Copper Looping with Copper Oxide as Carrier and Coal as Fuel

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1st International Conference on Chemical Looping

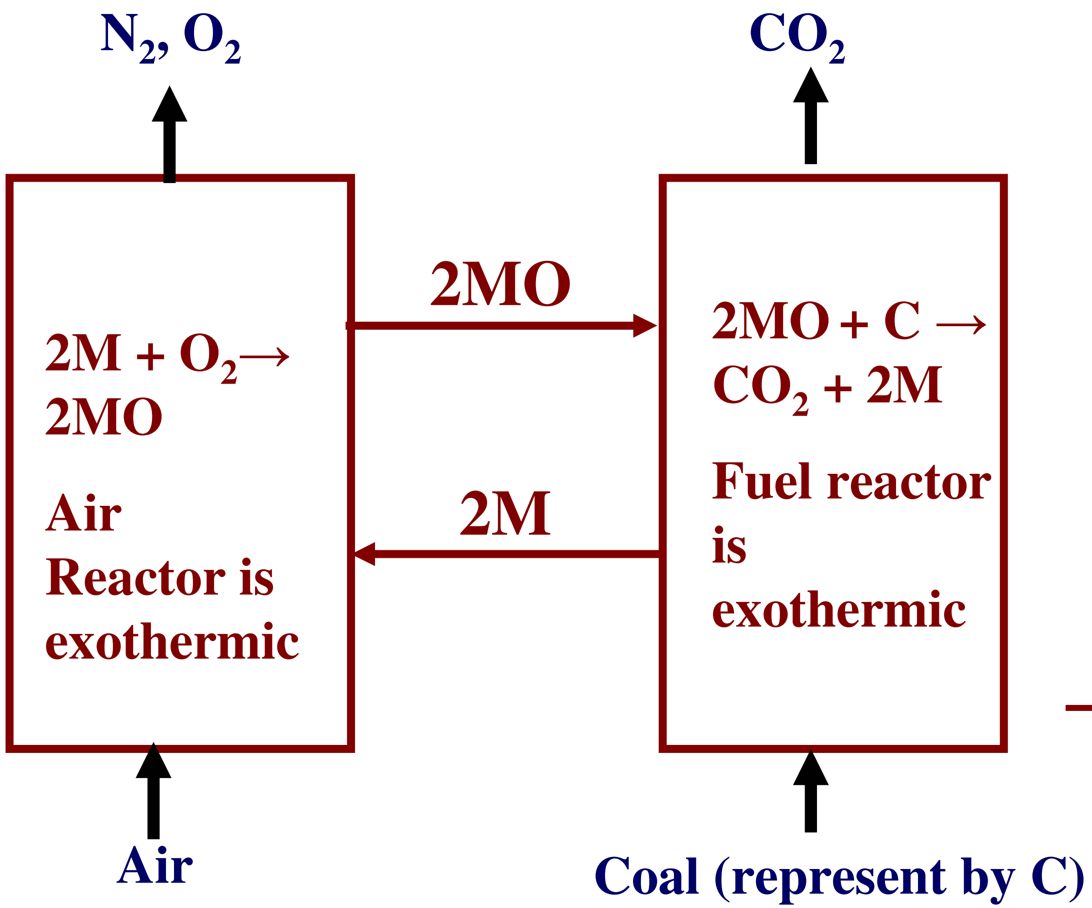
17 – 19 March, 2010

Lyon, France

Outline

- History of Chemical Looping Combustion with Oxygen Uncoupling (CLOU)
- Augmentation of Carbon Gasification with CLOU
- Kinetics of CuO decomposition and Cu_2O oxidation
- Order of Magnitude Design Considerations
- Concluding Comments

Chemical Looping Combustion with Oxygen Uncoupling (CLOU). The oxygen carrier dissociates at high temperature and the fuel (represented here by C) reacts with the O_2. CLOU proposed by Mattison, T., Lyngelt, A., and Lieon, L., J. Greenhouse Gas Control, 3, 11-19 (2009)



Air Reactor

$2M + O_2 = 2\ MO$ (Exo)

Fuel Reactor

oxidation occurs via dissociation of MO to yield O_2

$2MO = 2M + O_2$ (Endo)

$C + O_2 = CO_2$ (Exo)

$2\ MO + C = CO_2 + 2M$ (Exo)

Overall Reaction

$2M + O_2 = 2\ MO$ (Exo)

$2MO + C = CO_2 + 2M$ (Exo)

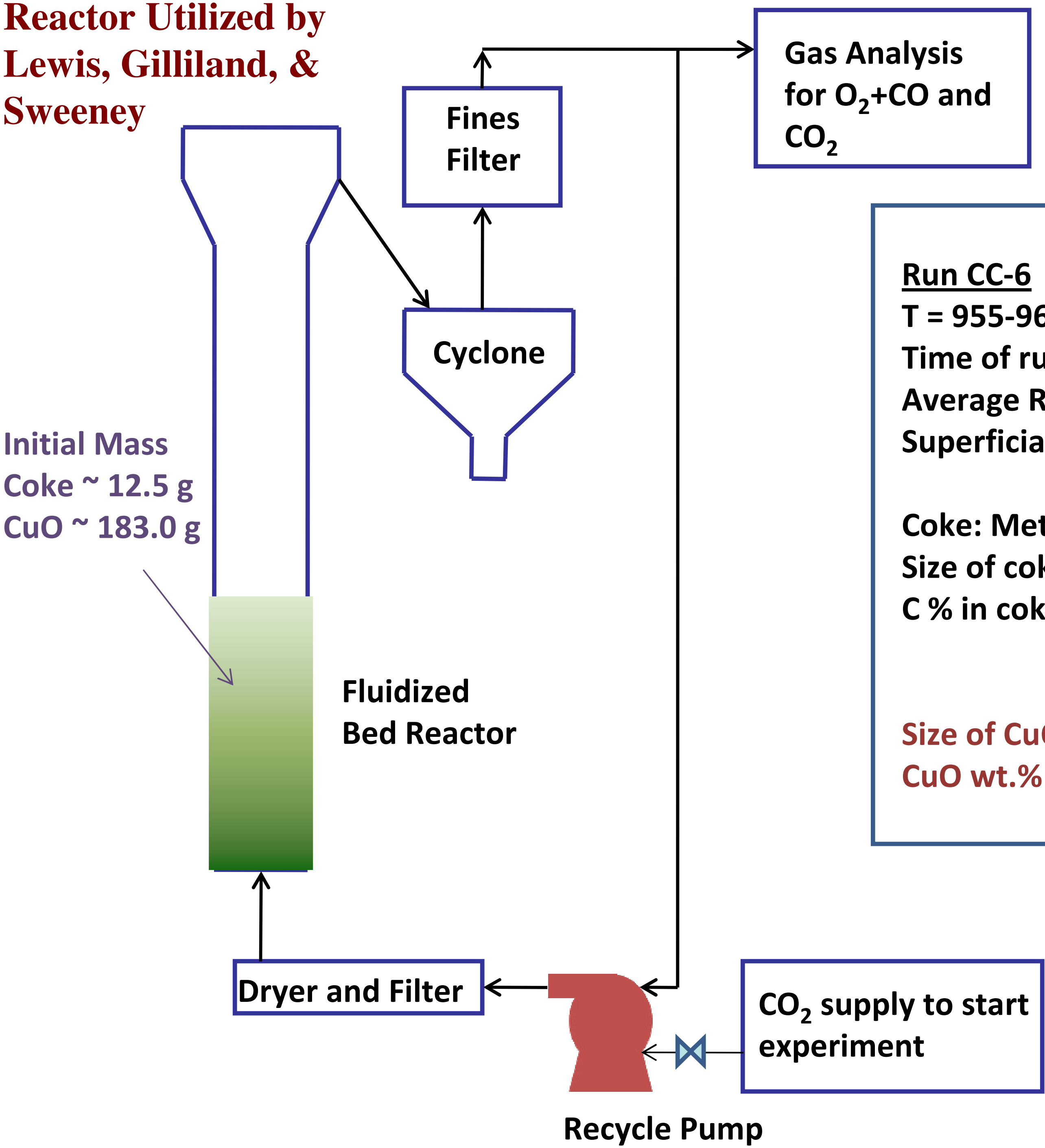
$C + O_2 = CO_2$ (Exo)

Earlier study of CLOU for non-combustion application

(Lewis, Gilliland, and Sweeney, Chem. Eng. Prog., 57(5), 251-257,1951) as well as U.S. Patent No. 2,665,972 for the "Production of Carbon Dioxide.

The experiment consisted of a batch, electrically-heated isothermal reactor; an initial batch of oxygen carrier was fluidized with an external CO_2 stream; after equilibration a batch of carbon was added; then the external CO_2 supply used for fluidization was replaced by the CO_2 generated in the reactor and recycled after cleaning and drying. Progress of the reaction was followed by analysis of 1. the product gas for CO_2 and $CO + O_2$ and 2. the solids for carbon content and O/Cu ratio of the bed material.

Reactor Utilized by Lewis, Gilliland, & Sweeney

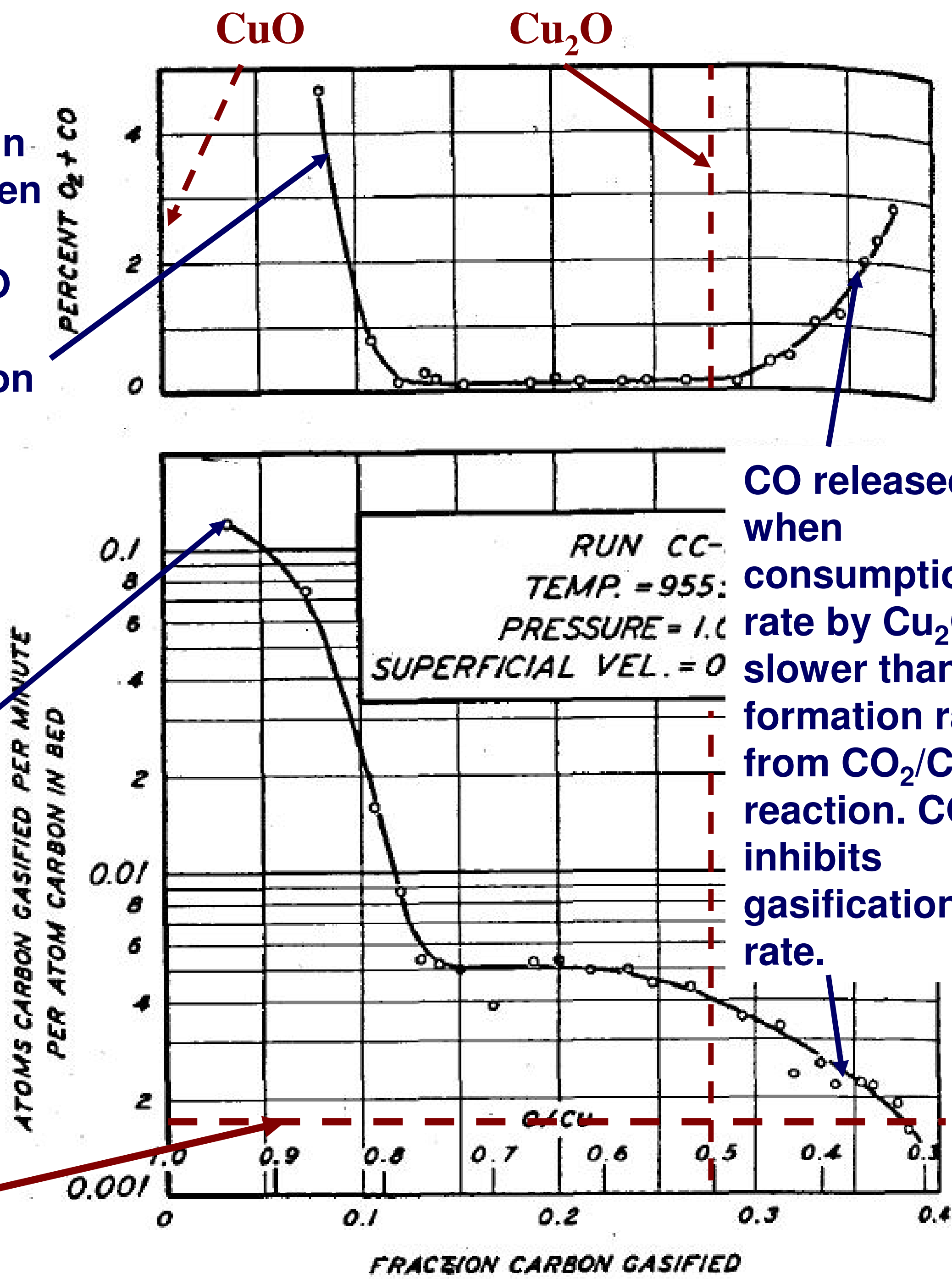


<u>Run CC-6</u>
T = 955-960 ℃
Time of run = 113.8 min
Average Reactor Pressure =1.095 atm.
Superficial Velocity = 0.236 m/s

Coke: Metallurgical Koppers Type
Size of coke particles : 100-150 µm
C % in coke = 88.25%

Size of CuO on Silica Gel : 150-600 µm
CuO wt.% on silica gel = 10-15%

Run
CC-6 from Lewis, Gilliland, & Sweeney
Temp. = 955±5°C
P = 1.095 atm.
Vel. = 0.236 m/s



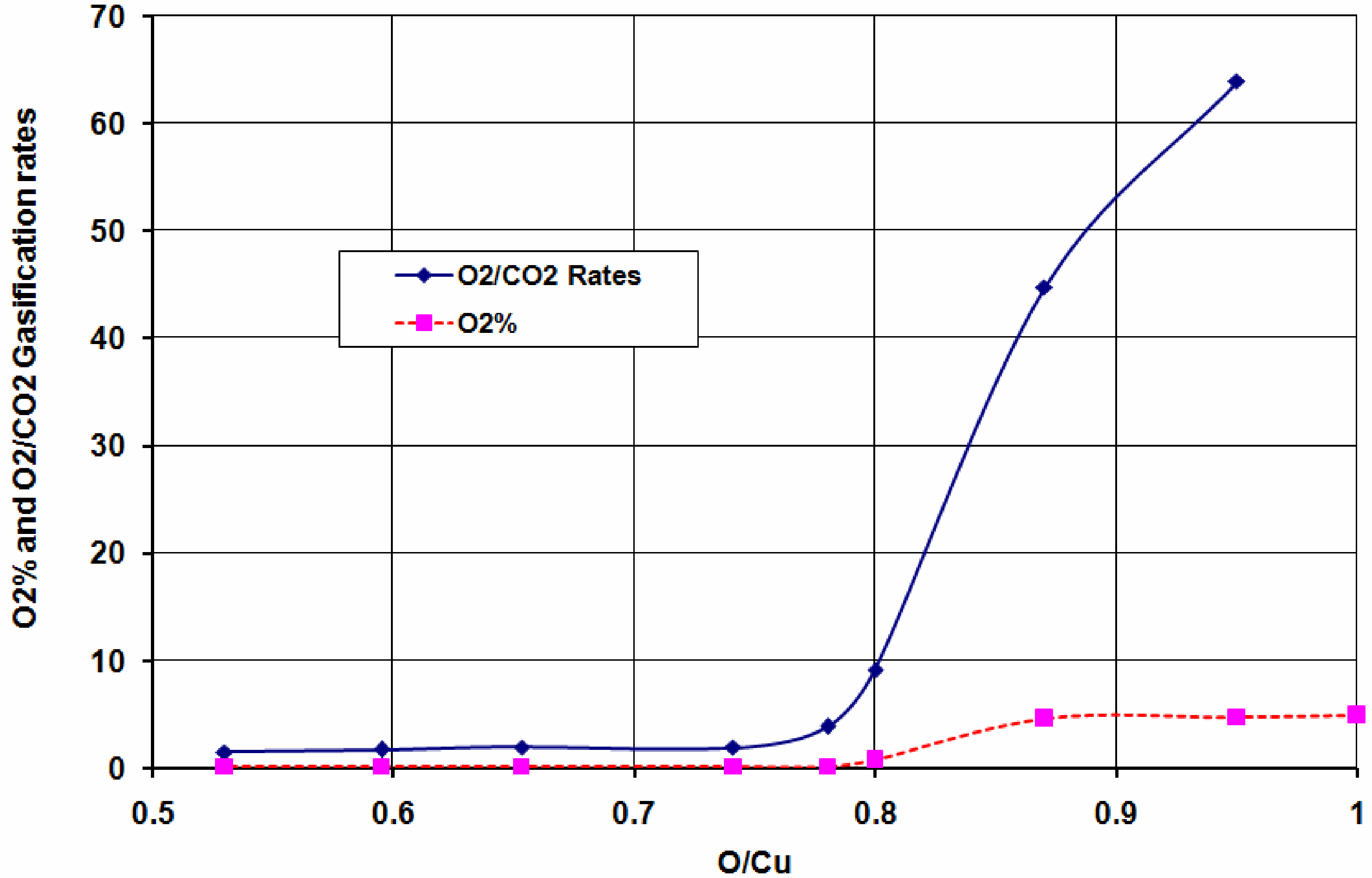
Excess O_2 in effluent when O_2 release rate by CuO exceeds consumption rate by C

Peak gasification rate > 60 times that for Fe carrier at about same T.

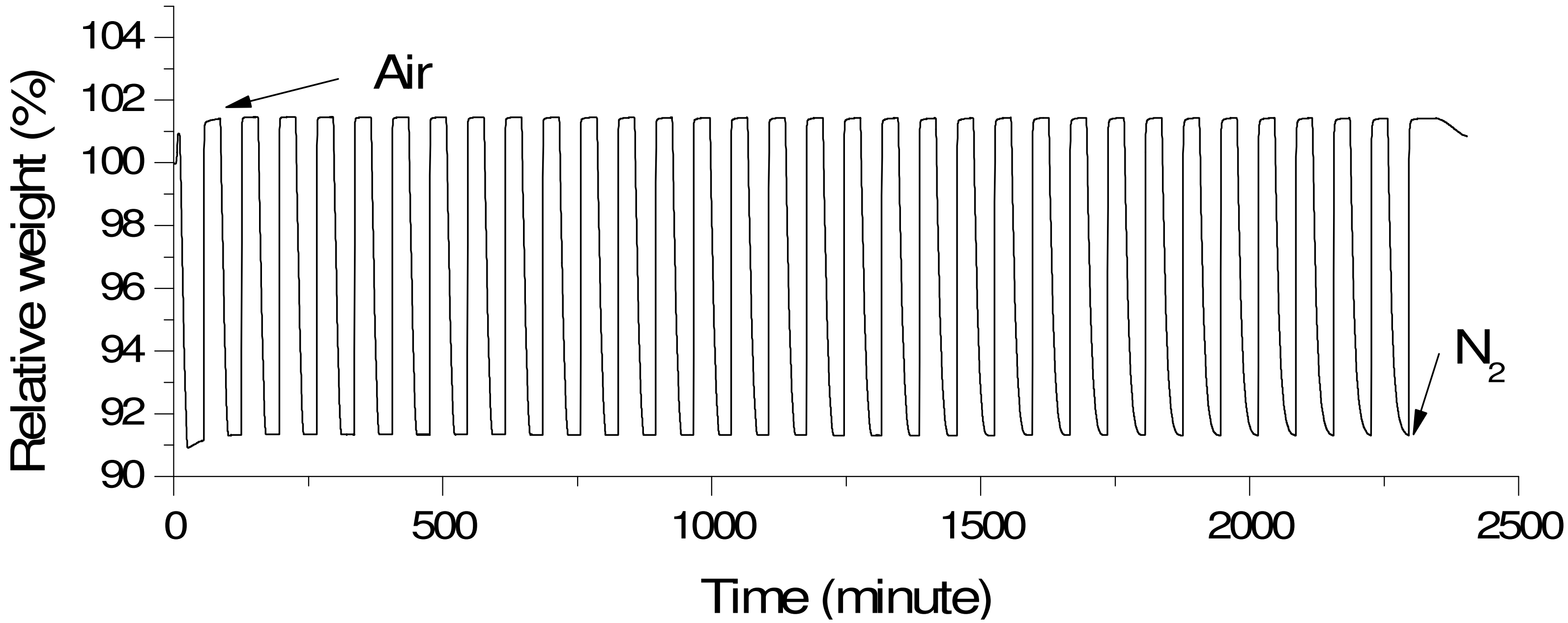
CO released when consumption rate by Cu_2O slower than formation rate from CO_2/C reaction. CO inhibits gasification rate.

Gasification rate due to 100% CO_2

Relative rates of gasification by O_2 and CO_2 (relation to local O_2 concentration)



Cycling atmosphere to TGA between air (30 min) and nitrogen (40 min) at 850°C to determine stability of CuO as an oxygen carrier.



Results suggest that 1. CuO decomposes to Cu_2O based on weight loss (~10%), 2. Sintering at higher temperatures will necessitate the use of supported oxides.

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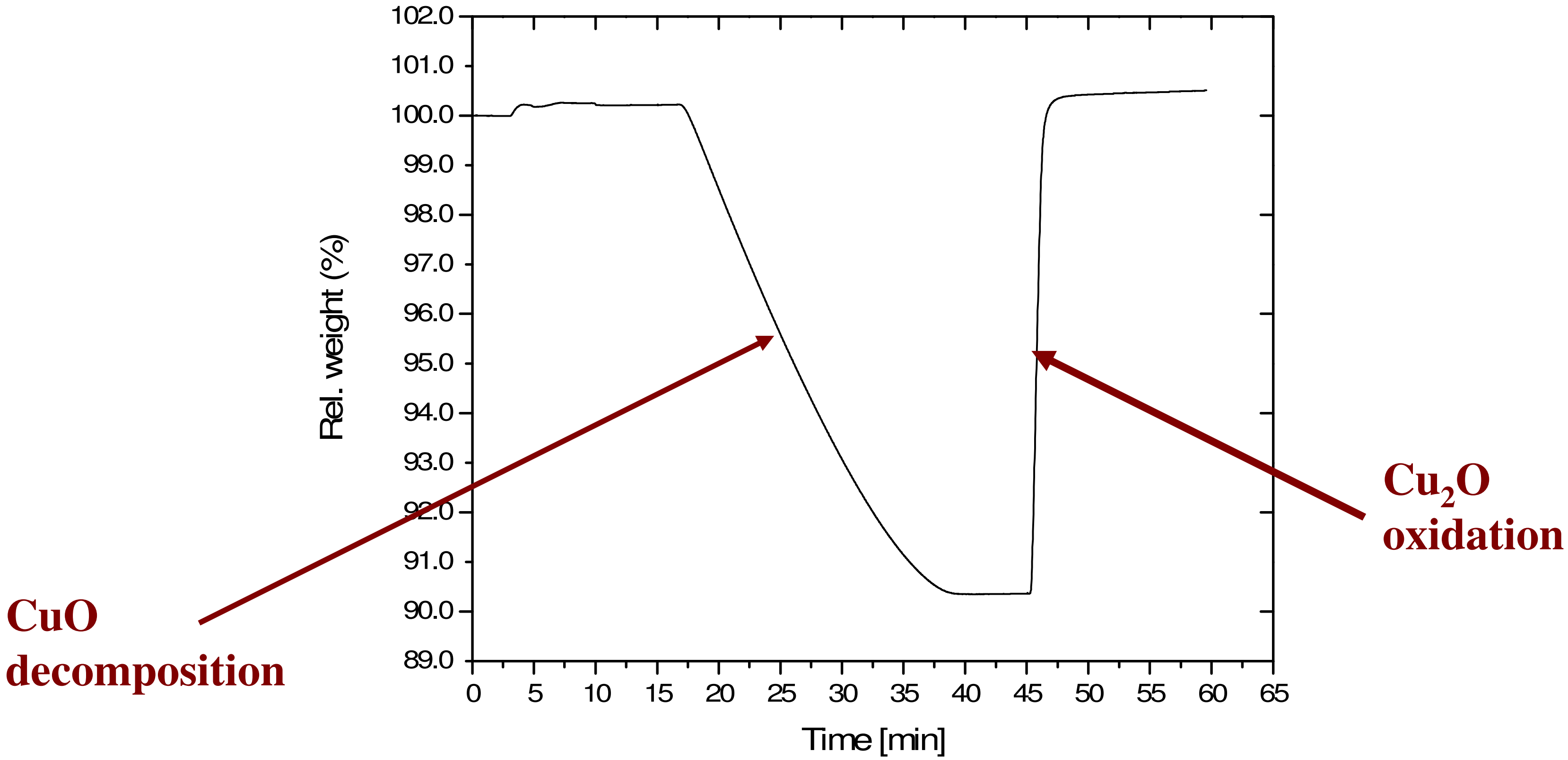
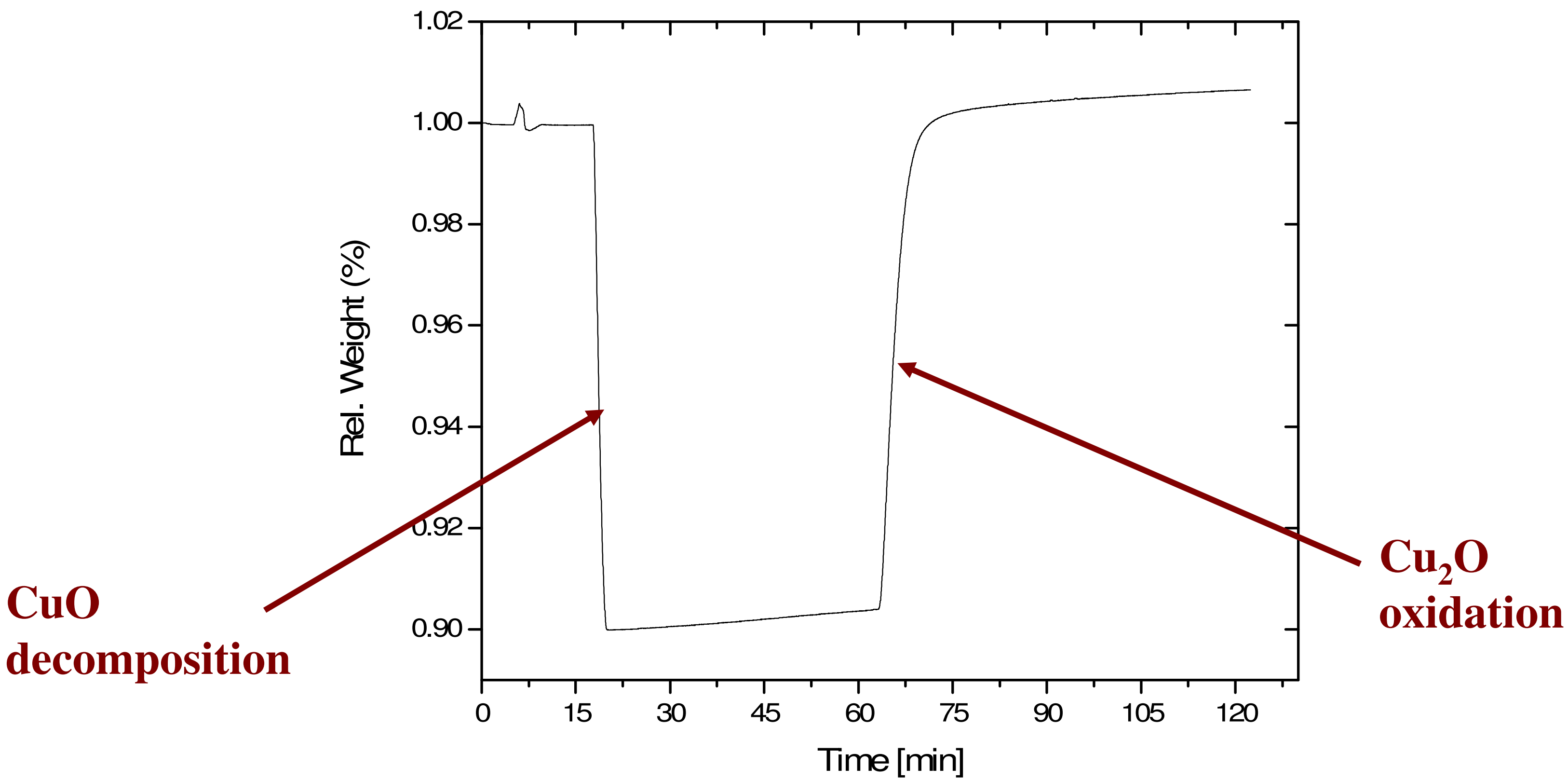
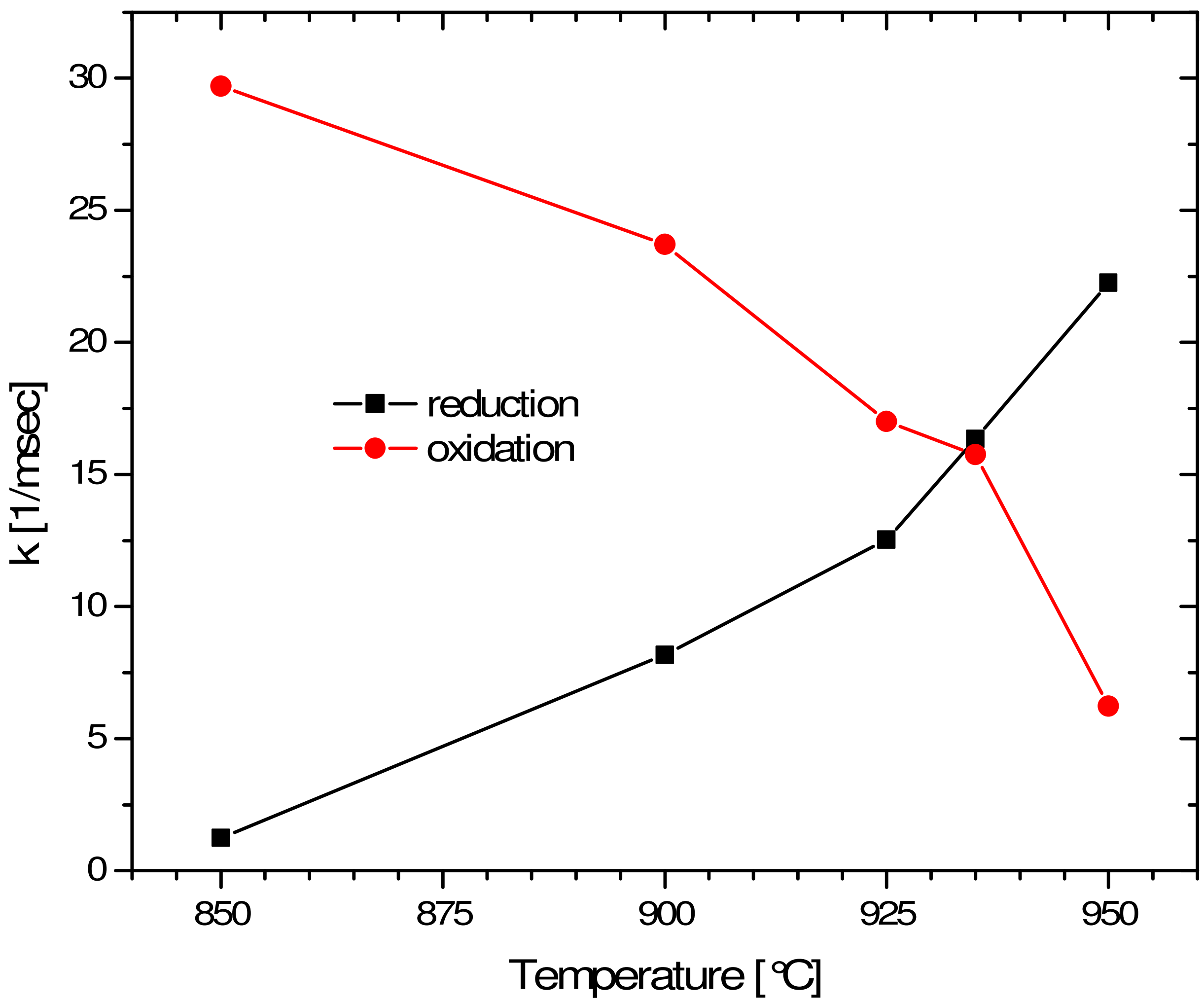
Isothermal 850°C (one cycle: nitrogen for 40 minutes and air for 30 minutes)



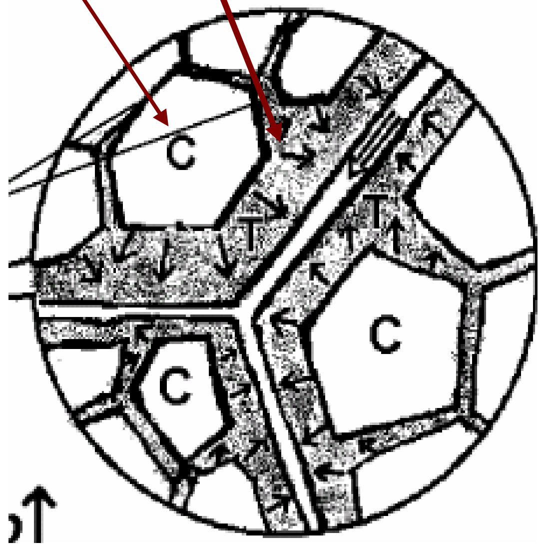
Isothermal 950°C (one cycle between nitrogen 40 minutes and air 30 minutes)



Rate constants for CuO decomposition and Cu_2O oxidation in air

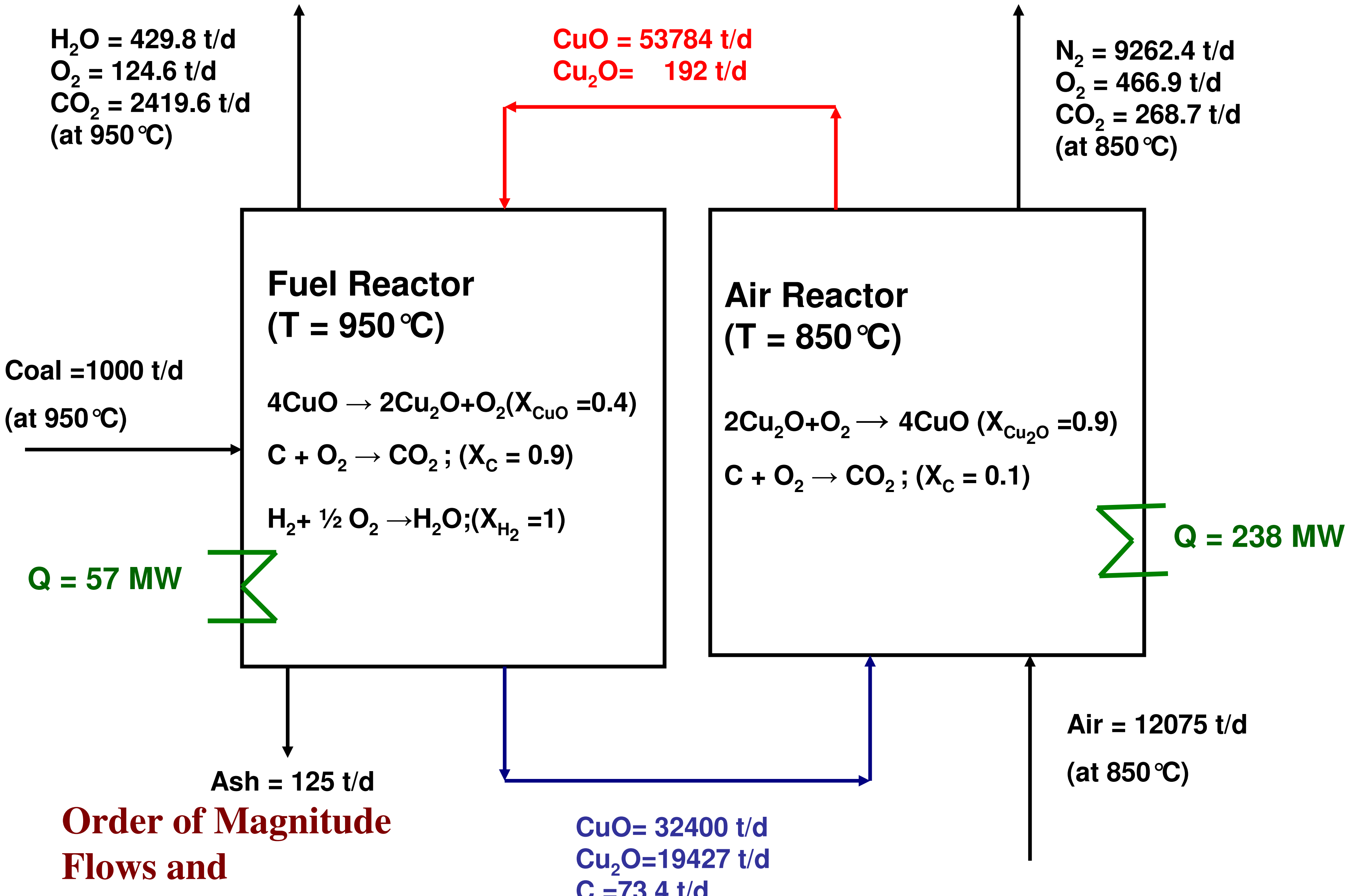


Prisedsky & Vinograd: Cu_2O grains surrounded by fractured CuO

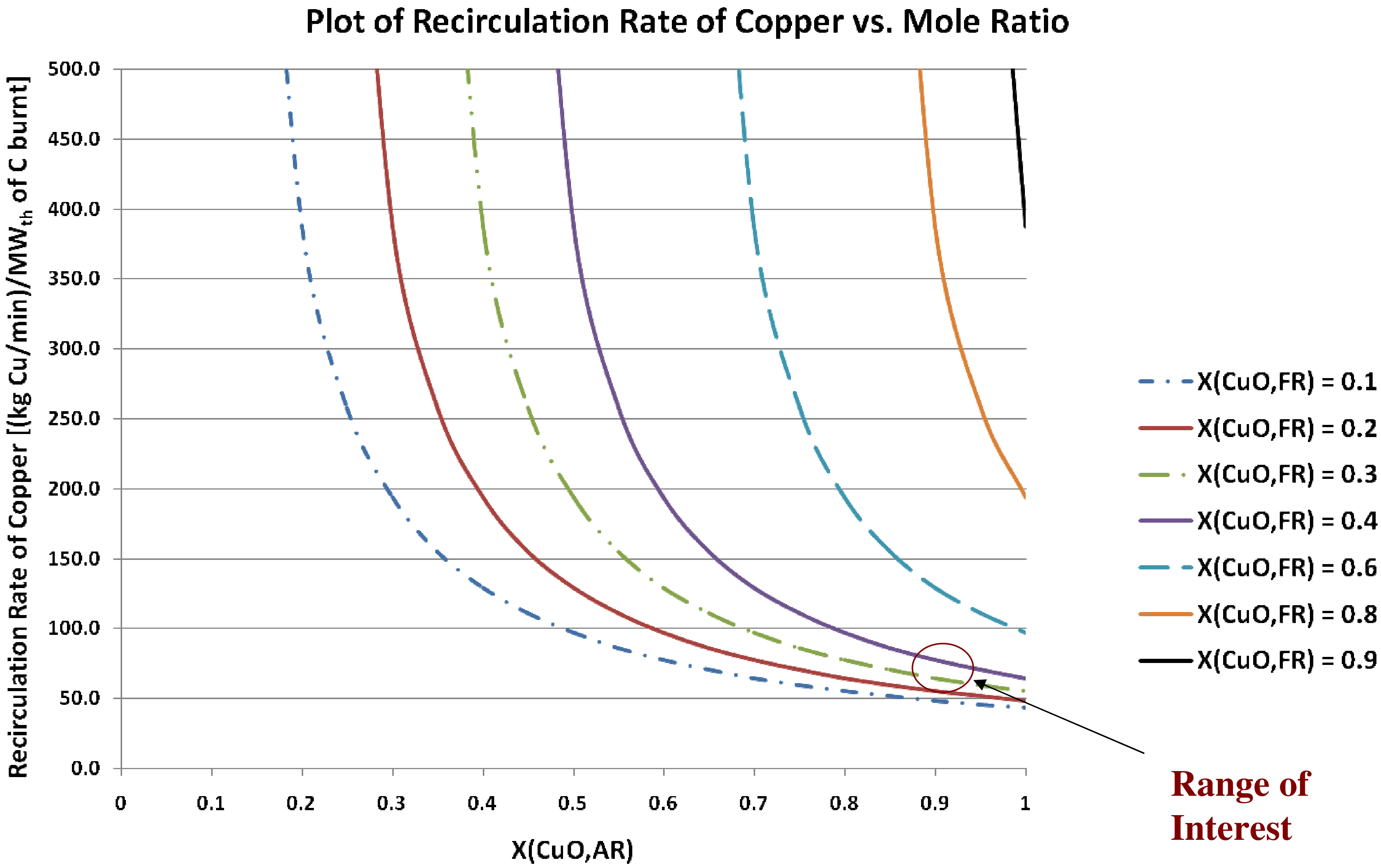


Zhu, Minura, and Isshiki:

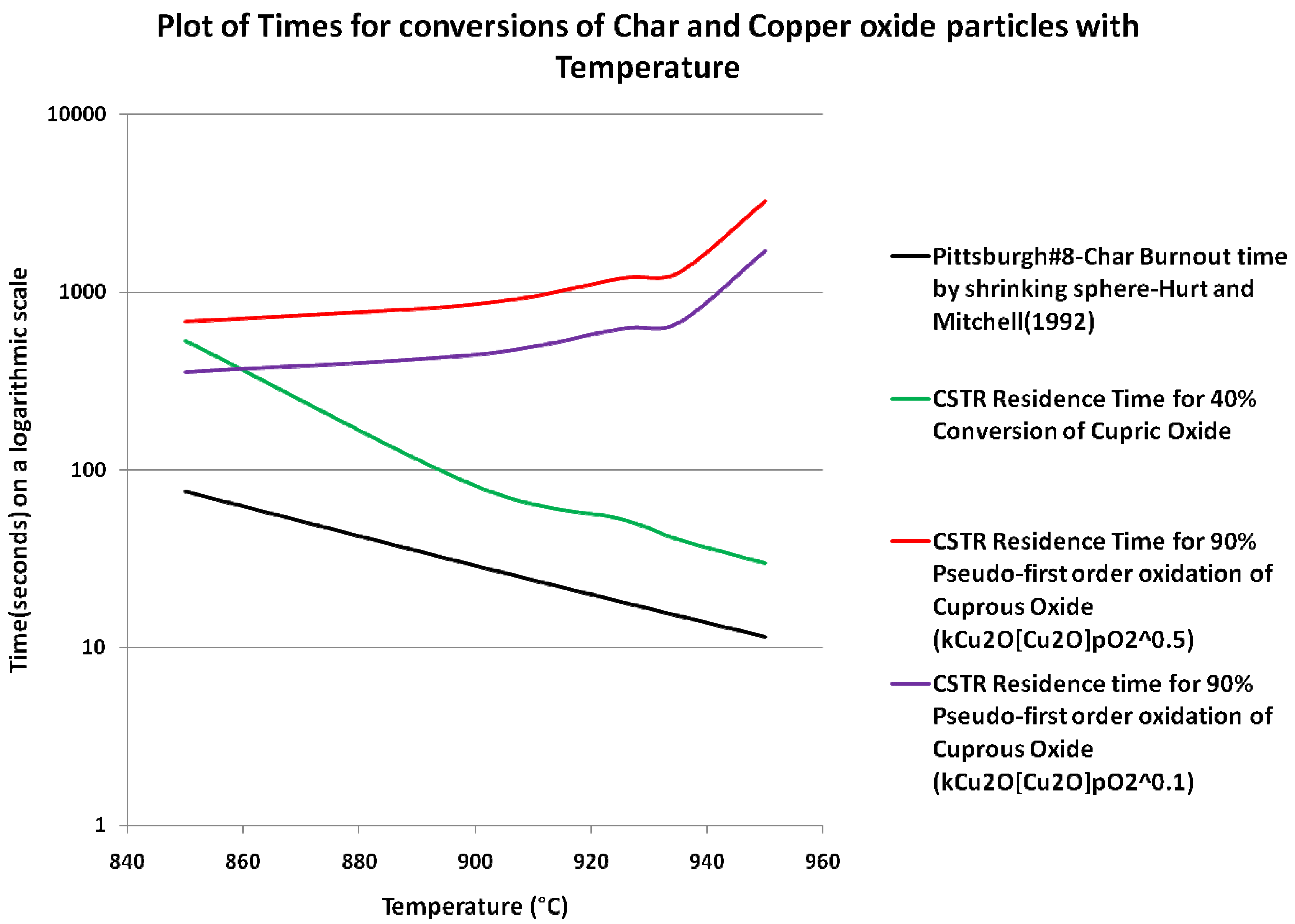
"The activation energy becomes..negative due to sintering of CuO grains" & decrease in grain boundary diffusion



Order of Magnitude Flows and Concentrations: Aspen Model



Objectives: Maximize [$(CuO)_{AR}$ – $(Cu)_{FR}$] to minimiz recirculation rate; Maximize $(CuO)_{FR}$ and minimize $(CuO)_{AR}$ to maximize reaction rates.



Plot of Times for conversions of Char and Copper oxide particles with Temperature
10000
1000
100
10
1
Time(seconds) on a logarithmic scale
840
860
880
900
920
940
960
Temperature (°C)
Pittsburgh#8-Char Burnout time by shrinking sphere-Hurt and Mitchell(1992)
CSTR Residence Time for 40% Conversion of Cupric Oxide
CSTR Residence Time for 90% Pseudo-first order oxidation of Cuprous Oxide (kCu2O[Cu2O]pO2^0.5)
CSTR Residence time for 90% Pseudo-first order oxidation of Cuprous Oxide (kCu2O[Cu2O]pO2^0.1)

Concluding Comments

- CLOU offers a potential for greatly reducing times for carbon gasification, as has been previously shown by Lewis and Gilliland and Mattison, Leion and Lyngfelt.
- CuO decomposition kinetics and Cu_2O are being generated to enable quantitave assessment of the potential of CLOU.
- Order of magnitude calculations show benefits of CLOU of 1. low oxygen carrier (OC) circulation rate, 2. low OC inventory, 3. Flexibility in selecting temperatures of fuel and air reactor because of exothermicity in both. Issues of OC support, contamination, attrition, sintering, and optimum reactor configuration and operation need yet to be adequately resolved.

Acknowledgments

The authors wishes to acknowledge:

- **Support by DOE under Award Number: DE-FC26-06NT42808.**
- **Lewis and Gilliland for introducing one of the authors (AFS) to the principles of chemical engineering.**
- **Andres Lynfelt, Tobias Mattison and Henrik Leion for introducing the same author to CLC and CLOU.**