Reforming landfill gas to syngas

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Outline

- Background / Motivation
- Experimental Results
  - Pre-reduced vs “As-prepared”
  - Kinetic parameter estimation
  - BET and EDX
- Future work
- Conclusions

Biogas: Landfill Gas (LFG)

Facts about landfills and landfill gas.

- Landfill gas is created when waste in a landfill decomposes.
- 50% CH_4 & 50% CO_2,
  - Oxygen, nitrogen, and hydrogen, and trace amounts of hazardous air pollutants (less than 0.2%).
- Largest anthropogenic (human-made) source of methane in the United States.
- ***Combustion of landfill gas in an engine, turbine, boiler significantly reduces odors and emissions of methane and hazardous air pollutants*.**

Background

LFG = Landfill Gas - 50 % CO_2, 50 % CH_4

LFGE = Landfill Gas to Energy

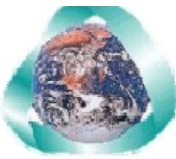
- Electricity generation
  - on site
  - sell to the grid
- Cogeneration
- Thermal applications – boiler, kiln, greenhouse, etc.
- Treatment of leachate

Convert it to synthesis gas (H_2 and CO) which can be used:

- As a feed gas for a fuel cell
- Enhanced combustion processes
- Possible Chemical Synthesis (methanol, acetic acid, or hydrocarbons)

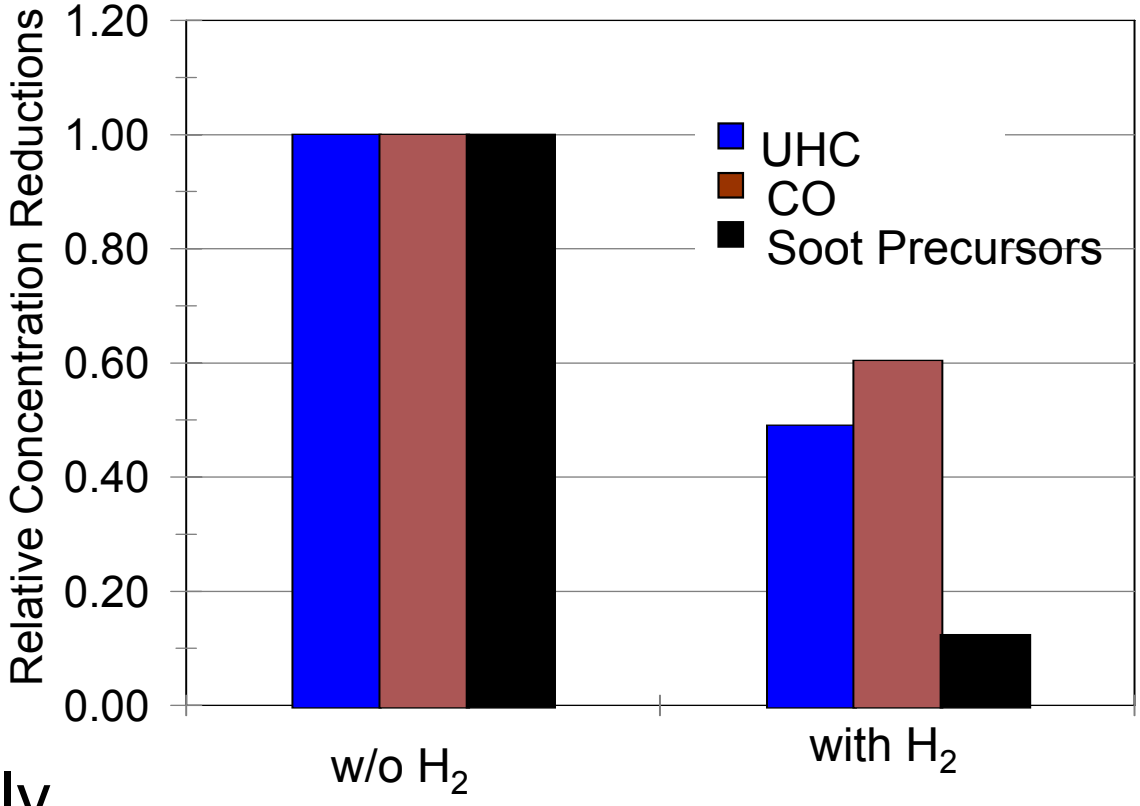
Background

- Steam Reforming
  - $CH_4 + H_2O \rightarrow CO + 3\ H_2$ $\Delta H = +226$ kJ/mol
- Partial Oxidation of Methane
  - $CH_4 + \frac{1}{2}\ O_2 \rightarrow CO + 2\ H_2$ $\Delta H = -44$ kJ/mol
    - Problem: At the stoichiometric CH_4-to-O_2 ratio there is significant carbon formation on many catalysts
- Dry Reforming
  - $CH_4 + CO_2 \rightarrow 2\ CO + 2\ H_2$ $\Delta H = +261$ kJ/mol



H_2 Spiking Data

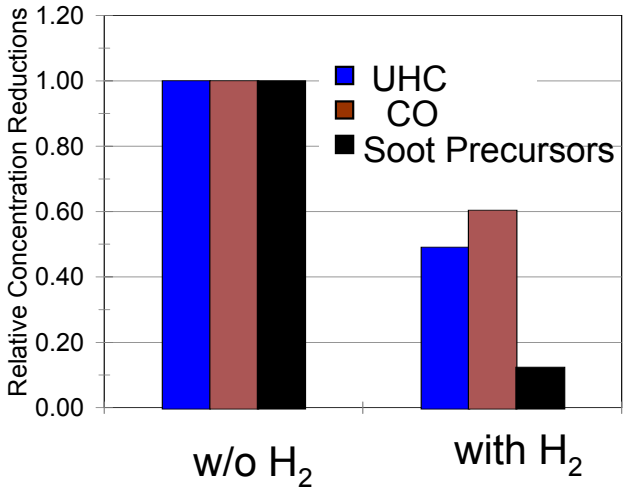
- ~15% H_2 added to a flame
- Typical boiler combustor flame
- medium BTU gas (300 BTU/ft^3)



- Reduces NO significantly
  - Reduced CH radical concentration
  - Leaner flammability limit – lower thermal NO

H_2 Spiking for Lower Emissions

- Lower NO_x, CO and HC:
  - NO_x emissions as low as 0.11 g/hp-hr
  - NO_x reduction > 80% in a gasoline fueled SI engine
  - Experiment w. ~15% H_2 added to a flame
  - Flame represents process-heating combustor
  - Low BTU refinery fuel gas used (~300 BTU/ft^3)



- Reduced GHG
  - Eliminates LFG purging and flaring

- Advantages of H_2 in natural gas engines well documented:
  - L.Bromberg, D.R.Cohn, A.Rabinovich and J.Heywood "Emissions Reductions Using Hydrogen from Plasmatron Fuel Converters" at Diesel Engine Emission Reduction Workshop, San Diego, CA, Aug 2000
  - Hydrogen Consultants, Inc. of Littleton, Colorado, has also demonstrated that methane blended with only 5% hydrogen (Hythane®) can result in NOx and CO reduction of up to 50%.

Emissions Benefits

- Reduction in CO and HC.
- Improvements in lean limit stability
- NO_x emissions as low as 0.11 g/hp-hr over a range of equiv. ratios
- NO_x reduction > 80% in a gasoline fueled SI engine
- Advantages of H_2 in natural gas engines well documented:

- R.Breashes, H.Cotrill and J.Rupe, "*Partial Hydrogen Injection into Internal Combustion Engines – Effect on Emissions and Fuel Economy*" First Sympos. on Low Pollution Power Systems Development, Ann Arbor MI, 1973
- J.Houseman and F.W.Hohn, "A Two Charge Engine Concept: Hydrogen Enrichment", SAE 741169 (1974)
- S.R.Bell and M.Gupta, "Extension of the Lean Operation Limit for Natural Gas Fueling of a Spark Ignited Engine Using Hydrogen Blending". Combust. Sci. and Tech., **123** pp. 23-48 1997
- F.E Lynch and R.W.Marmaro; US Patent 5,139,002, 1992
- L.Bromberg, D.R.Cohn, A.Rabinovich and J.Heywood "Emissions Reductions Using Hydrogen from Plasmatron Fuel Converters" at Diesel Engine Emission Reduction Workshop, San Diego, CA, August 20-24, 2000
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H_2 Generation Approach

- 2 reaction pathways

  Preferred: $CH_4 + 1/2\ O_2 \xrightarrow{\text{Catalytic Partial Ox}} 2H_2 + CO$

  Undesirable: $CH_4 + 2O_2 \xrightarrow{\text{Deep Ox}} CO_2 + 2H_2O$

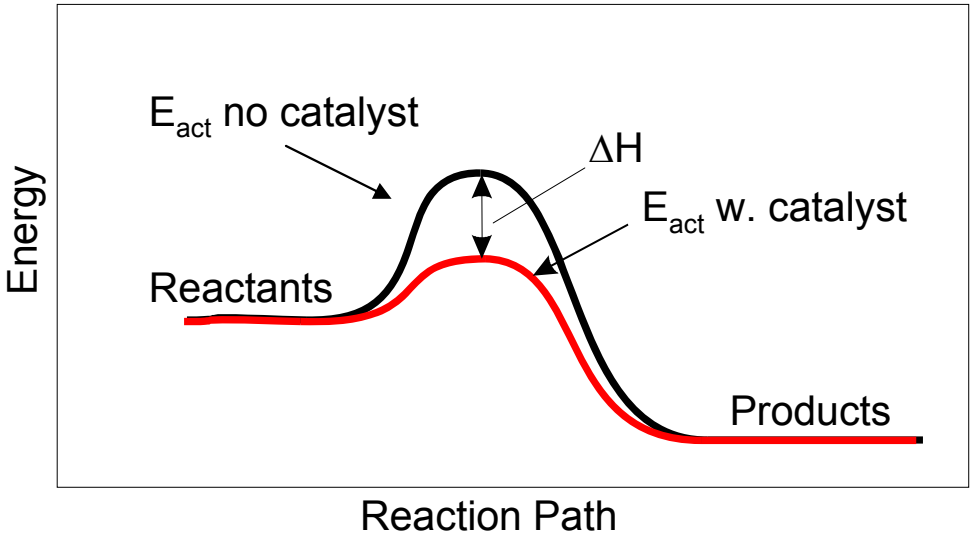
- Novel catalytic reactor design identified
  - extremely compact, efficient & lightweight
- Selective catalysts
- Low operating temp
  - Non-exotic materials of construction
- Robust, durable, stable reactor
  - Low temp gradients

Net effect: Temp rise; Reactive partial ox. products (CO, H_2)

Catalyst Attributes

- **Activity** – Initiate or speed up reaction w/o being consumed.

– However, catalyst may undergo changes during process



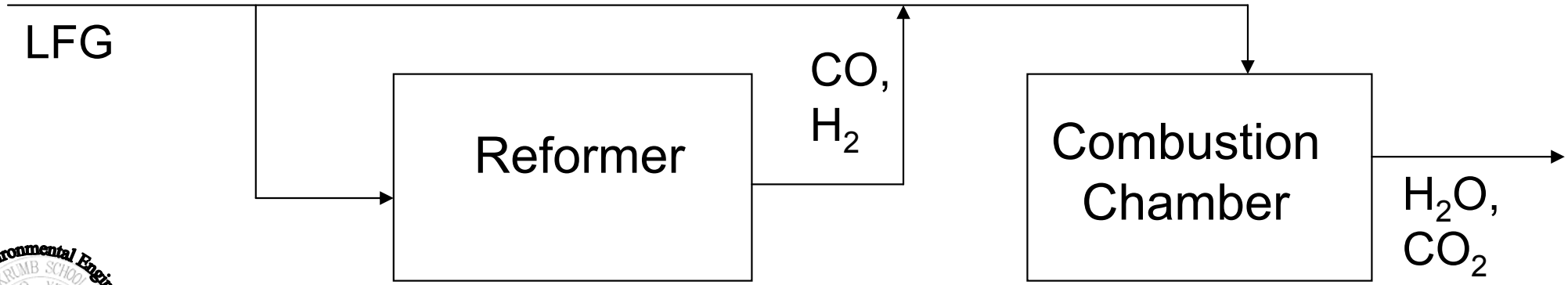
$$CH_4 + O_2 \xrightarrow{\text{Catalyst A}} CO_2 + H_2O$$

$$CH_4 + O_2 \xrightarrow{\text{Catalyst B}} H_2 + CO$$

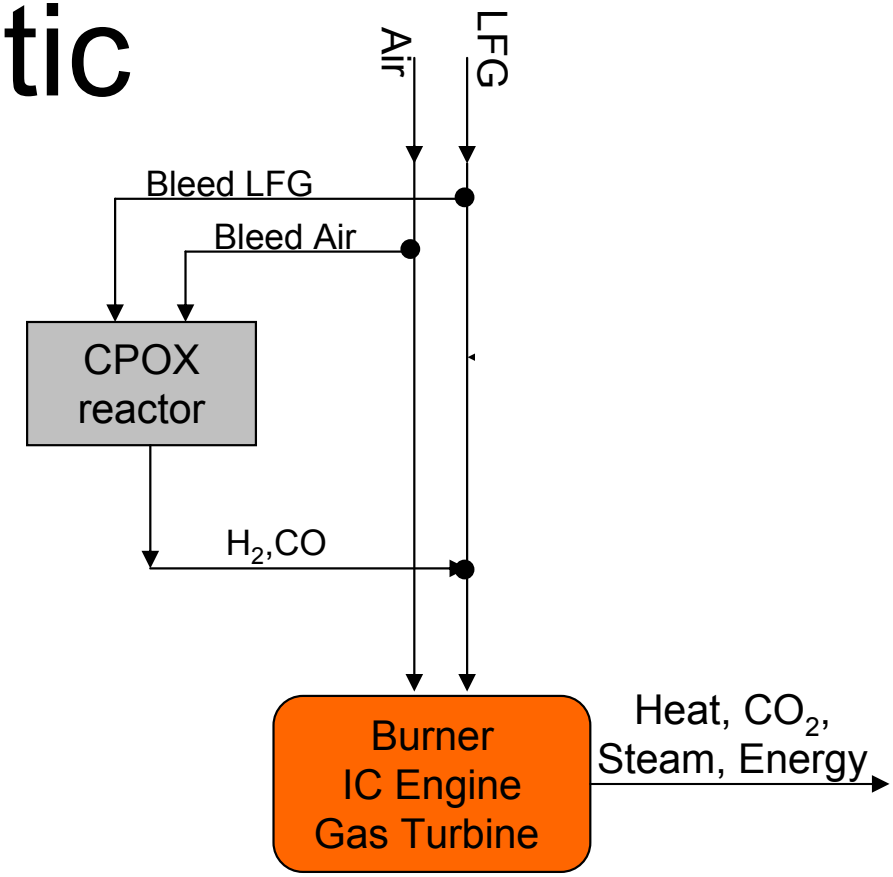
- **Selectivity** –Ability to speed up desired rxn
- Fuel to air ratio affects catalyst selectivity

Background

- Combustion benefits from H_2
  - Flame stability at low ϕ
  - Ignition at low ϕ
  - Low temperature operability
- Emission benefits
  - Reduced GHG
  - Lower NOx, CO, UHC



System Implementation Schematic

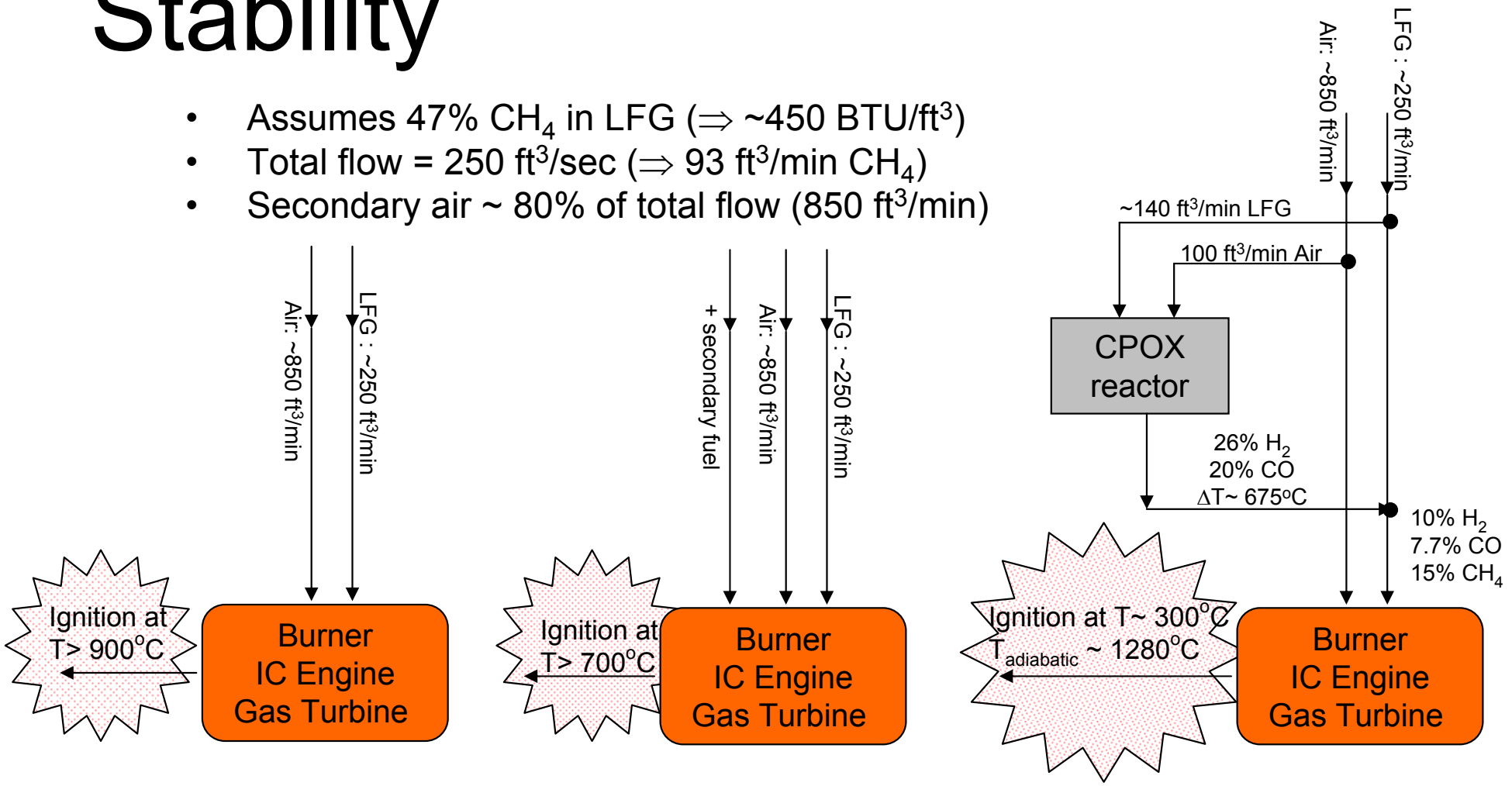


- Flow Splitter/mixer

More reactive system; Reduce/eliminate secondary fuel usage

Lower Ignition Temperature for Stability

- Assumes 47% CH_4 in LFG ($\Rightarrow$ ~450 BTU/ft^3)
- Total flow = 250 ft^3/sec ($\Rightarrow$ 93 ft^3/min CH_4)
- Secondary air ~ 80% of total flow (850 ft^3/min)



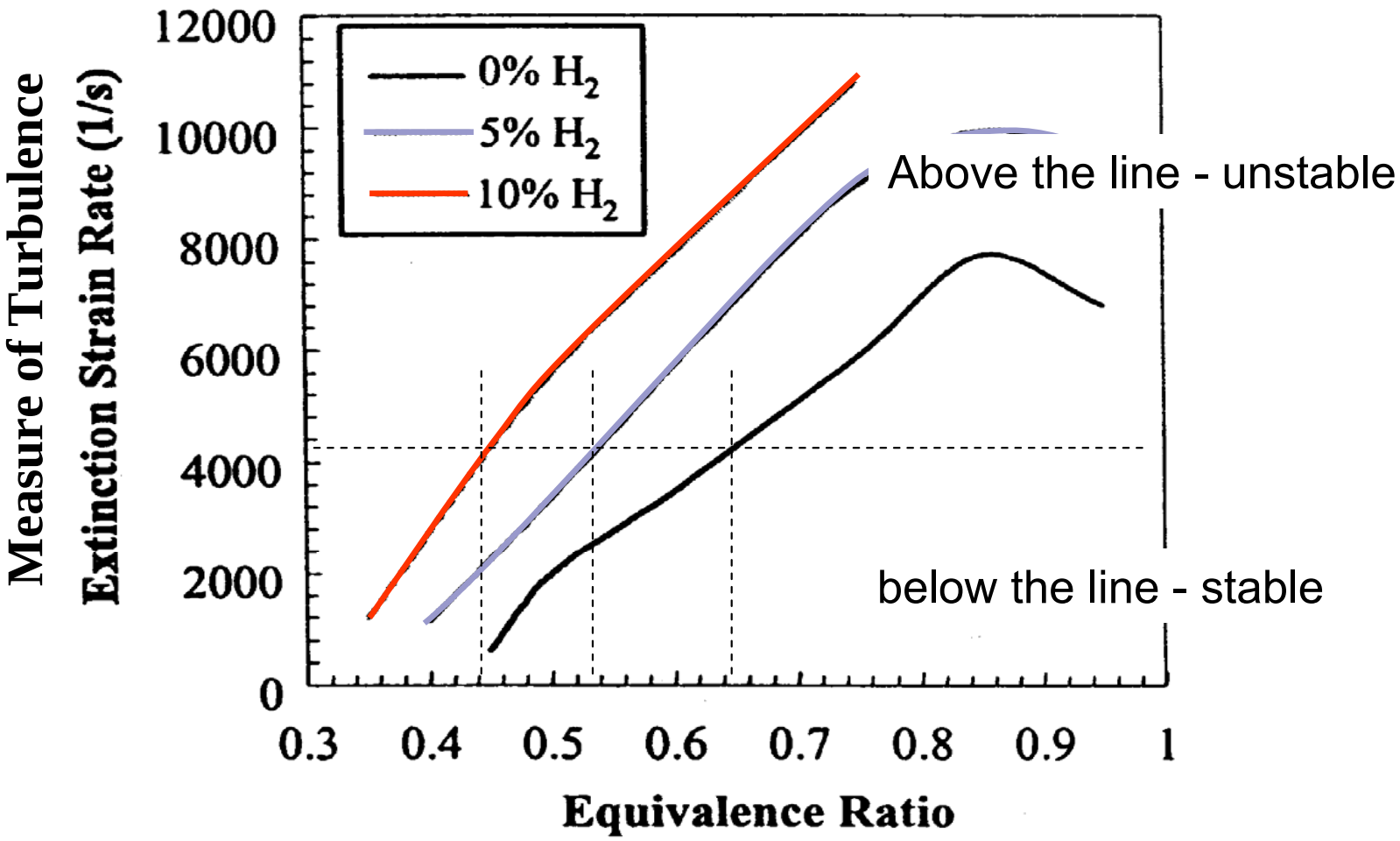
Requires lower net energy & ignition temp. CH_4 fluctuation permissible

Combustion Enhancements

- Reformed LFG or biogas
  - Better combustion performance
  - Reduced emissions
  - Little or no engine modifications

- $CH_4 + ½ O_2 \rightarrow CO + H_2$
  - Use the H_2 to enhance the combustion

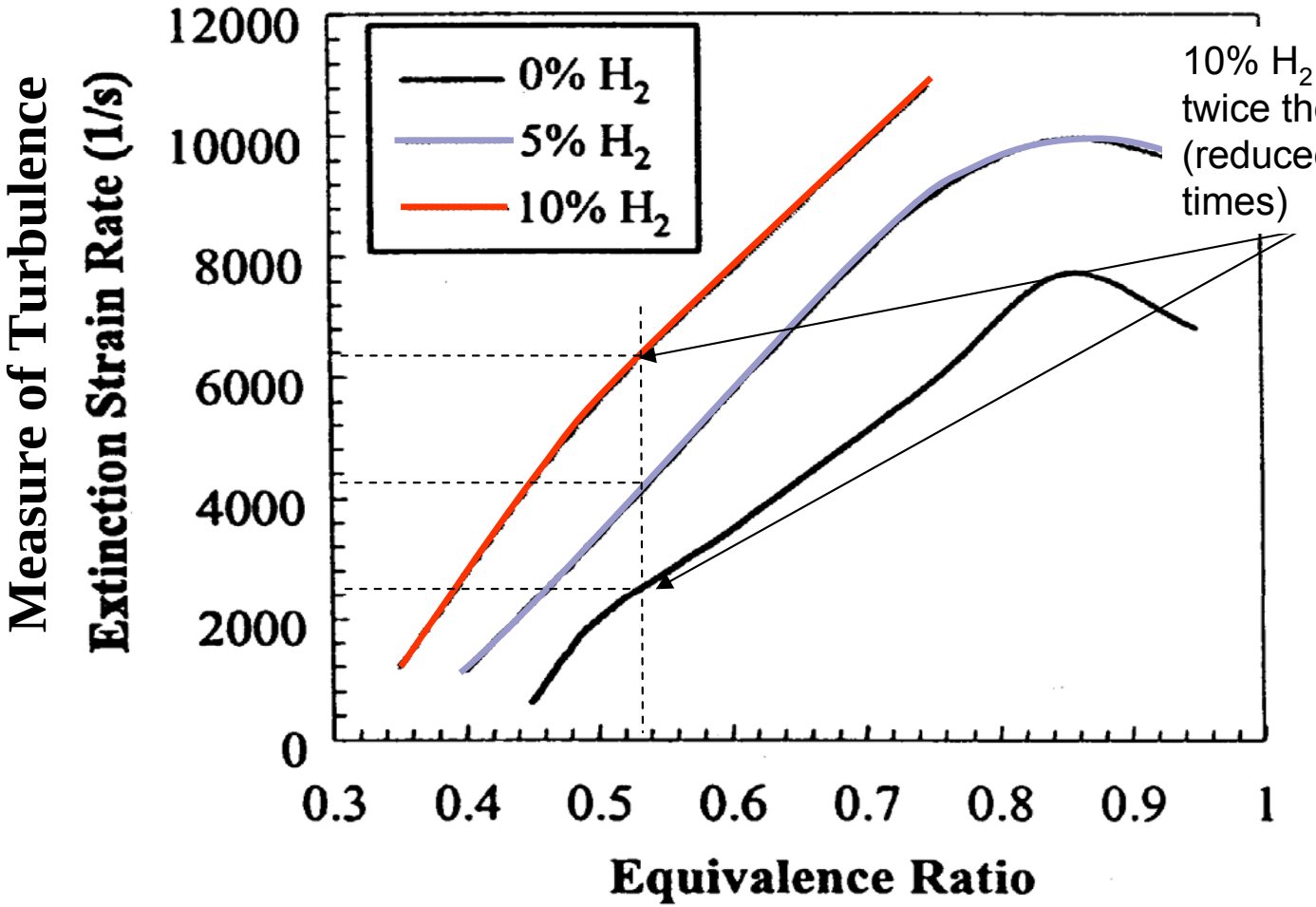
Combustion Benefits from H_2



H_2 addition increases reactivity, extending stability/blowout limits

Calculation, GRI 2.1 mechanism for CH_4 @ 1 atm, 400 C inlet; Cong & Jackson (1999)

Combustion Benefits from H_2



10% H_2 yields stability at twice the turbulence levels (reduced ignition delay times)

CO_2 as a potential feedstock.

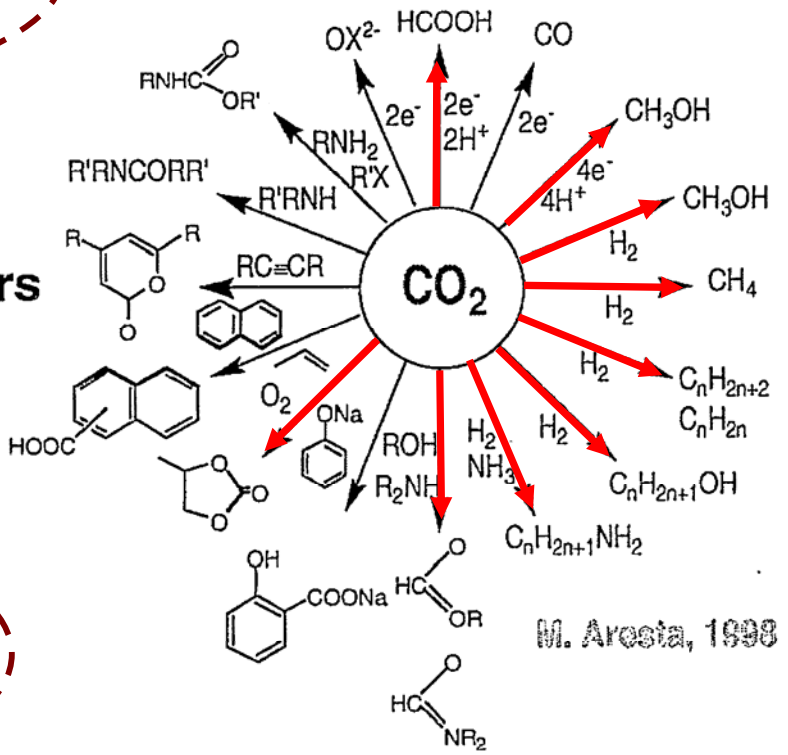
Intermediates or fine chemicals for the chemical industry

- -C(O)O- : ~~Acids~~, esters, lactones
- -O-C(O)O- : Carbonates
- -NC(O)OR- : Carbamic esters
- -NCO : Isocyanates
- -N-C(O)-N : Ureas

Use as a solvent

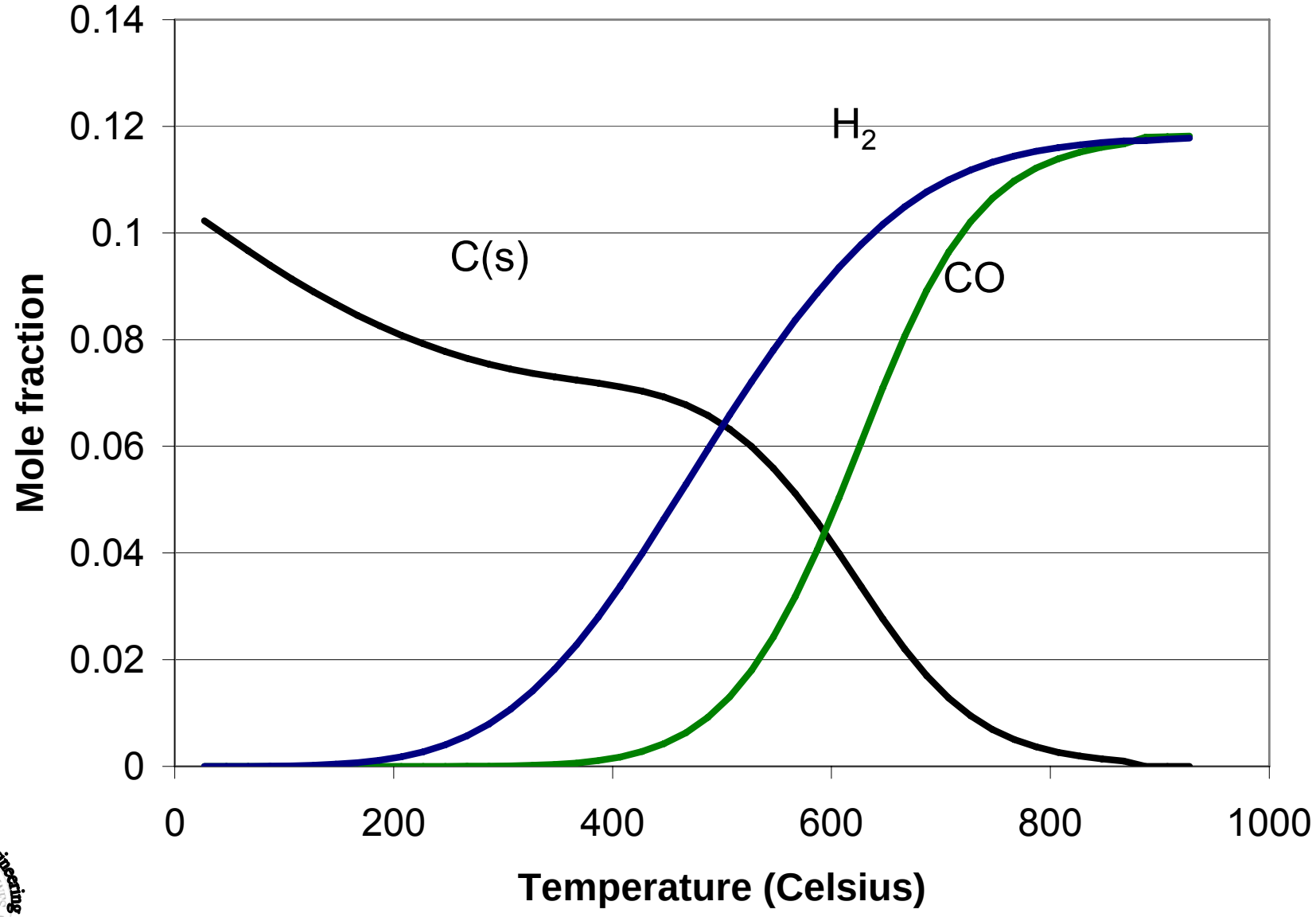
Energy rich products

- CO, CH_3OH
- Hydrocarbons and their derivatives

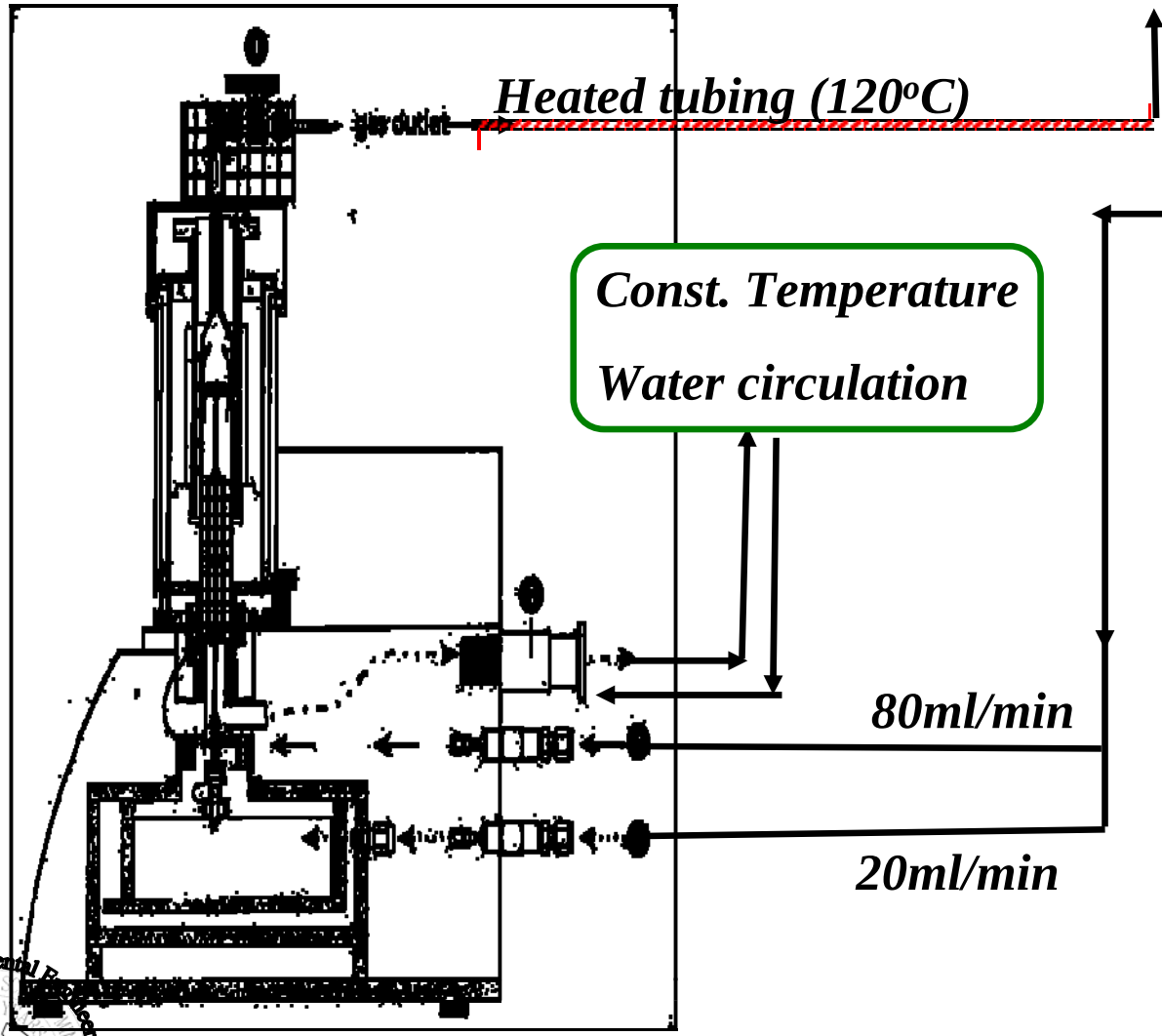


Equilibrium Calculation

$$CH_4 + CO_2 + N_2 \Leftrightarrow H_2 + CO + N_2 + H_2O(g) + C(s) + CO_2 + CH_4$$



Experimental Setup



Micro-GC

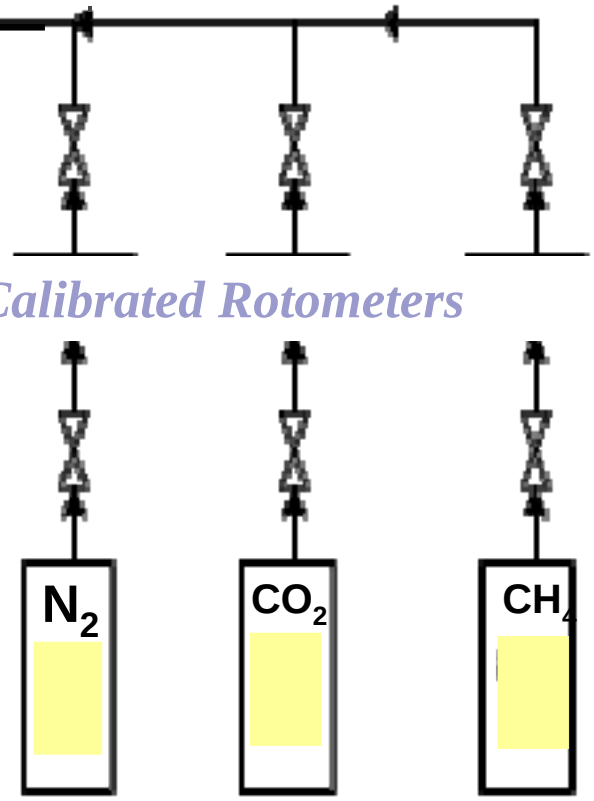
Heated tubing (120°C)

Const. Temperature

Water circulation

80ml/min

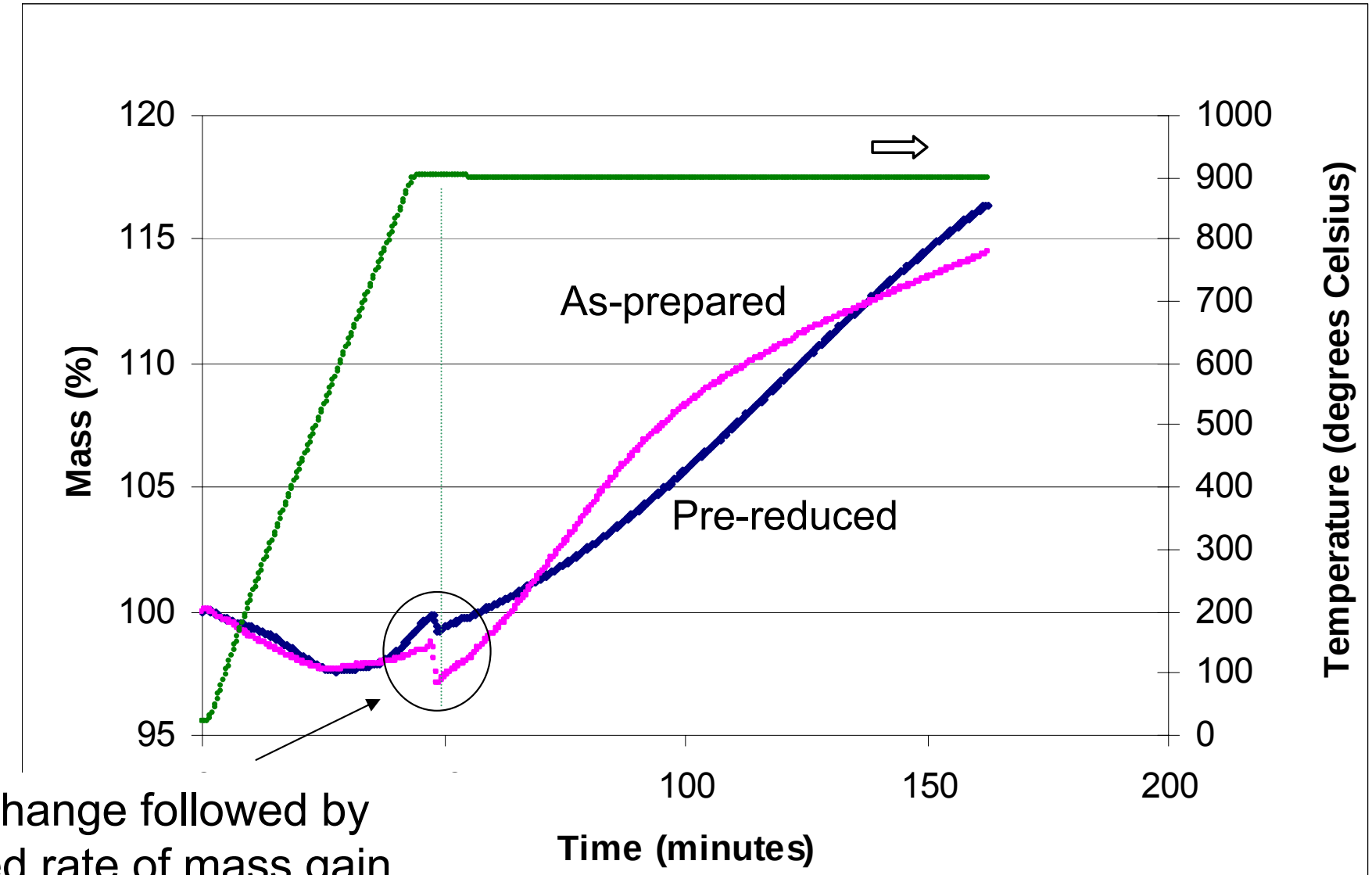
20ml/min



Calibrated Rotometers

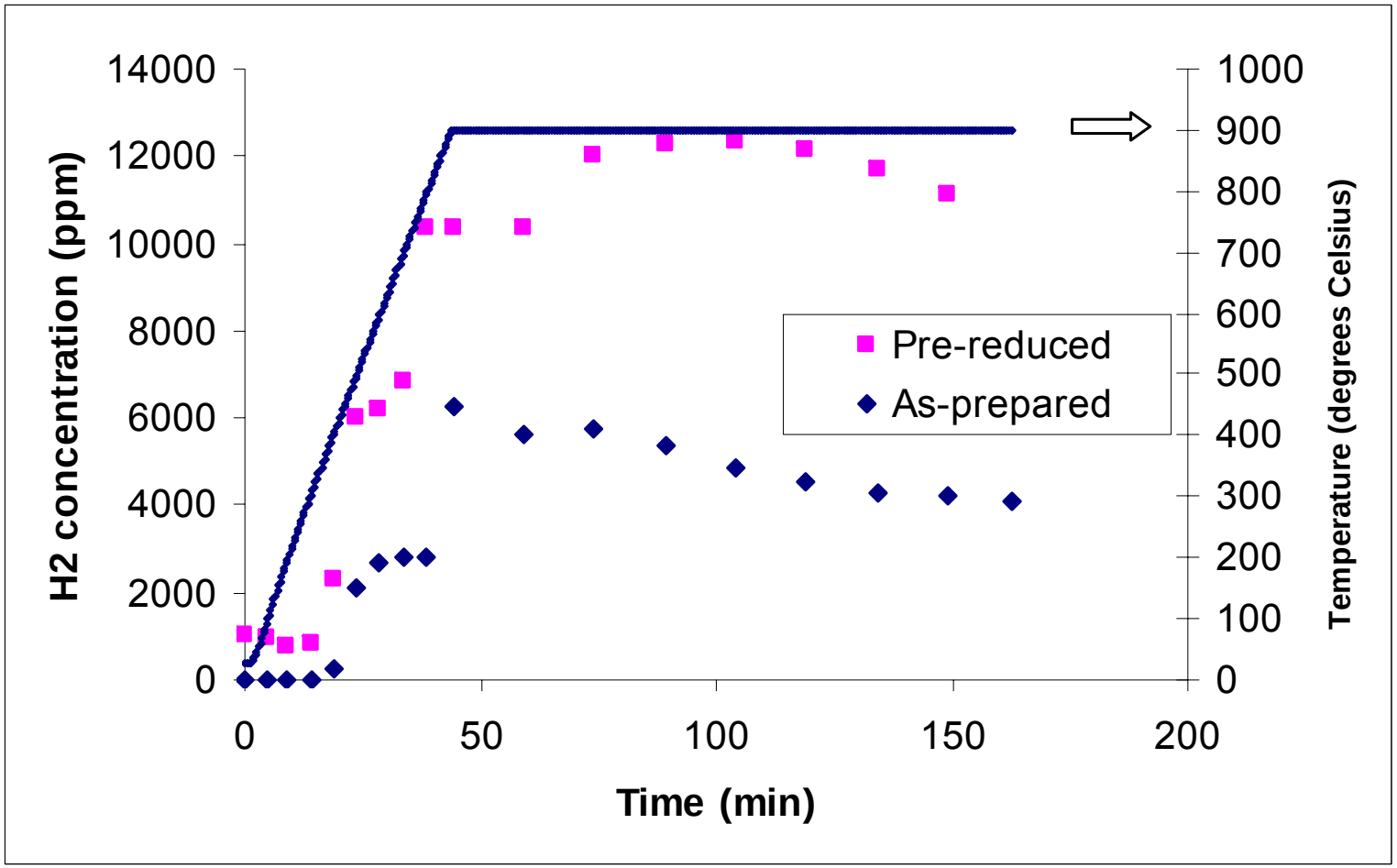
Certified gases (pure and mixtures)

Pretreatment - Results



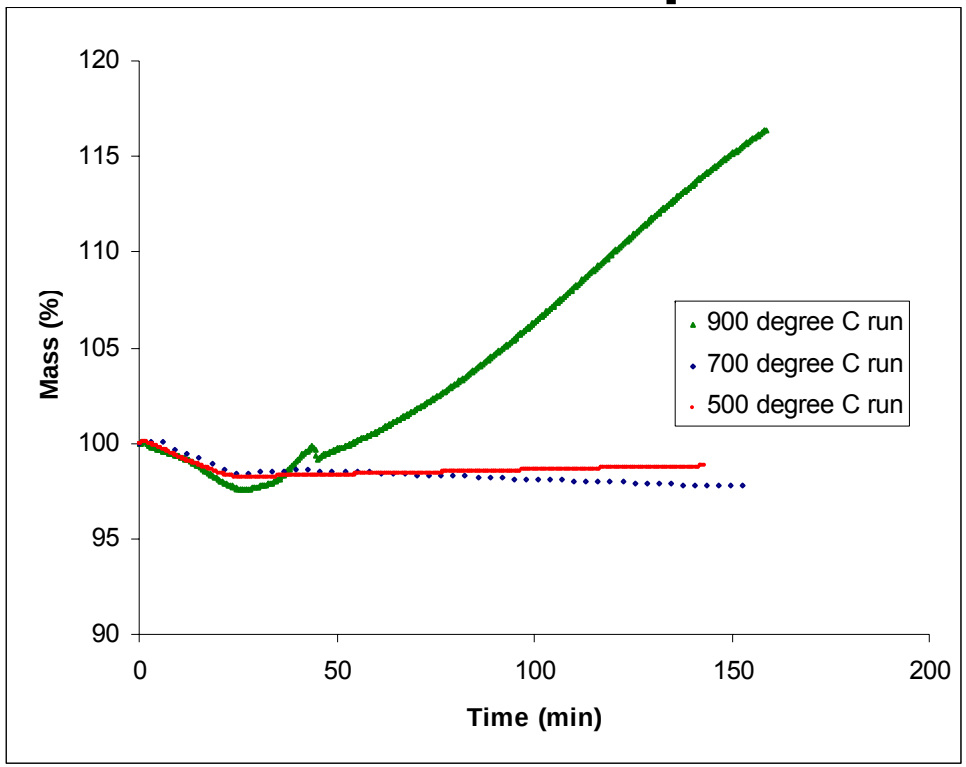
Abrupt change followed by increased rate of mass gain (carbon deposition)

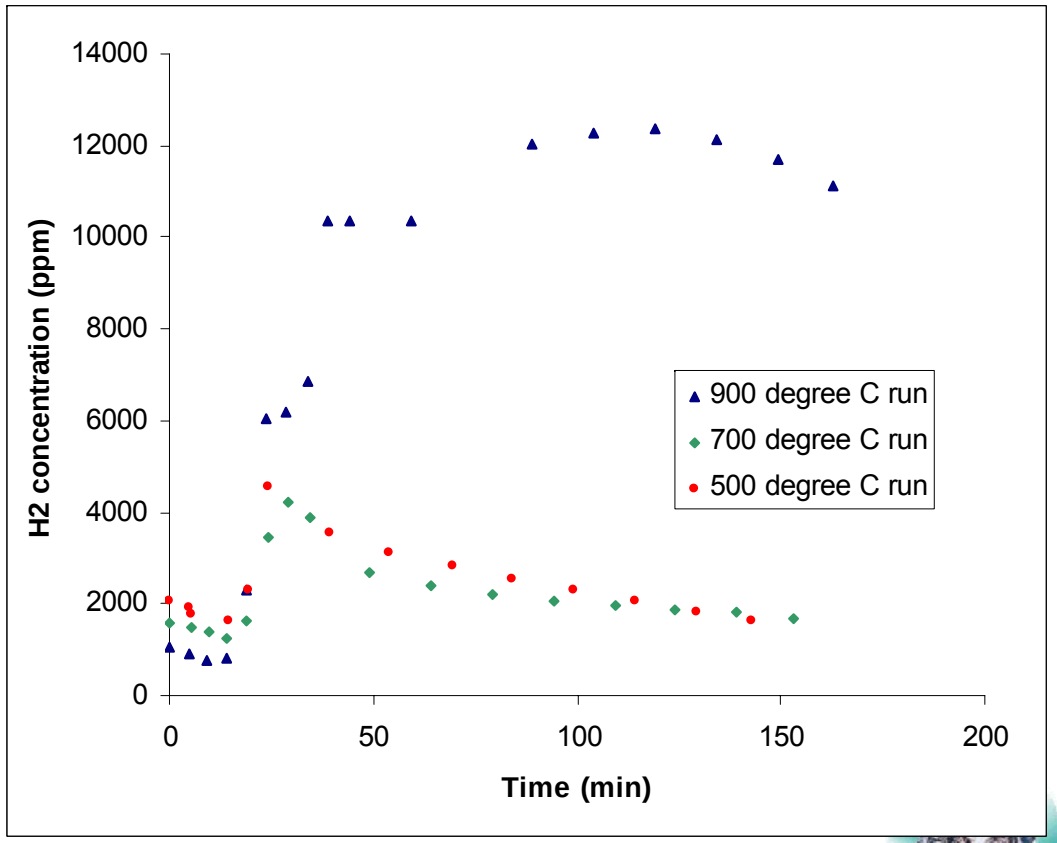
Pretreatment - Results



The reduced catalyst shows a higher production of both H_2 and CO

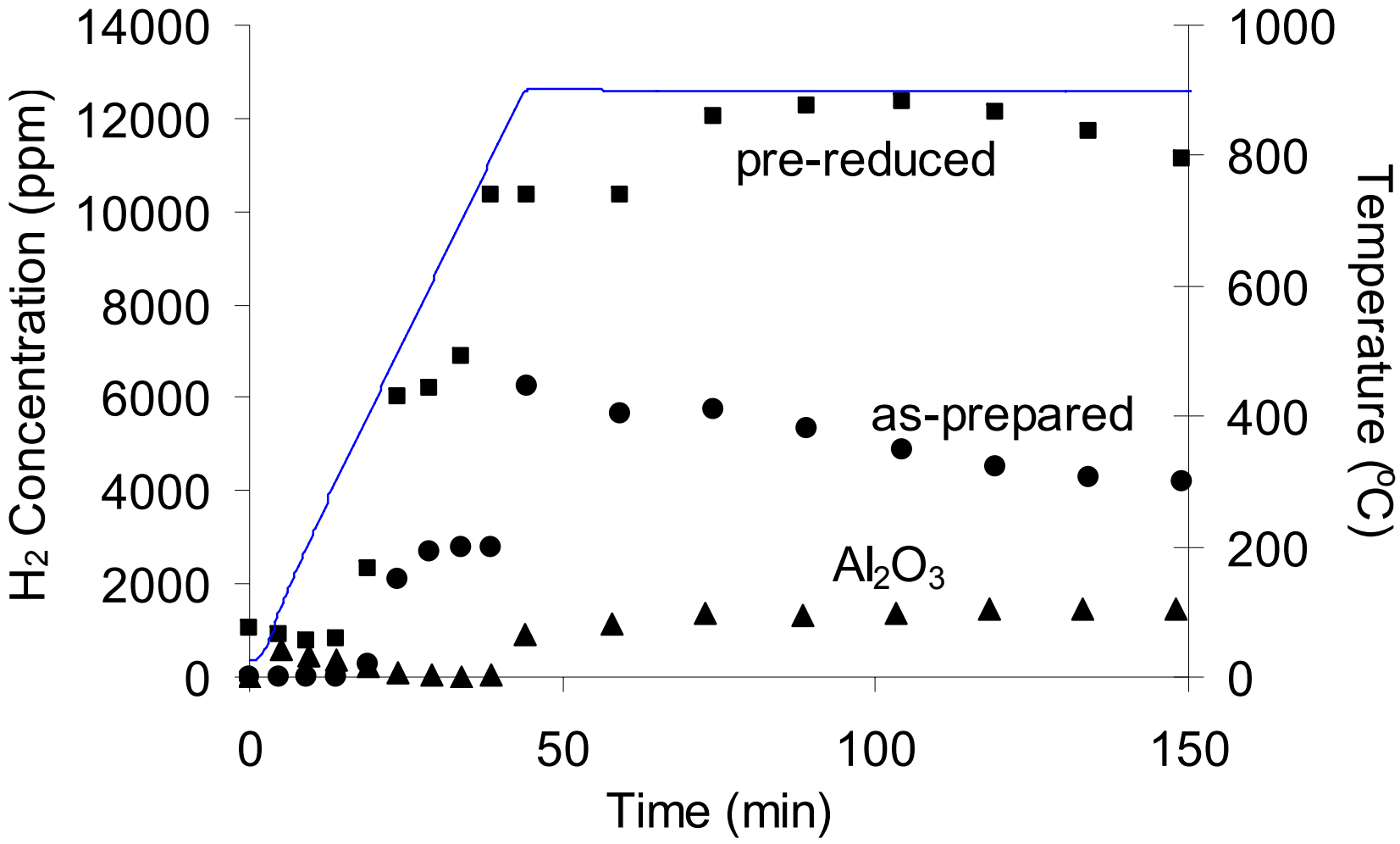
Various Temperatures - Results



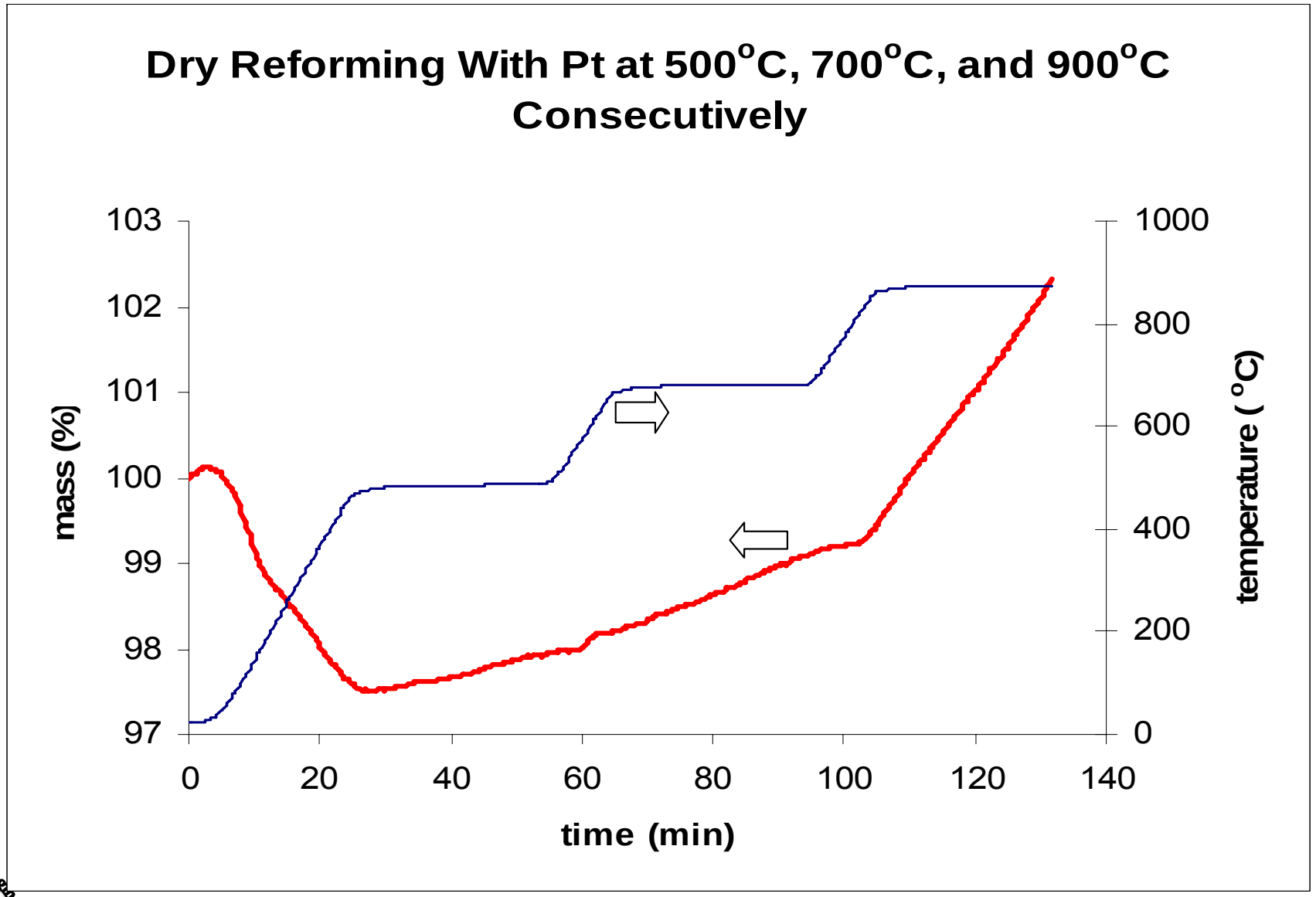


Higher mass gain for 900 C

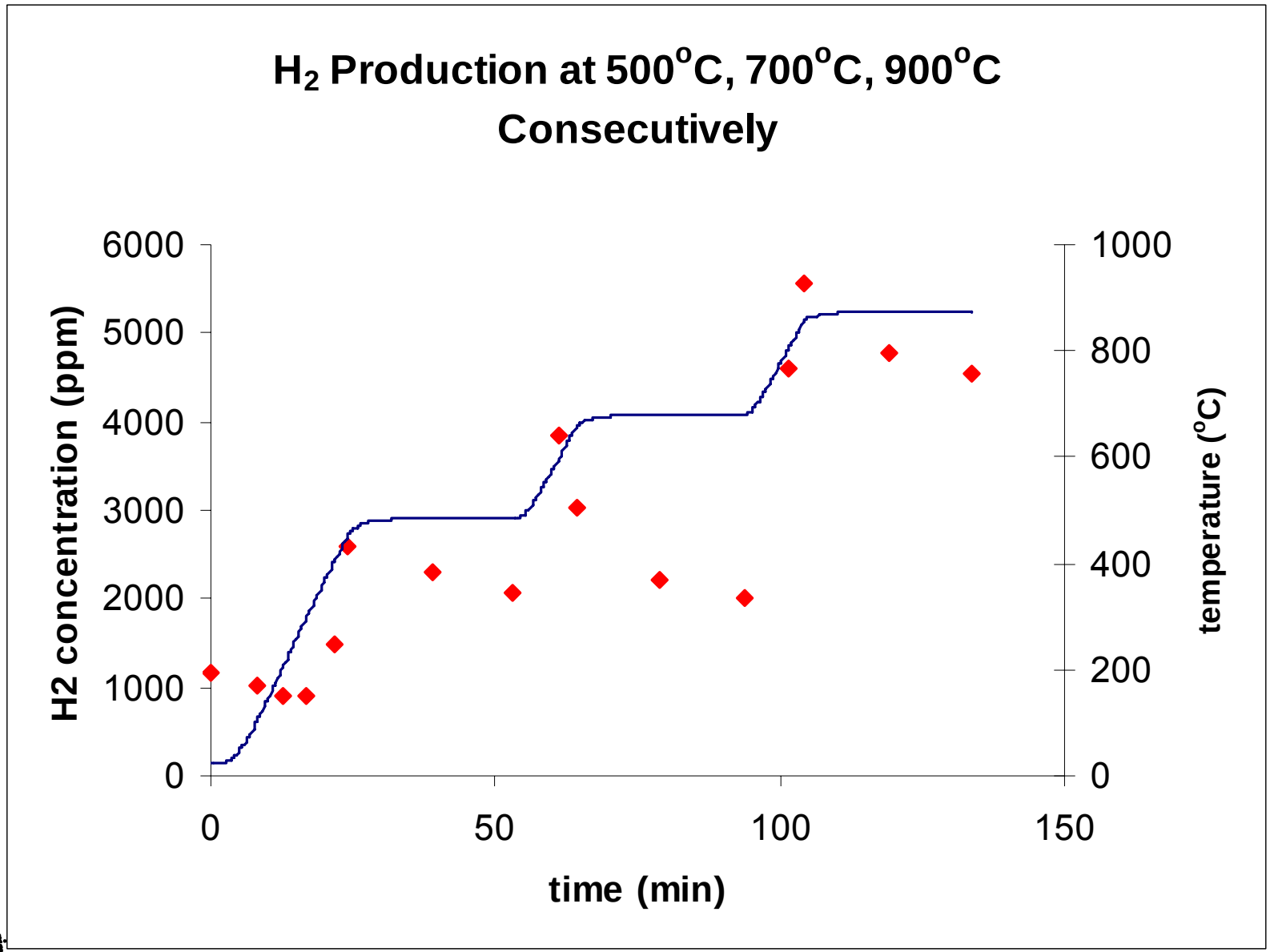
Yet high activity


14000
12000
10000
8000
6000
4000
2000
0
H2 Concentration (ppm)
1000
800
600
400
200
0
Temperature (°C)
pre-reduced
as-prepared
Al2O3
0
50
100
150
Time (min)

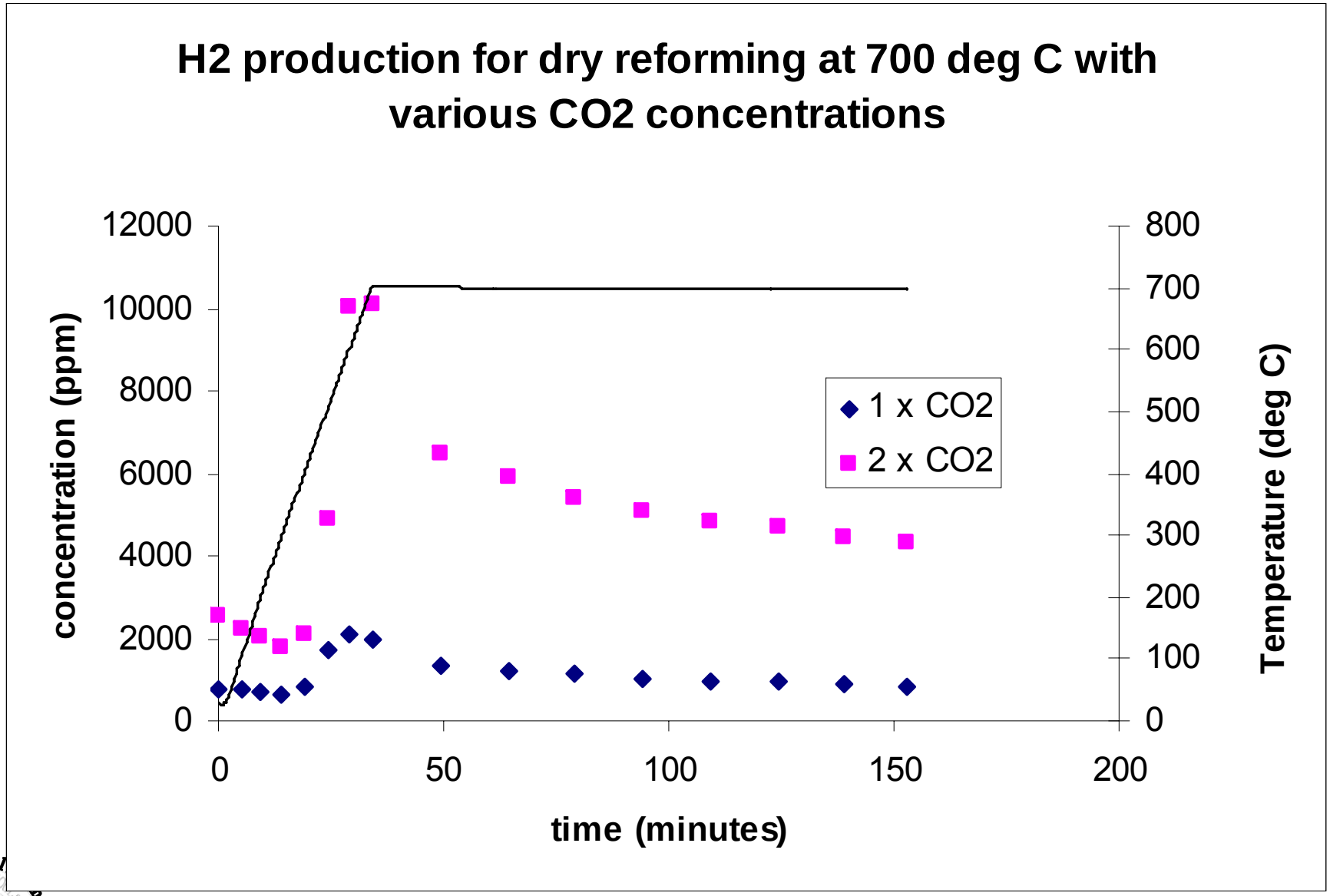
Ramp - Soak Results



Ramp - Soak Results



Various CO_2 Amounts – 700°C



BET Analysis

Sample Description	Surface Area (m^2/g)
Fresh Al_2O_3 support	188
Fresh Pt catalyst	152
DR at 900°C, As-prepared	159
DR at 900°C, reduction at 900°C	163

Active site (Pt metal) surface may be decreasing

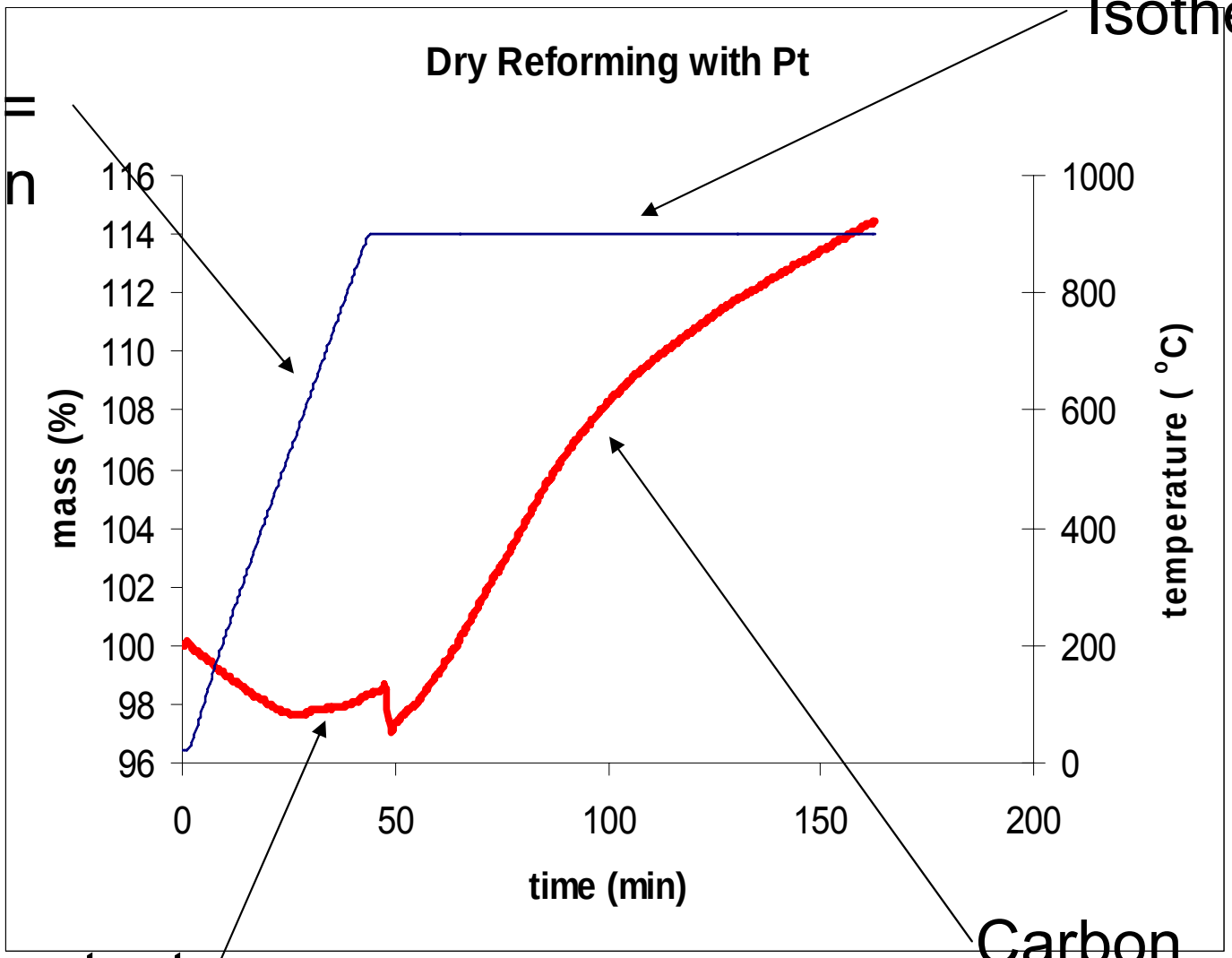
EDX Results

DR temp = 900, no reduction	C	19 %
DR temp = 900, no reduction	C	24 %
DR temp/red temp = 900°C	C	28 %
DR temp/red temp = 900°C	C	22 %
DR temp/red temp = 700°C	C	10 %
DR temp/red temp = 500°C	C	4 %

- Questions
  - Not reducing = less carbon deposition
  - more carbon deposition at higher temperatures = thermal breakdown of CH_4: $CH_4 \rightarrow 2\ H_2 + C$

Kinetic Analysis

Heating rate =
β = 20 K/min



Isothermal

Reactant Deposition

Carbon Deposition

Kinetic Analysis: Basic Equations

- All kinetic models have same basic equations:

$d\alpha/dt = k f(\alpha)$

$k = A \exp(E/RT)$

$d\alpha/dt = k (1-\alpha)^n$

α = conversion factor

A = pre-exponential factor

E = apparent activation energy

T = absolute temperature

n = apparent order of reaction

- Conversion factor, α:

decomposition: $\alpha = w_i - w / w_i - w_f$

deposition: $\alpha = w - w_i / w_f - w_i$

w_i = initial weight

w_f = final weight

w = weight at some time t

Kinetic Analysis – Coats-Redfern Method

- Heating rate, β:

$$\beta = dT/dt$$

$$\beta = d\alpha/dT = A \exp(-E/RT)(1-\alpha)^n$$

Separation of variables, integrate, take log of each side:

For $n \neq 1$

$$\log \{(1-(1-\alpha)1\text{-}n)/(T2(1-n))\} = \log AR/\beta E\,[1\text{-}2RT/E] - E/2.3RT$$

For $n = 1$

$$\log \{(-\log(1-\alpha))/T2\} = \log AR/\beta E\,[1 - 2RT/E] - E/2.3RT$$

Both are in the form $y = mx + b$:

$$n \neq 1: y = \log \{(1-(1-\alpha)1\text{-}n)/(T2(1-n))\}$$

$$n = 1: y = \log \{-\log(1-\alpha)/T2\}$$

$$x = 1/T$$

$$m = -E/2.3\,R$$

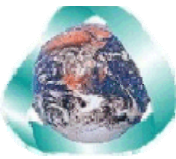
$$b = \log AR/\beta E\,[1\text{-}2RT/E]$$

Kinetic Analysis – Carbon Deposition

Sample Description	n	E (kcal/mol)	A (min^{-1})
DR at 900°C, reduction at 900°C, double CO_2	2	7.96	$0.25*10^{12}$
DR at 700°C, reduction at 700°C, double CO_2	2	60.70	$2.19*10^{12}$

Conclusions

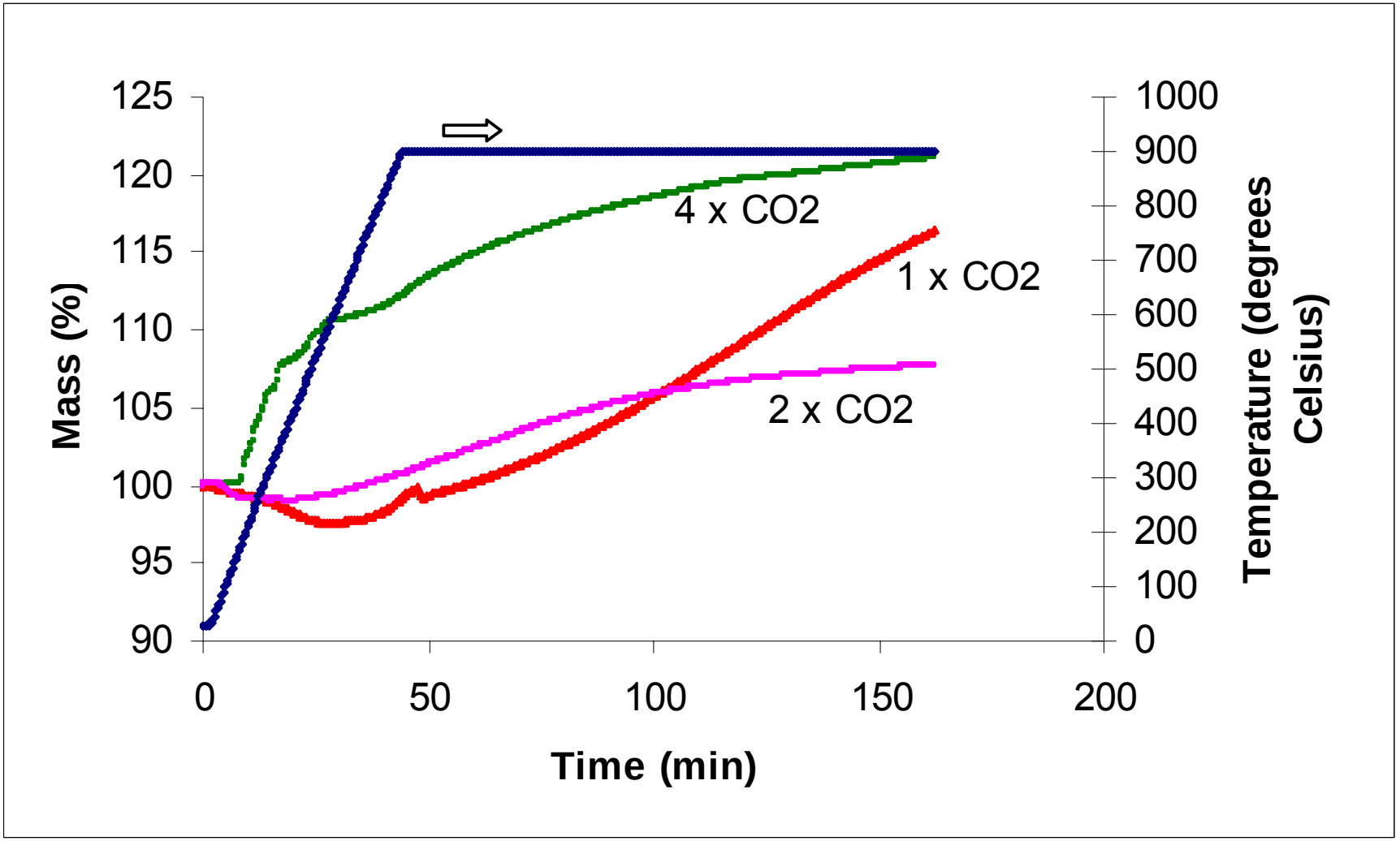
- Higher temperatures yields higher mass gains
- Higher temperatures yields more H_2/CO
- No real significant change in BET
  - Active sites may be changing
- EDX results show correct trends in terms of C
  - Verified by subsequent burn-off experiments
- Kinetic parameters calculated
  - Model development
  - Estimation of Durability – long term deactivation
- Flow reactor experimentation beginning
  - Durability – long term deactivation
- No appreciable performance on Au / Al_2O_3



Acknowledgements

- National Science Foundation – CTS SGER grant
- Tracy Jackson
- Noah Whitmore
- Thank You for listening

Various CO_2 Amounts – 900°C



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