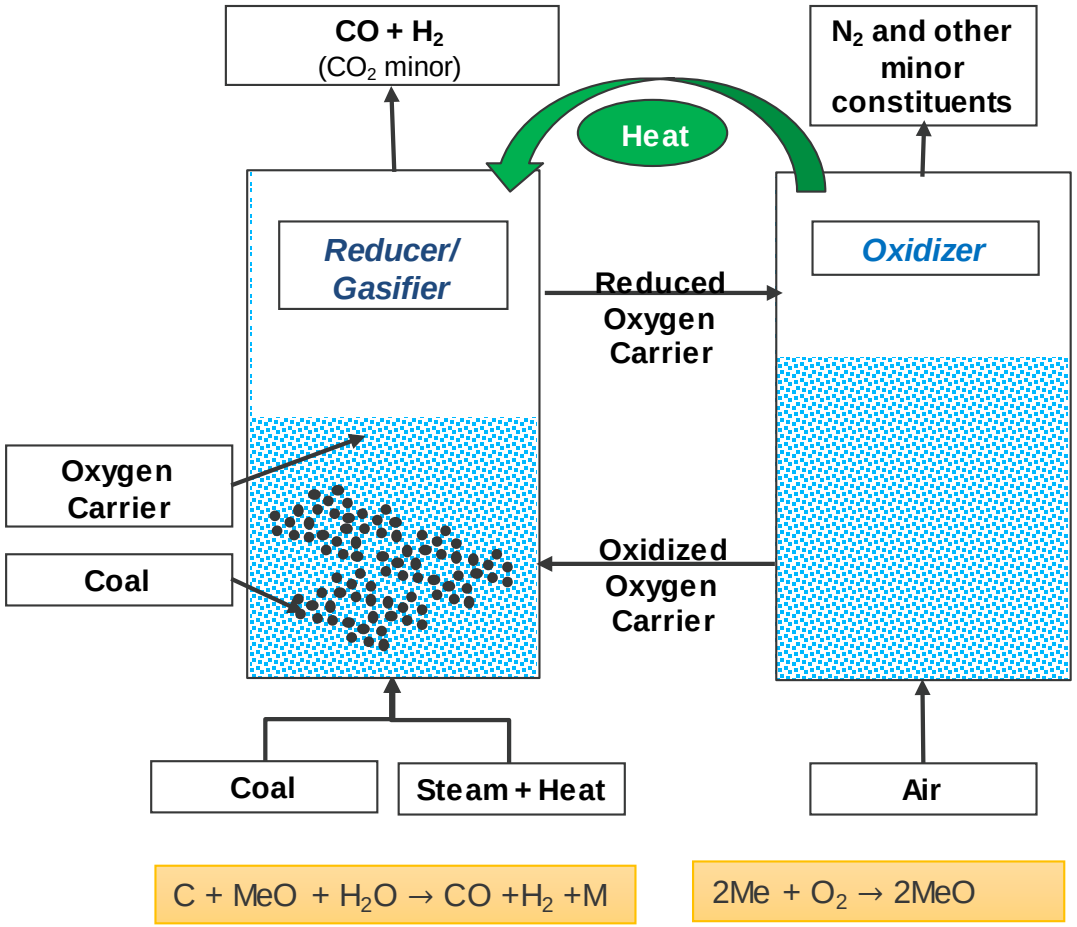
Outline:

- **Background**
  - Chemical Looping Gasification
  - Motivation
- **Methods**
  - Experimental Setup
  - Modeling Approach
- **Results and discussion**
  - Identifying the oxygen carrier reduction pathway
  - Model representation
  - Impact of OC size on model representation
- **Conclusions**

Introduction: Chemical Looping Gasification Concept

- **Configuration:**
  - Dual reactor design:
    - Fuel Reactor (Reducer/Gasifier)
    - Air Reactor (Oxidizer)
- **Foundation: Selective Oxygen Carrier with unique properties**
  - React directly with coal via solid-solid reactions to produce synthesis gas
  - Minimal reactivity with synthesis gas
  - **Applied Energy 165 (2016) 952–966**
- **Advantages:**
  - No direct contact between fuel and air.
  - Synthesis gas stream not diluted with Nitrogen
  - No need for pure oxygen via cryogenic separation



Solid-solid: MeO + C* → CO + Me

Introduction: Motivation

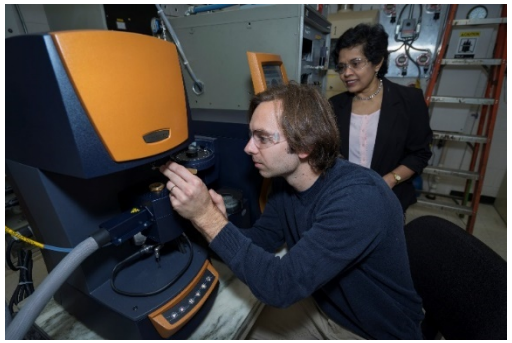
Motivation for this work:

- ***Provide particle scale kinetic model representation for both oxygen carrier and char with respect to solid mediated reactions***
- ***Accurate model representation need for scale up and optimization***
- ***Determine kinetic rate parameters for the solid mediated interactions between coal char and metal oxide (Ca-Ferrite)***

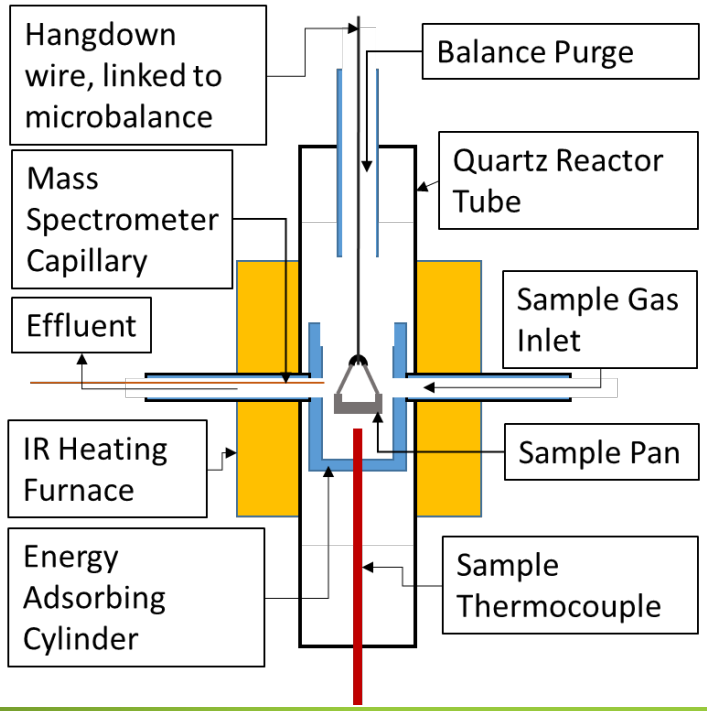
Addressing this problem:

- ***Thermogravimetric Analysis, Mass Spectrometry and other coupled characterization techniques***
- ***Solid state decomposition modeling approaches***

Methods: Experimental Setup



TA Discovery TGA-MS Reactor Setup



TGA-MS

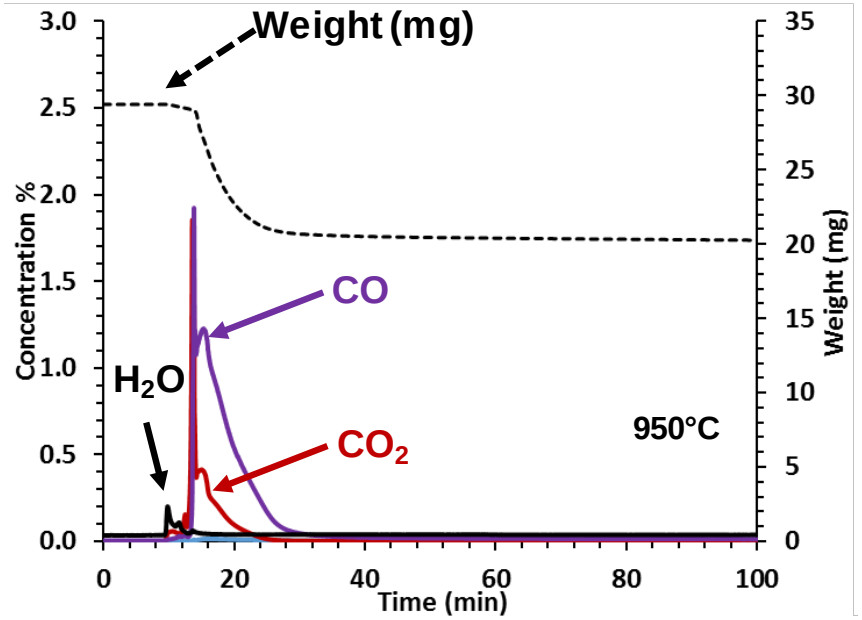
- **Experimental Parameters:**
- Loading: ~30 mg of sample
  - 24 mg $CaFe_2O_4$
  - 6 mg Coal Char
- Ramp 200°C/min to Desired Temp
- Temperature Range:
  - **850°C, 900°C & 950°C**
- Hold isothermal 240 min
- Oxidize: 80% Air for 60 minutes
- **On-line MS for Gas product analysis**

Other Characterization Techniques

- **XRD and SEM**

Methods: Kinetic Modeling using TGA-MS

TG-MS $CaFe_2O_4$ & Wyodak Coal Char



Conventionally:

Extent of conversion: (Overall conversion, TGA)

Solid conversion based on instantaneous weight change data

$$X(t) = \frac{m_0 - m(t)}{m_0 - m_f}:$$

- m_0 = initial mass (Ca-Ferrite + Char) (mg)
- $m(t)$ = instantaneous mass at time, t
- m_f = final mass (Reduced Ca-Ferrite + Ash)
  - Theoretical mass associated with full reduction of $CaFe_2O_4$ to CaO and Fe^0
  - Full char utilization (only ash remains)

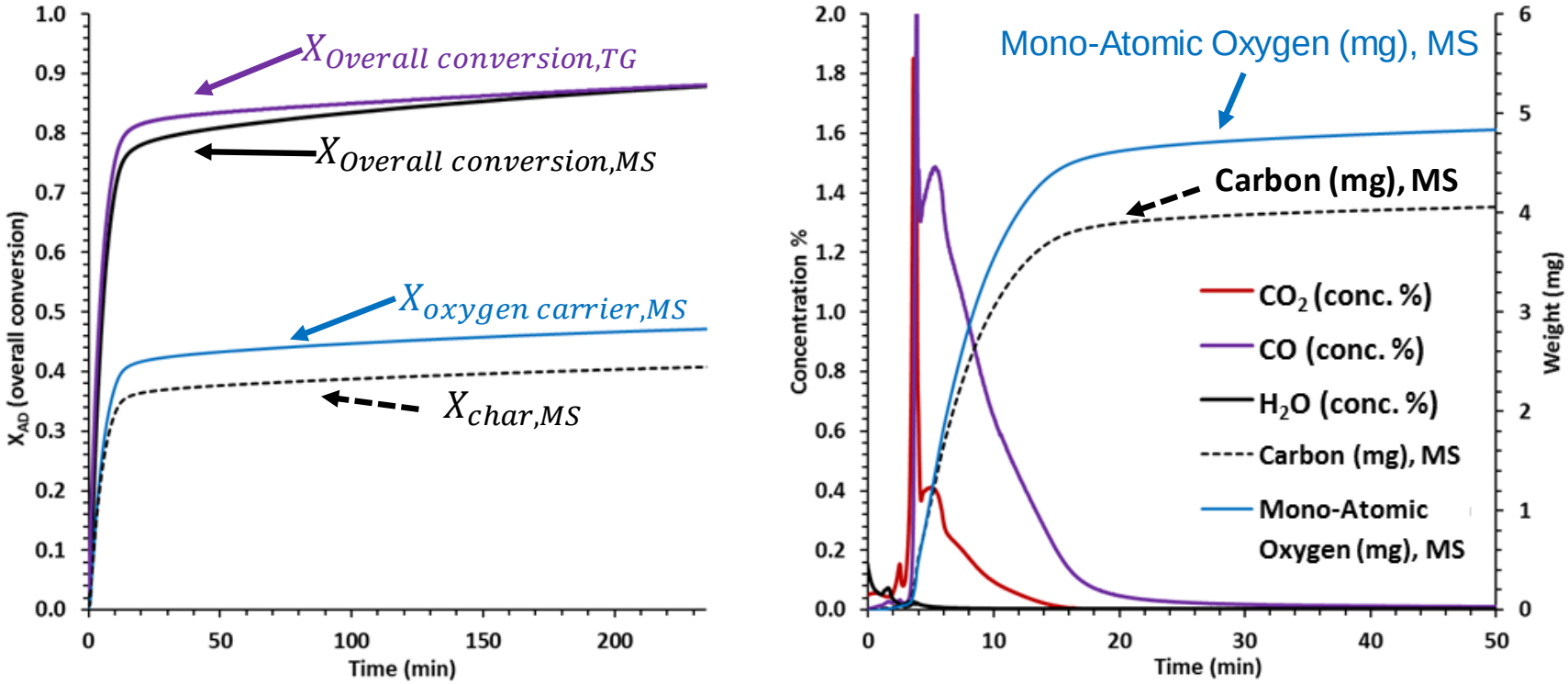
***Complex System*: Both Char and OC change with time**

Deconvolute individual weight changes (char + OC) based on EGA (Evolved gas anlysis).

Overall reaction: $2C^* + CaFe_2O_4 \xrightarrow{k'} CO + CO_2 + CaO + 2Fe^0$

Methods: Kinetic Modeling using TGA-MS

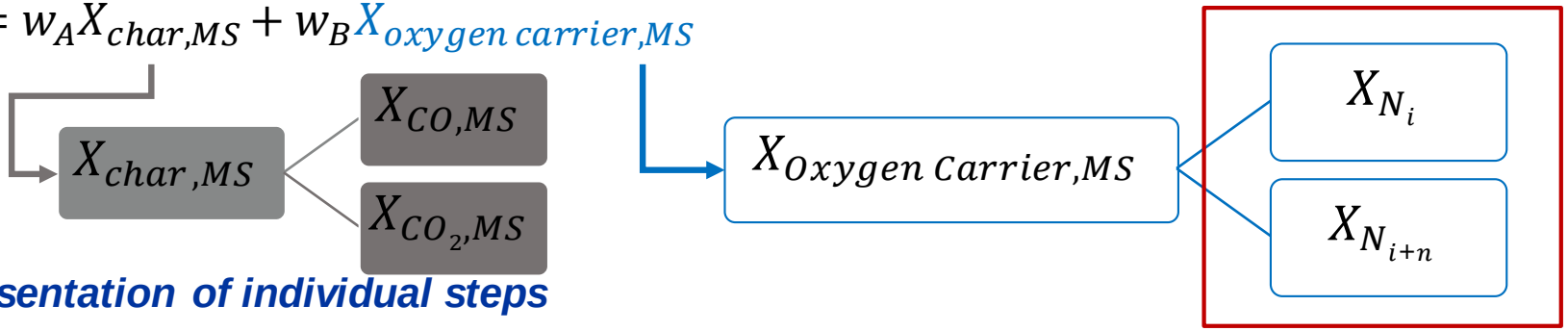
- **Both char and OC change with time**
  - Overall conversion must be separated to understand char and OC contributions
    - $X_{char,MS}$: char conversion based Mass Spectra
    - $X_{oxygen\ carrier,\ MS}$: oxygen carrier conversion based on Mass Spectra



- $X_{overall\ conversion} = \sum_n^i w_i X_i = w_A X_{char,MS} + w_B X_{oxygen\ carrier,MS}$

Methods: Kinetic Modeling using TGA-MS

- $\sum_n^i w_i X_i = w_A X_{char,MS} + w_B X_{oxygen\ carrier,MS}$



Model Representation of individual steps

- $\frac{dX_i}{dt} = k\,(T) f(X_i)$: **Rate of decomposition of solid**
  - $f(X_i)$: representative kinetic model function
- $g(X_i) = \int_0^X \frac{d(X_i)}{f(X_i)} = k(T)t$: **Integral form**
- $X_i = h(t)$ *Explicit form*
- $k(T) = Ae^{\left(\frac{-E_a}{RT}\right)}$: **Arrhenius rate constant**
  - A = frequency factor (1/s)
  - E_a = Activation energy (J/mol)
  - R = gas constant (J/mol-K)
  - T = reaction temperature (K)
- $D_{O^{2-}}(T) = D_i e^{\left(\frac{E_a^*}{k_B T}\right)}$: **Oxygen ion diffusion coef.**
  - D_i = jump frequency (cm^2/s)
  - k_B = Boltzmann const

Established Kinetic models for Solid State Reactions

Kinetic Model	Mechanism	f(x)	g(x)	X = h(t)
Order of Reaction	1st Order	$(1-X)$	$-\ln(1-X)$	$1-e^{(-k(T)t)}$
	2nd Order	$(1-X)^2$	$((1-X)^{-1}-1)$	$1-(k(T)t+1)^{-1}$
	3rd Order	$(1-X)^3$	$((1-X)^{-2}-1)$	$1-(k(T)t+1)^{-1/2}$
	nth Order	$(1-X)^n$	$((1-X)^{-(n-1)})-1)$	$1-(k(T)t+1)^{-1/(n-1)}$
Diffusion	1-D	$^1/_2 X$	X^2	$-(k(T)t)^{1/2}$
	3-D (SCM PLD)	$^3/_2 (1-X)^{\frac{2}{3}}[1-(1-X)^{\frac{1}{3}}]$	$(1-(1-X)^{\frac{1}{3}})^2$	$(1-(1-(\tau(T)t)^{\frac{1}{3}})^2)$
Contraction	2-D	$2(1-X)^{1/2}$	$1-(1-X)^{1/2}$	$1-(1-k(T)t)^2$
	3-D (SCM KC)	$3(1-X)^{2/3}$	$1-(1-X)^{1/3}$	$1-(1-\tau(T)t)^3$
JMA (nucleation)	nth Order	$n(1-X)(-\ln(1-X))^{(1-\frac{1}{n})}$	$[-\ln(1-X)]^{\frac{1}{n}}$	$1-e^{(-k(T)t)^n}$
	n = 1	-	$[-\ln(1-X)]$	$1-e^{(-k(T)t)^1}$
	n = 2	-	$[-\ln(1-X)]^{\frac{1}{2}}$	$1-e^{(-k(T)t)^2}$
Ginstling-Brounshtein (GB-SCM PLD)	SCM Product Layer Radial Diffusion	$(1-3(1-X)^{\frac{2}{3}}+2(1-X))$	$3/2((1-X)^{-\frac{1}{3}}-1)^{-1}$	-

Methods: Kinetic Modeling using TGA-MS

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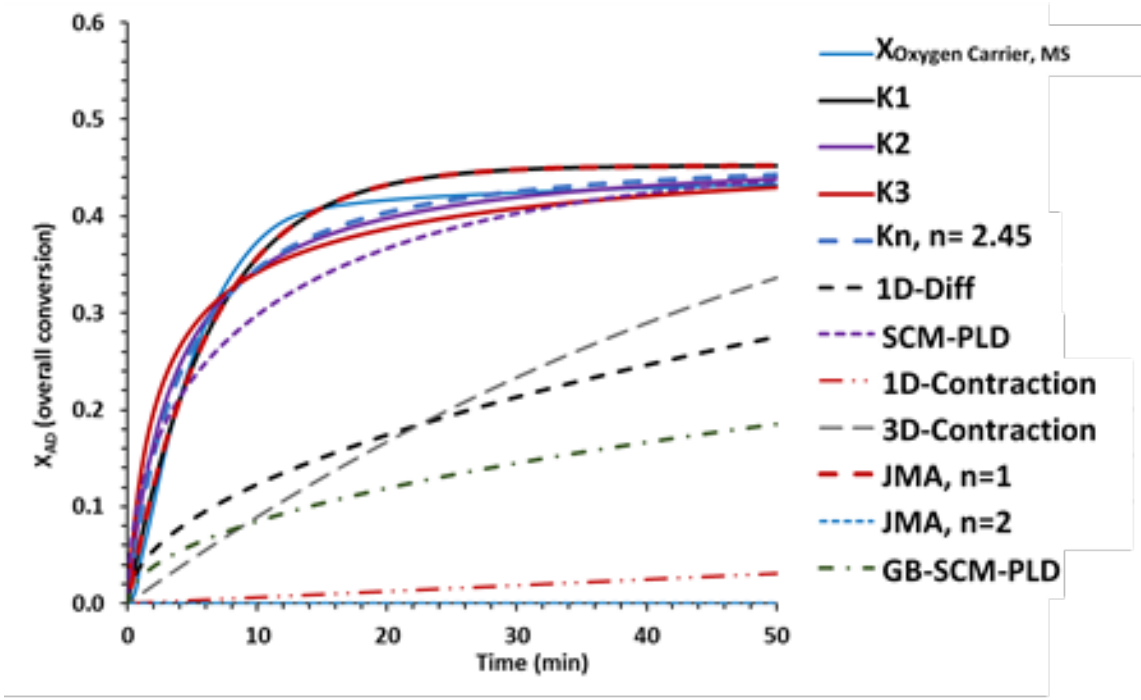
Initial Model Screening



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Diffusion	1-D	$^1/_2 X$
	3-D (SCM PLD)	$^3/_2 (1-X)^{\frac{2}{3}}[1-(1-X)^{\frac{1}{3}}]$
Contraction	2-D	$2(1-X)^{1/2}$
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Ginstling-Brounshtein (GB-SCM PLD)	SCM Product Layer Radial Diffusion	$(1-3(1-X)^{\frac{2}{3}}+2(1-X))$

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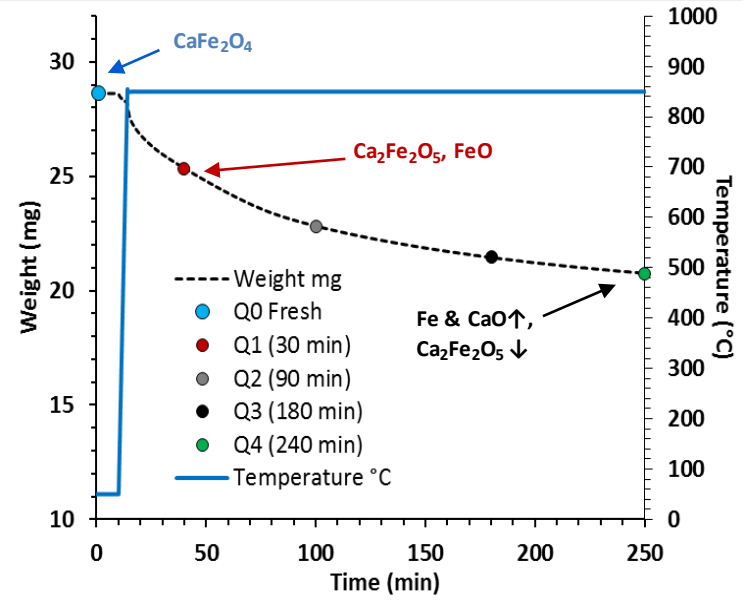
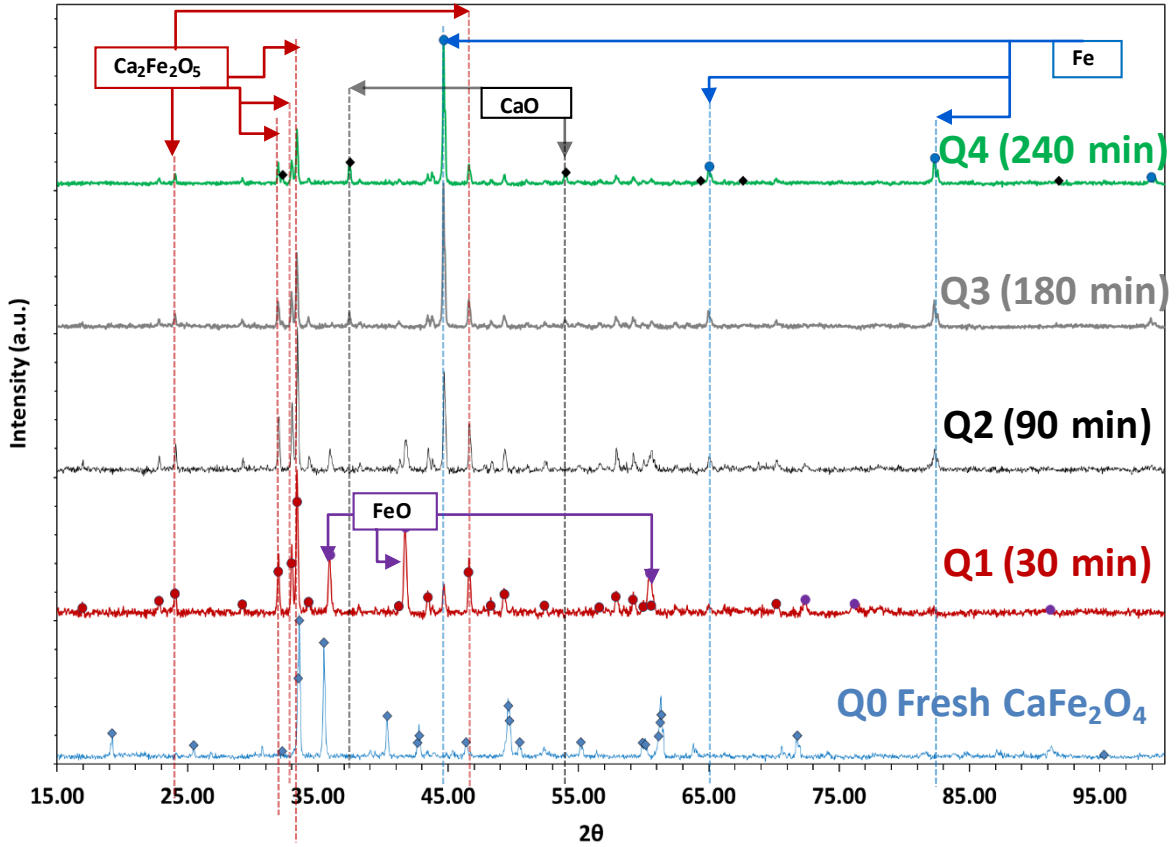
Identifying the reduction pathway for Ca-Ferrite

TGA (TA Discovery) & XRD (Panalytical X-pert Pro)

TGA: Reaction time impact on oxygen release (Controlled reduction sampling)



XRD: Phase reorientation w.r.t. sampling interval



$$\textit{Initial} \qquad \textit{Partial Reduction} \qquad \textit{Full Reduction}$$
$$CaFe_2O_4 \rightarrow Ca_2Fe_2O_5 \;\&\; FeO \rightarrow CaO \;\&\; Fe^0$$

Further examination of the condensed phase reaction mechanism after determination of the reduction pathway

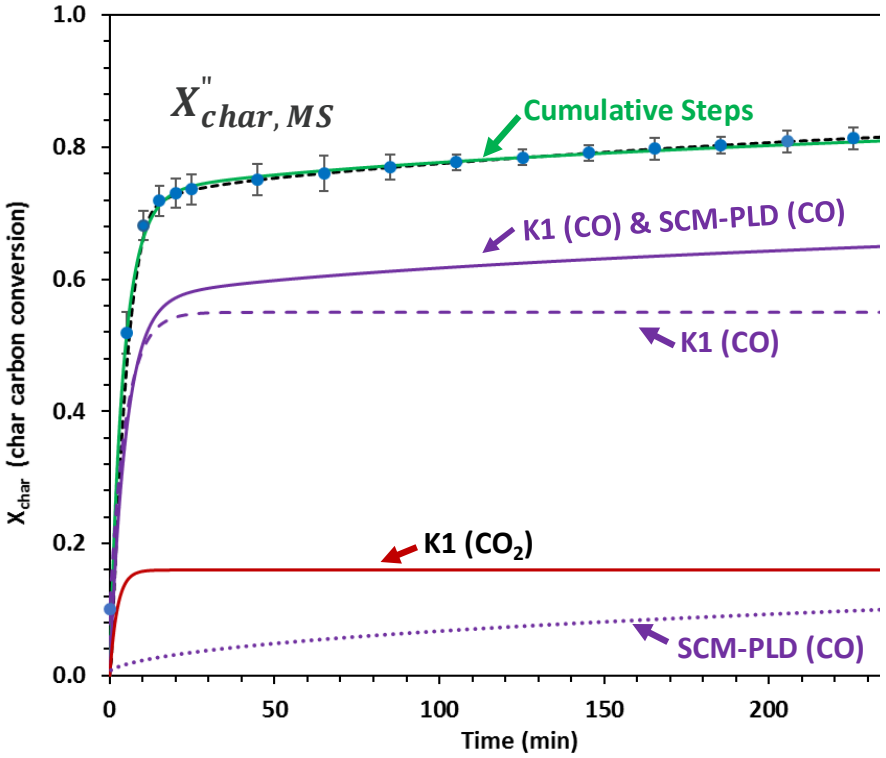
Condensed phase reaction mechanism (Direct Solid-Solid reaction):

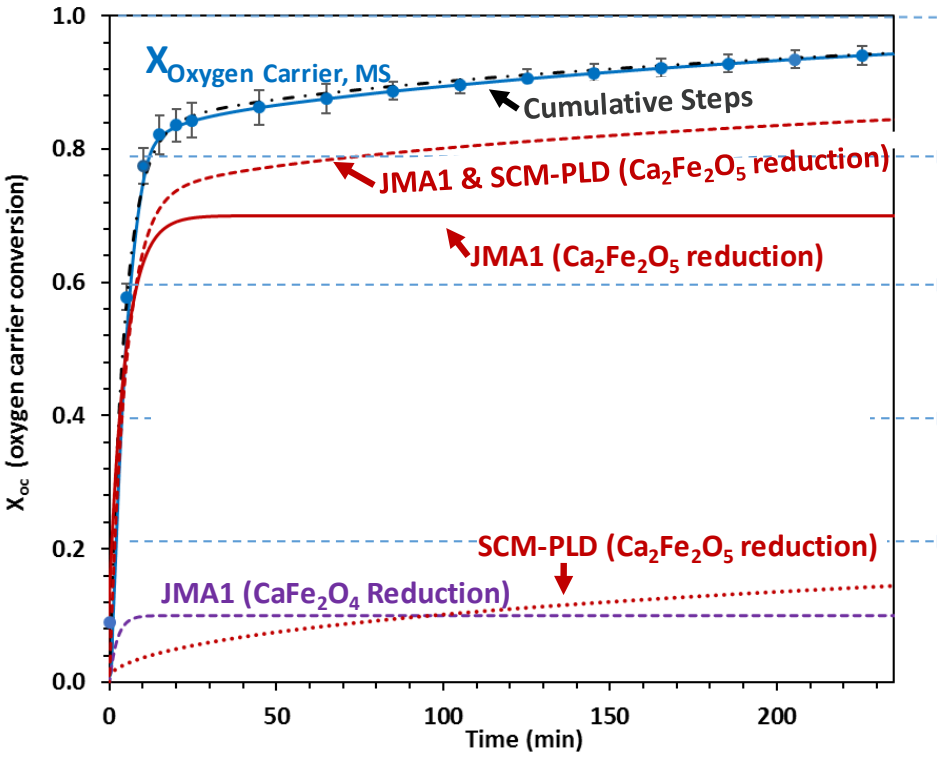
- Overall Reaction:
  - $2C^* + CaFe_2O_4 \xrightarrow{k'} CO + CO_2 + CaO + 2Fe^0$
- Individual components of condensed phase mechanism:
  - Char Oxidation:
    - R1 Desired: $C^* + O^{2-} \xrightarrow{k_A} CO$
    - R2 Undesired: $C^* + 2O^{2-} \xrightarrow{k_B} CO_2$
    - ***2 primary steps***
  - Oxygen Carrier Reduction
    - R3: $2CaFe_2O_4 \xrightarrow{k_C} Ca_2Fe_2O_5 + 2FeO + O^{2-}$
    - R4a: $Ca_2Fe_2O_5 \xrightarrow{k_{D,1}} 2CaO + 2Fe^0 + 3O^{2-}$
    - ***2 primary steps***

- ***Model representation (multistep, parallel mech.)***

Model representation for the selective oxidation of Wyodak Char with $CaFe_2O_4$

Wyodak Char (40-50µm) & $CaFe_2O_4$ (40-50µm), 950°C



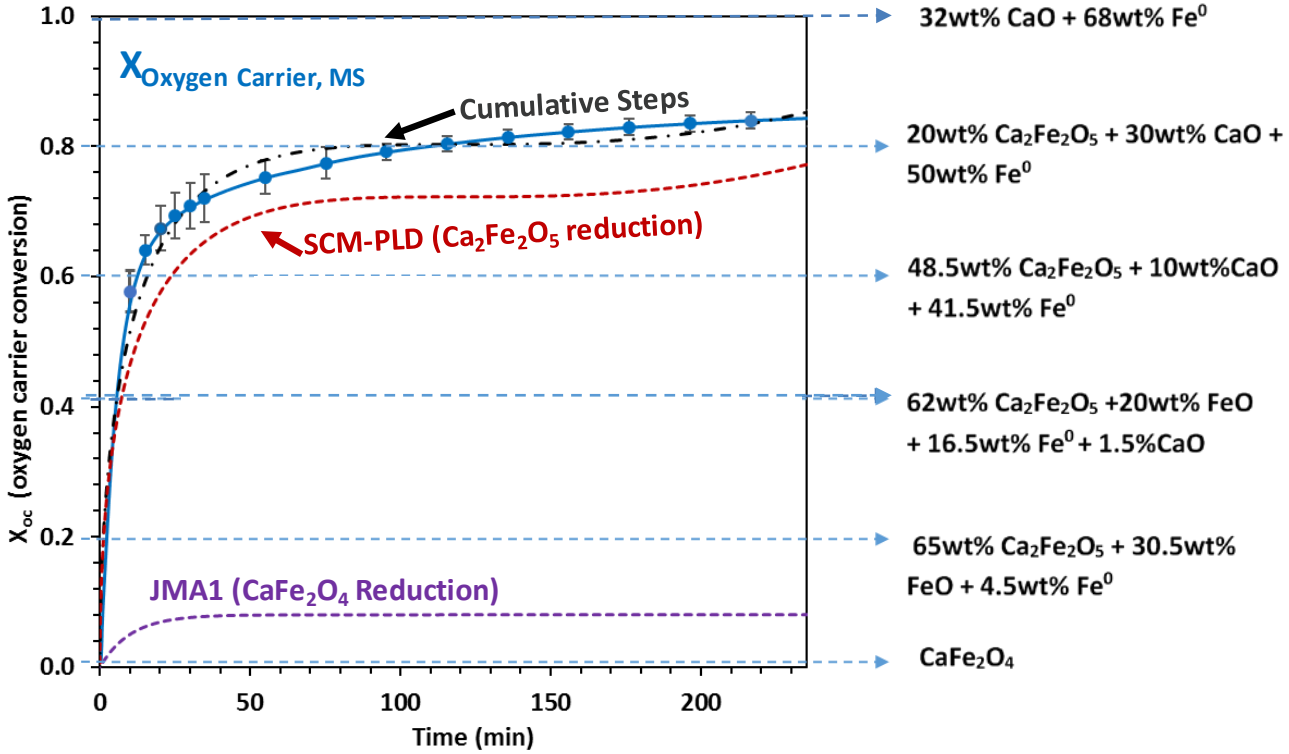


Model Representation:

- **Wyodak Char conversion:**
  - Carbon oxidation to CO_2, & CO primarily first order *[K1]* (kinetic controlling regimes)
- **$CaFe_2O_4$ Reduction Conversion:**
  - First order nucleation and growth *[JMA1]*:
    - Relatively fast, increased rate of oxygen ion transfer
    - Proximal contacts
  - Minor underlying oxygen ion diffusion resistance

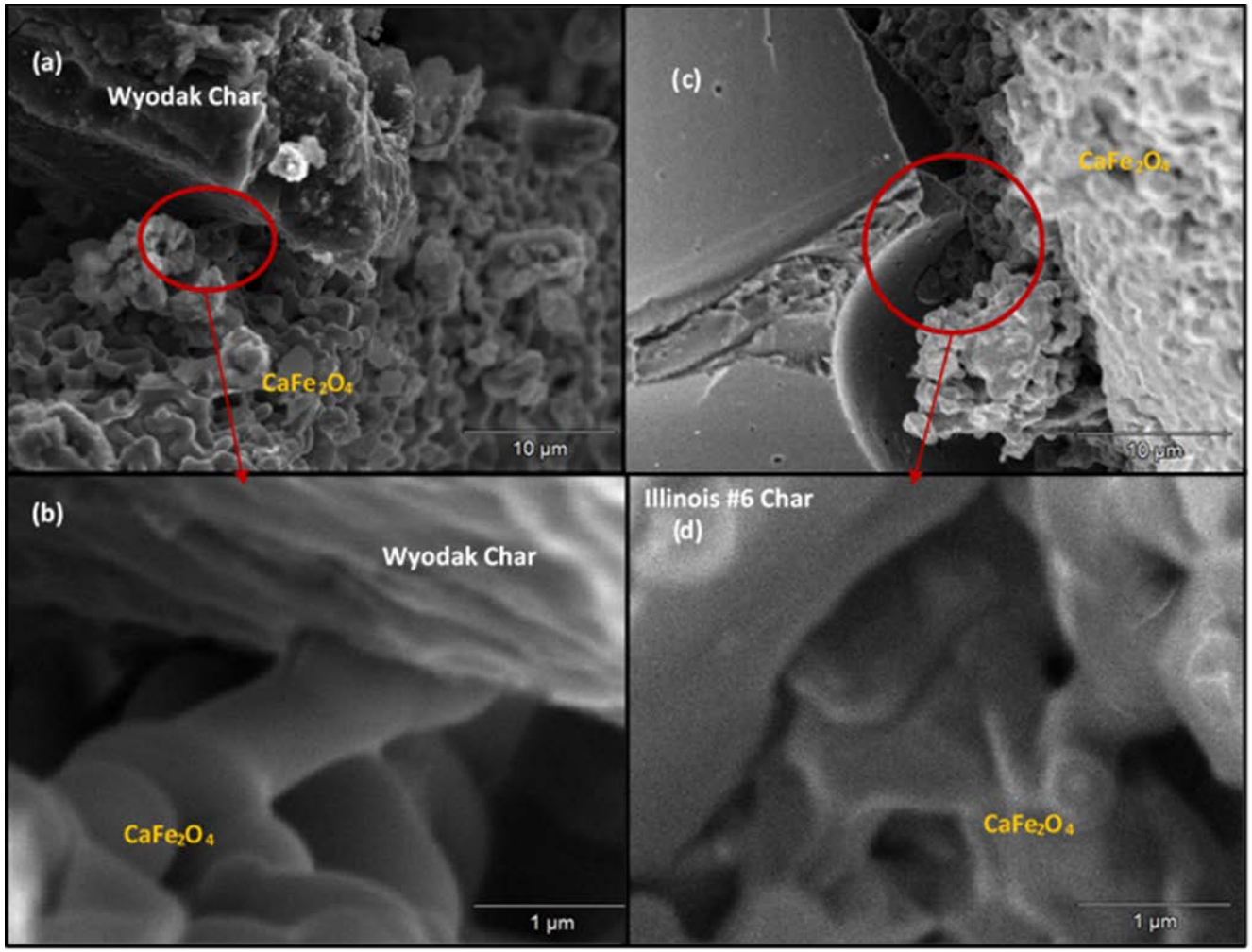
Assessing the impact of oxygen carrier particle size for the selective oxidation of Wyodak Char with $CaFe_2O_4$

Wyodak Char (~40-50µm) & $CaFe_2O_4$ (~125-180µm), 950°C



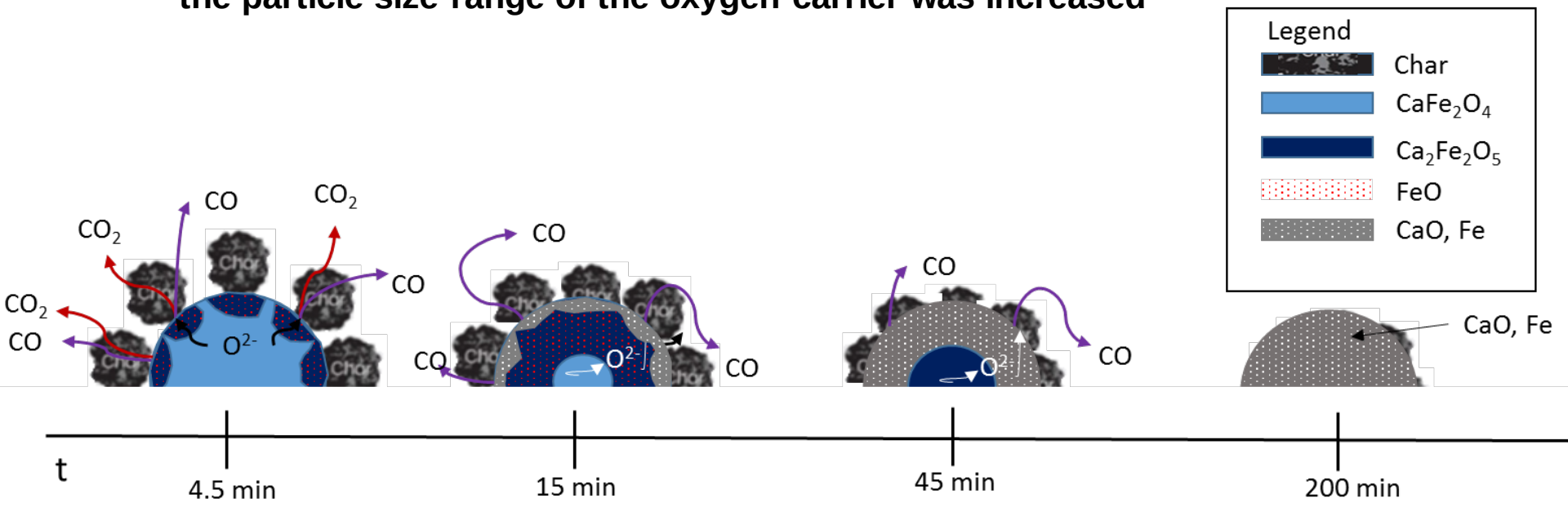
- **$CaFe_2O_4$ Size has a profound impact on the prevailing mode of oxygen transfer**
- **Doubling the OC size, shifts reduction to predominantly SCM-PLD representation with oxygen ion diffusion controlling regime**
  - Important coefficients determined: $D_{O^{2-}}$

SEM Imaging of char-$CaFe_2O_4$ reaction interface



Conclusions:

- Provide particle scale model representation for both char and OC
- Combination of the modified shrinking core model (SCM) with planar oxygen ion diffusion control and reaction order (char) /nucleation and growth (OC) based models were applied for kinetic parameter determination
- Models Identified to represent mechanistic behavior for further advancement of the process concept
- $CaFe_2O_4$ particle size plays a major role in the prevailing mode of oxygen release
- The probability for oxygen ion diffusion controlling regimes increased when the particle size range of the oxygen carrier was increased



Acknowledgements

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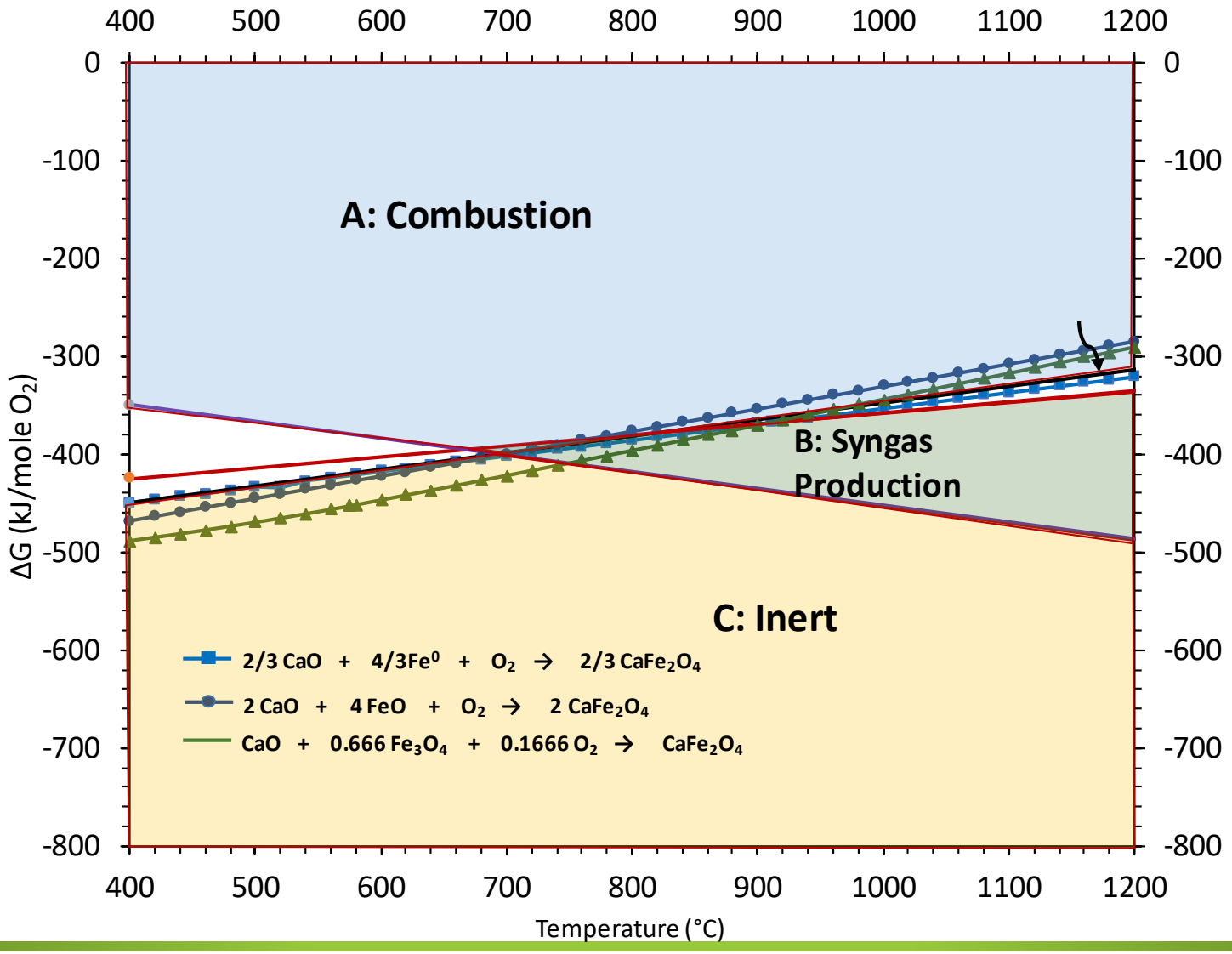
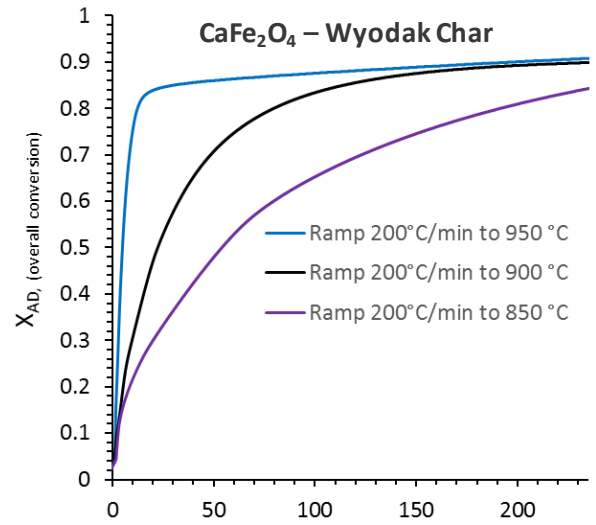
Questions ?

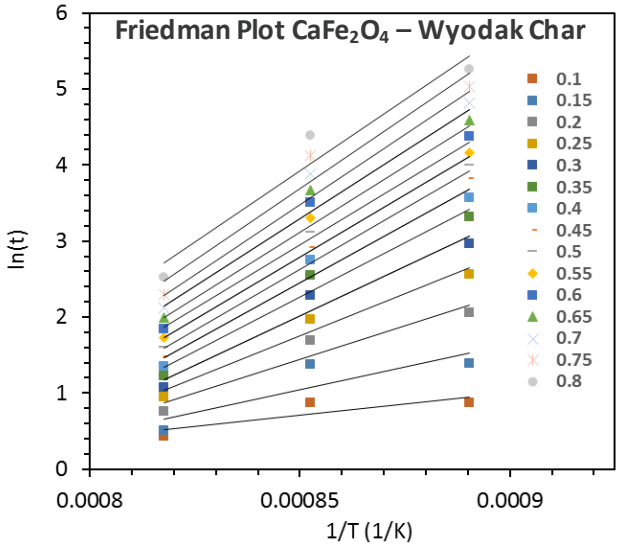
Modified Ellingham diagram for $CaFe_2O_4$ at 700-850 ^{0}C

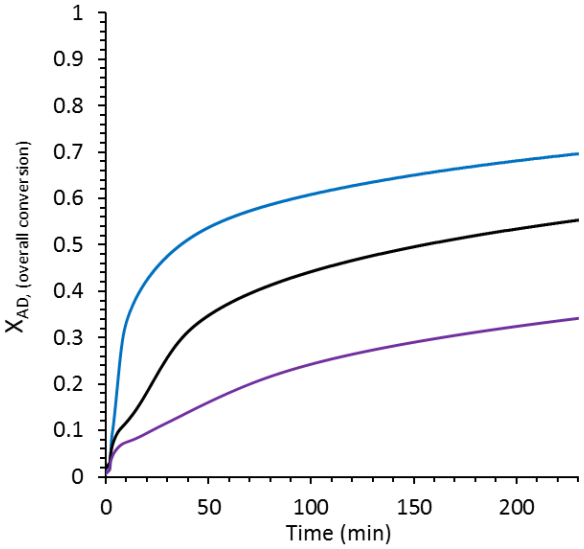
- ΔG in the synthesis gas production region

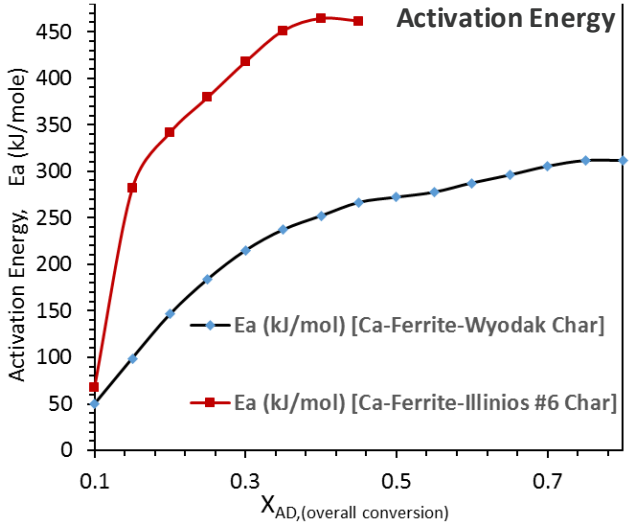


Estimation of the Activation energy for selective oxidation of Wyodak char with $CaFe_2O_4$









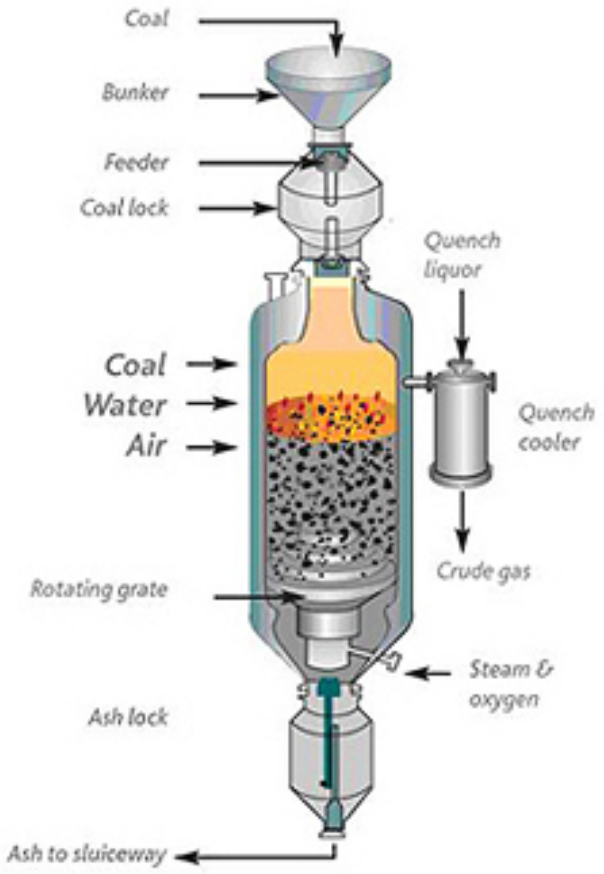
Estimation of the overall Activation Energy:

- Model Free Iso-conversional Methods
- $\ln(t) = \left(-\ln A + \ln \int_0^X \frac{dX}{f(x)}\right) + \frac{E_a}{RT}$
  - For fixed values of overall conversion (X_{AD}) : Plot 1/T vs. ln(t), fit and extrapolate slope
  - Advantage: Independent of model description

- Activation energy ranges from 50-450 kJ/mol depending upon extent of conversion

Lurgi Gasifier - Commercial Fixed Bed Gasifiers

http://www.netl.doe.gov/research/coal/energy-systems/gasification/gasifipedia/lurgi



- The Lurgi gasifier is a pressurized, dry-ash, moving bed gasifier that produces syngas from lump coal, steam, and oxygen as an oxidant.
- A high ratio of steam to oxygen helps moderate the temperature such that the ash does not melt, but is removed as dry ash.
- Coal enters the top of the gasifier through a lock hopper and is handled by a rotary distributor as it begins its descent through the gasifier.
- Steam and oxygen enter from the bottom, while ash is removed at the bottom by a rotating grate and lock hopper.
- A top temperature of about 1,000°F and bottom temperature of about 1,800°F creates a temperature gradient in the gasifier.
- Exiting raw syngas at up to 1,000°F is cooled and quenched using recycle water to condense tars and oils.
- A water jacket cools the gasifier vessel and generates part of the steam needed by the gasifier.