WTE Research at the Combustion and Catalysis Laboratory (CCL)

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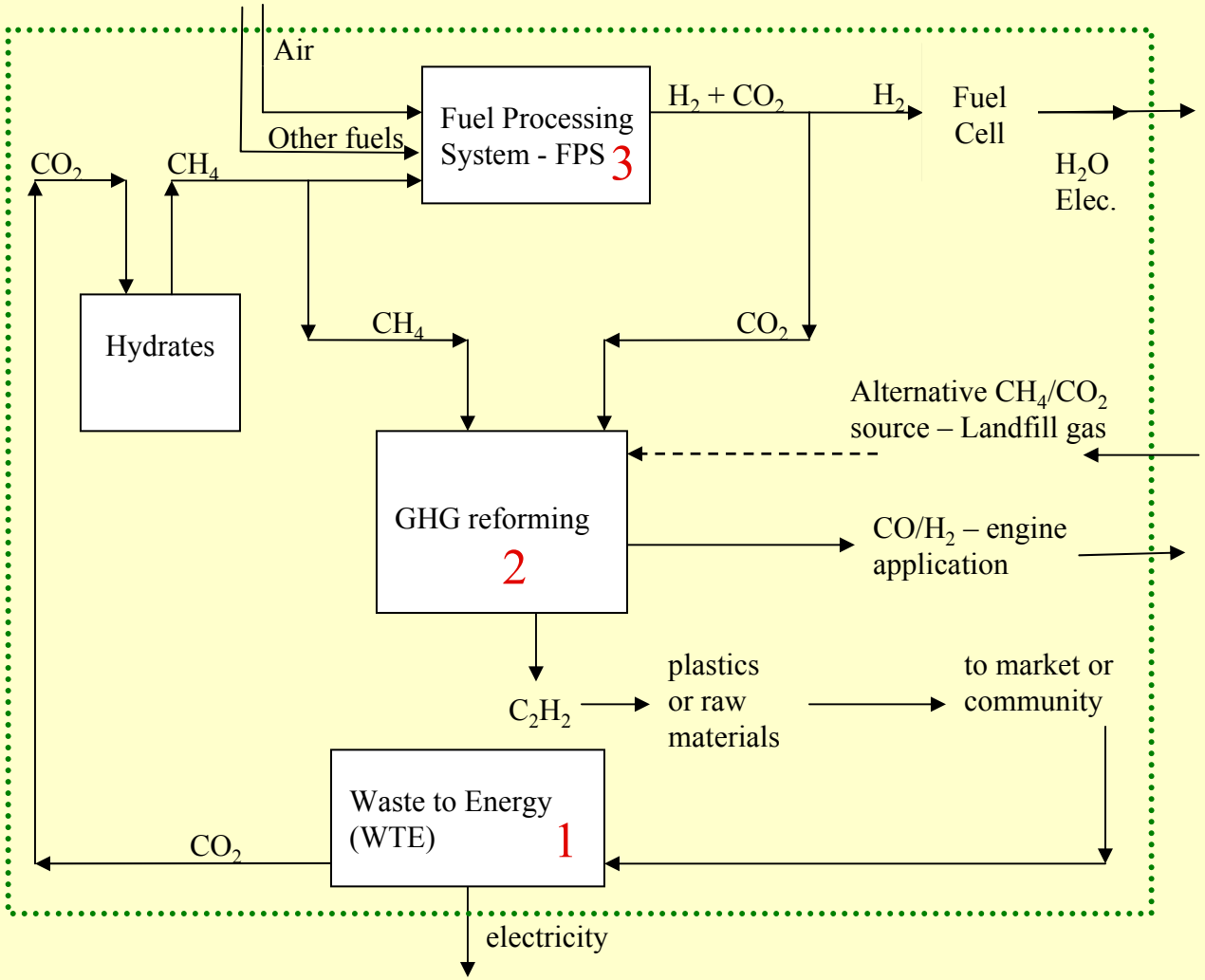
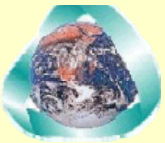
Columbia University

Presentation Outline

- Technologies
  - Waste to Energy
  - Greenhouse Gas Reforming
  - H_2 Generation from waste
- Conclusions
- Acknowledgements

Overview:
CCL @ Columbia University



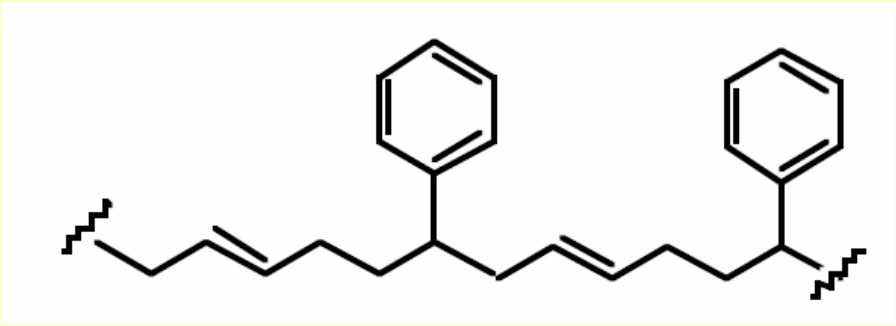


Waste to Energy: Tires

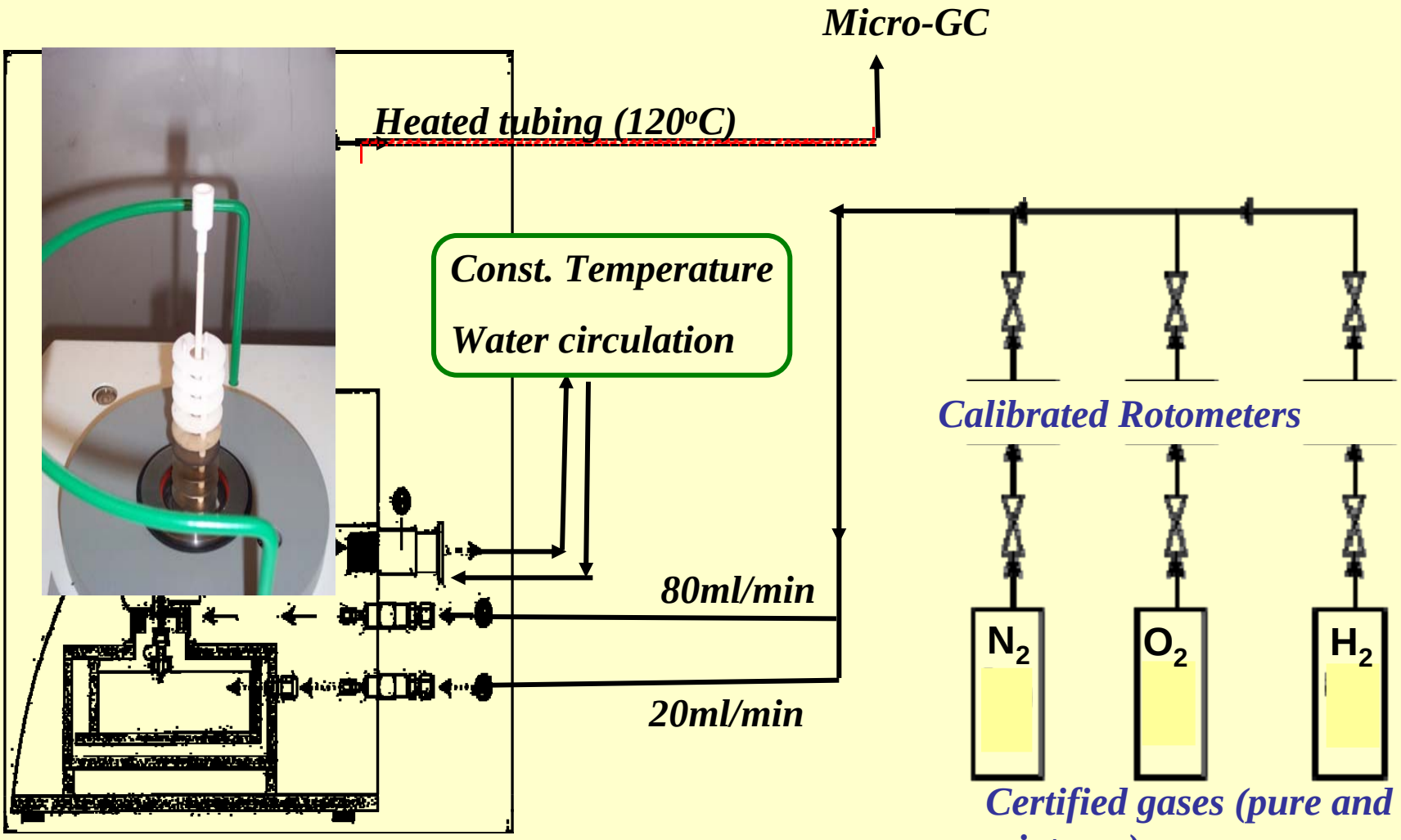
- Makeup (rubber and inorganic content) are well suited for energy production and material recovery
- Understand kinetics of combustion process
- Develop mechanism for modeling efforts
  - PAH, Chemical reaction pathways

Experimental Setup

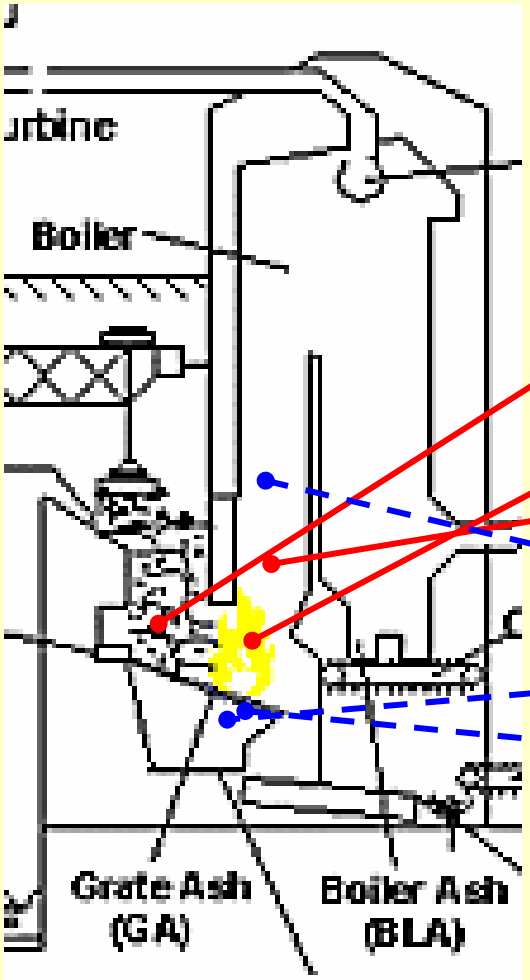
- Major synthetic rubbers
  - ***Styrene Butadiene Rubber (SBR)***
  - Poly-isoprenes (***in progress***)
  - Butadiene Rubber (BR)



Experimental Setup



Experimental Conditions



Current conditions found in combustors

Gasification/ pyrolysis (100% N_2)

Air atmosphere (20% O_2, 80% N_2)

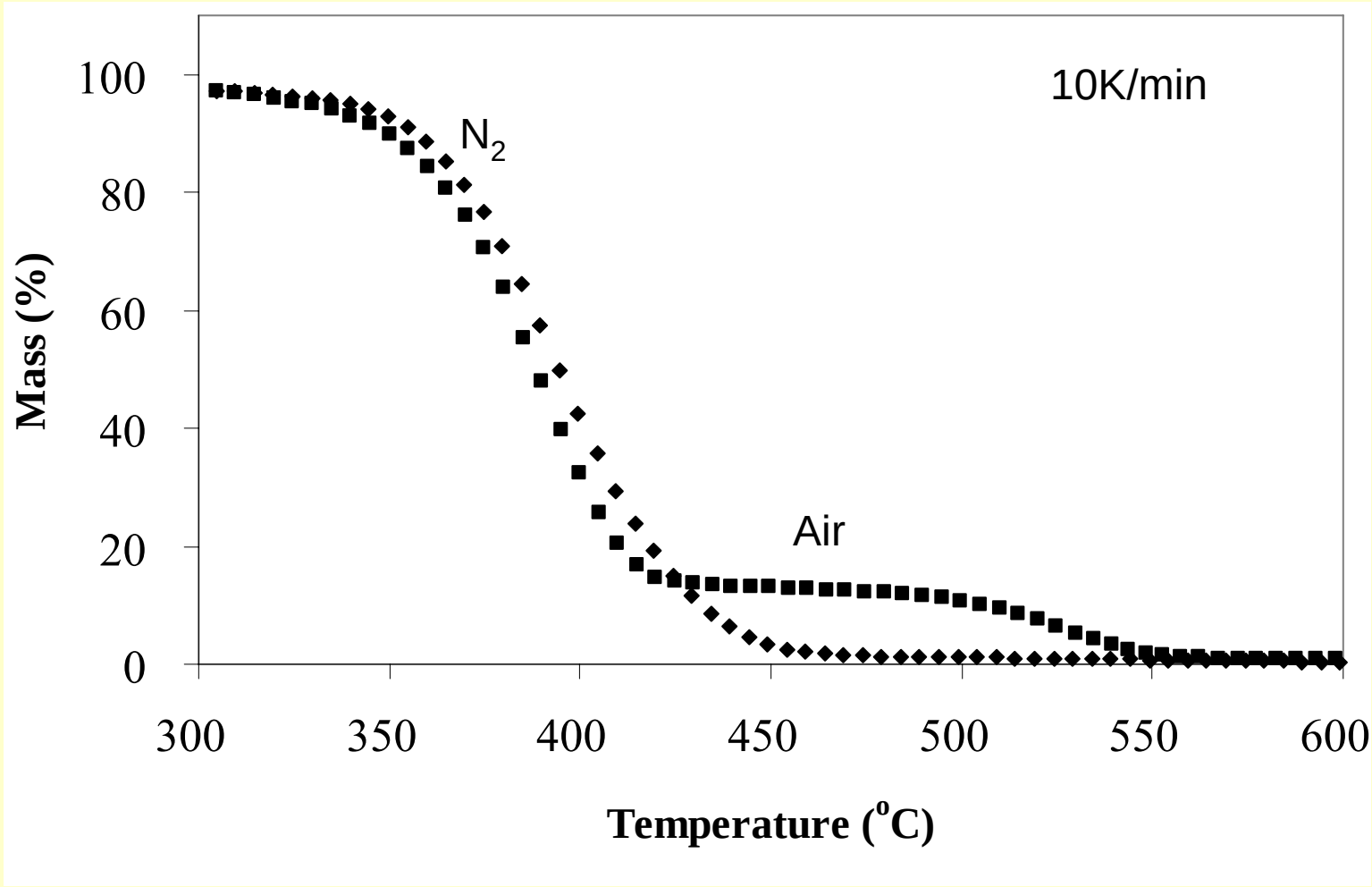
Lean atmosphere (6% O_2, 94% N_2)

Possible enhancements for higher efficiency

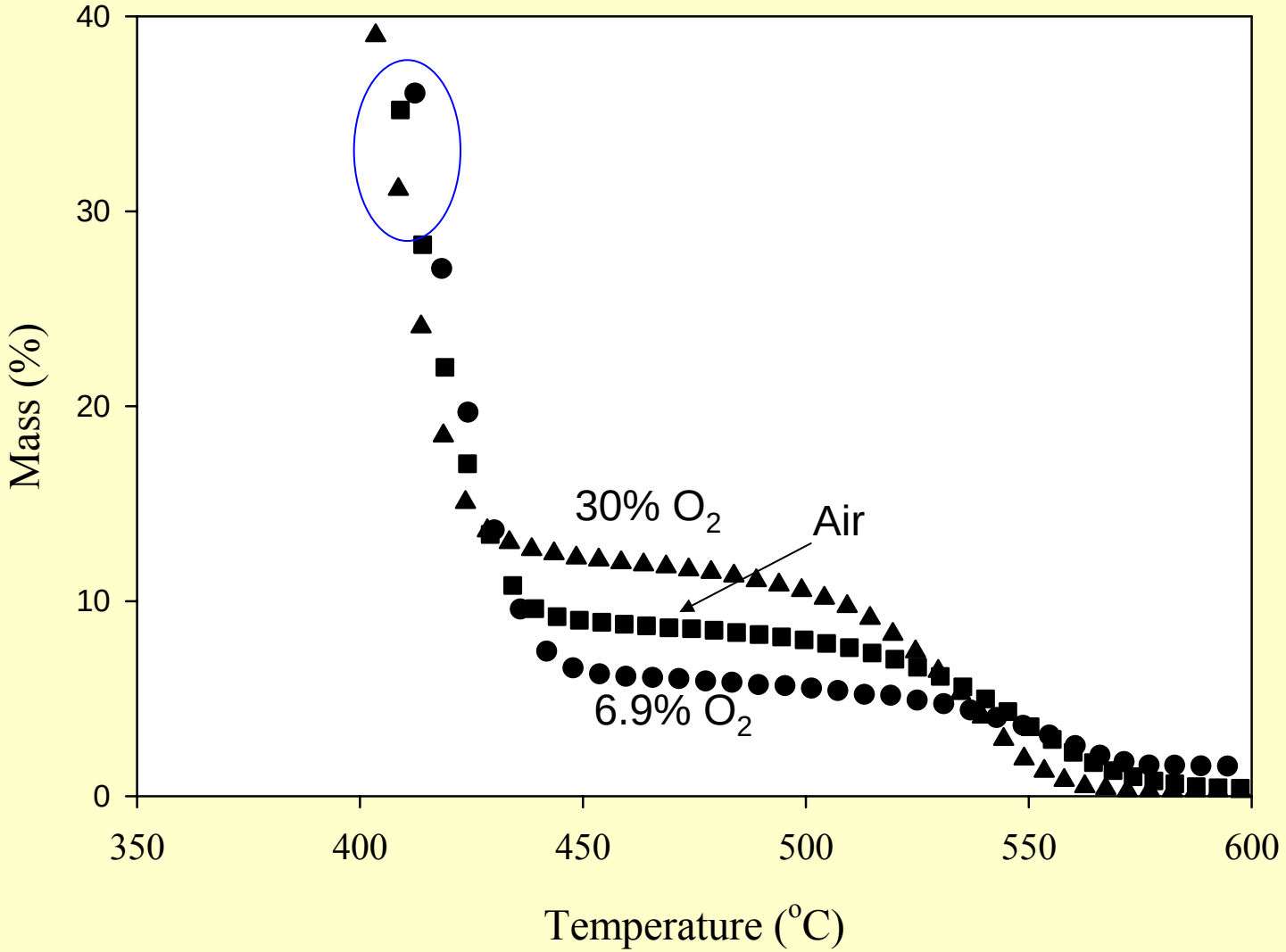
Enriched atmosphere (30% O_2, 70% N_2)

Hydrogen "spiking" (3% H_2, 97% N_2)

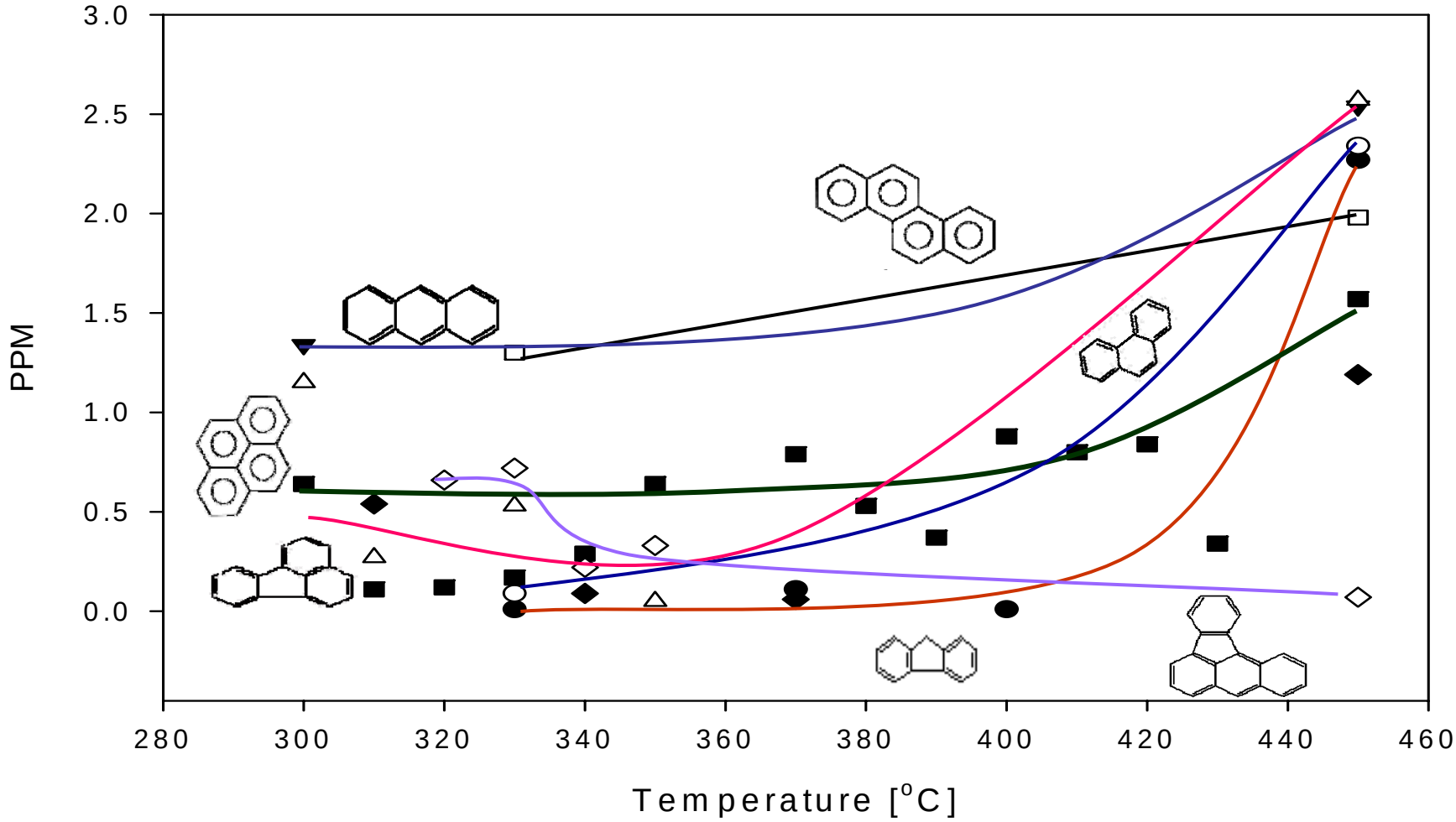
Combustion/Gasification Comparison



Combustion Comparisons

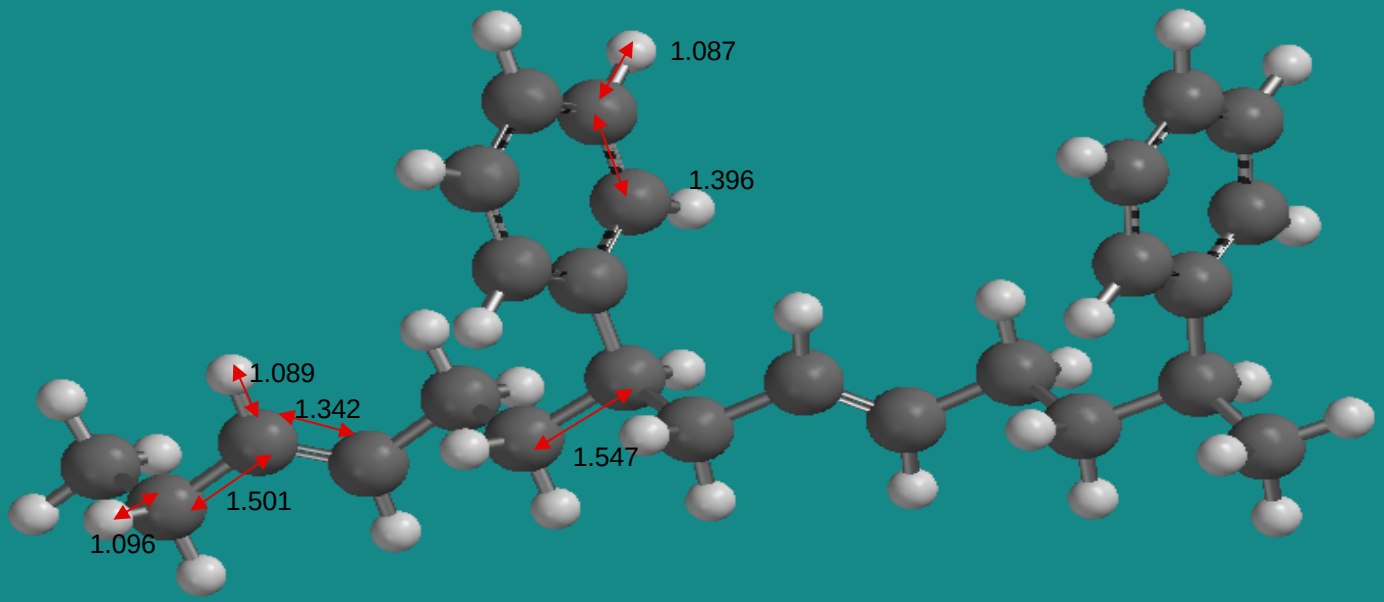


Polycyclic Aromatic Hydrocarbon (PAH) (detected to date)



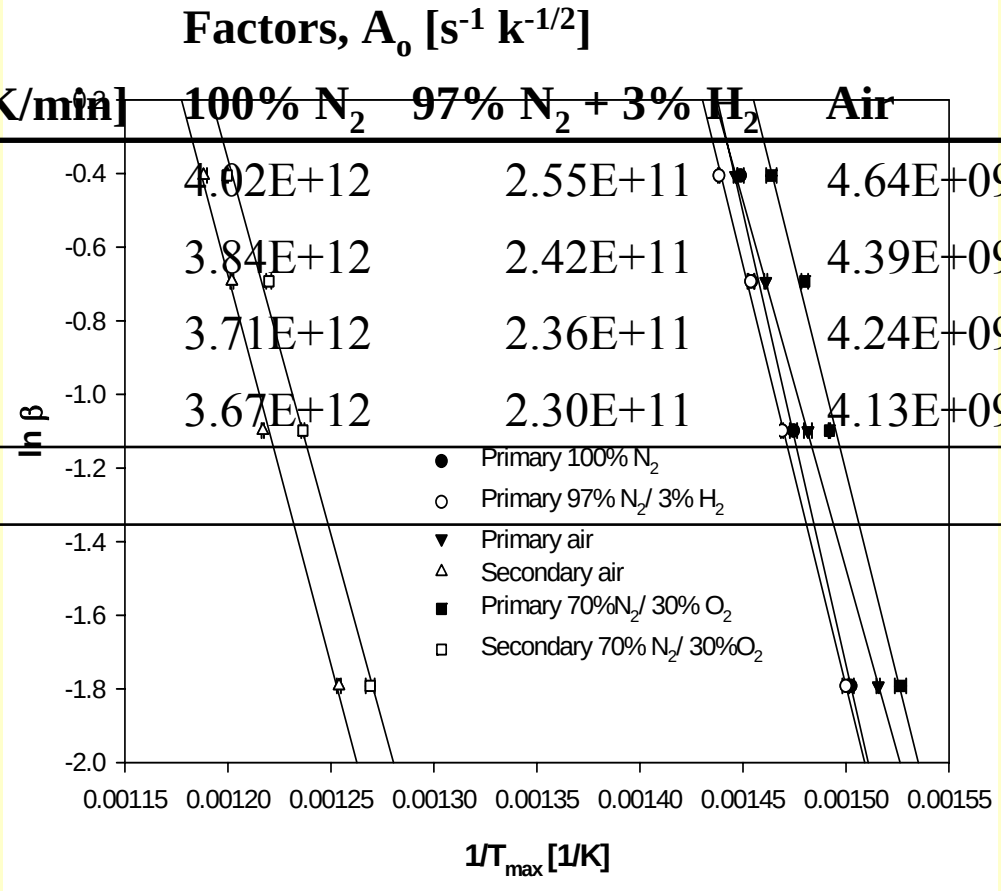
Chemical Structure of SBR;

25% Styrene, 75% Butadiene Cross linked Co-Polymer



Kinetic Expression Development

	Factors, A_o [s^{-1} $k^{-1/2}$]			
Heating rate, β [K/min]	**100% N_2**	**97% N_2 + 3% H_2**	**Air**	**O_2 enhanced**
10	4.02E+12	2.55E+11	4.64E+09	2.87E+11
20	3.84E+12	2.42E+11	4.39E+09	2.72E+11
30	3.71E+12	2.36E+11	4.24E+09	2.66E+11
40	3.67E+12	2.30E+11	4.13E+09	2.59E+11



Kinetic Expression Development

$$\alpha = \frac{W(t) - W_i}{W_i - W_f}$$

$$\frac{d\alpha}{dt} = k(1-\alpha)^n$$

$$k = AT^n \exp\left(\frac{-E}{RT}\right)$$

$$\frac{d\alpha}{dT} = \frac{A_0}{\beta} T^{1/2} (1-\alpha)^n \exp\left(\frac{-E}{RT}\right)$$

$$\frac{d^2\alpha}{dT^2} = \frac{1}{\beta}\left(\frac{d\alpha}{dt}\right)\left[n(1-\alpha)^{-1}\left(-\frac{d\alpha}{dT}\right) + \frac{E}{RT^2} + \frac{1}{2}T^{-1}\right]$$

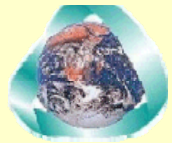
Reaction Order Calc.

$$n = \frac{\left[\beta\left(d^2\alpha/dT^2\right)/\left(d\alpha/dt\right) - E/RT^2 - 1/2\,T^{-1}\right](1-\alpha)}{\left(-d\alpha/dT\right)}$$

Activation Energy Calc.

$$E = RT \ln\left[\frac{\left(\frac{d\alpha}{dt}\right)}{A_0 T^{1/2}(1-\alpha)^n}\right]$$

Aspen™ Kinetic Simulation



Combustion[2]

$Tire + O_2 \rightarrow CO_2 + H_2O$ $\Delta H_r = -35$ MJ/kg

Boudouard[3]

$C_{(s)} + CO_2 \rightarrow 2\,CO$ $\Delta H_r = 11$ MJ/kg

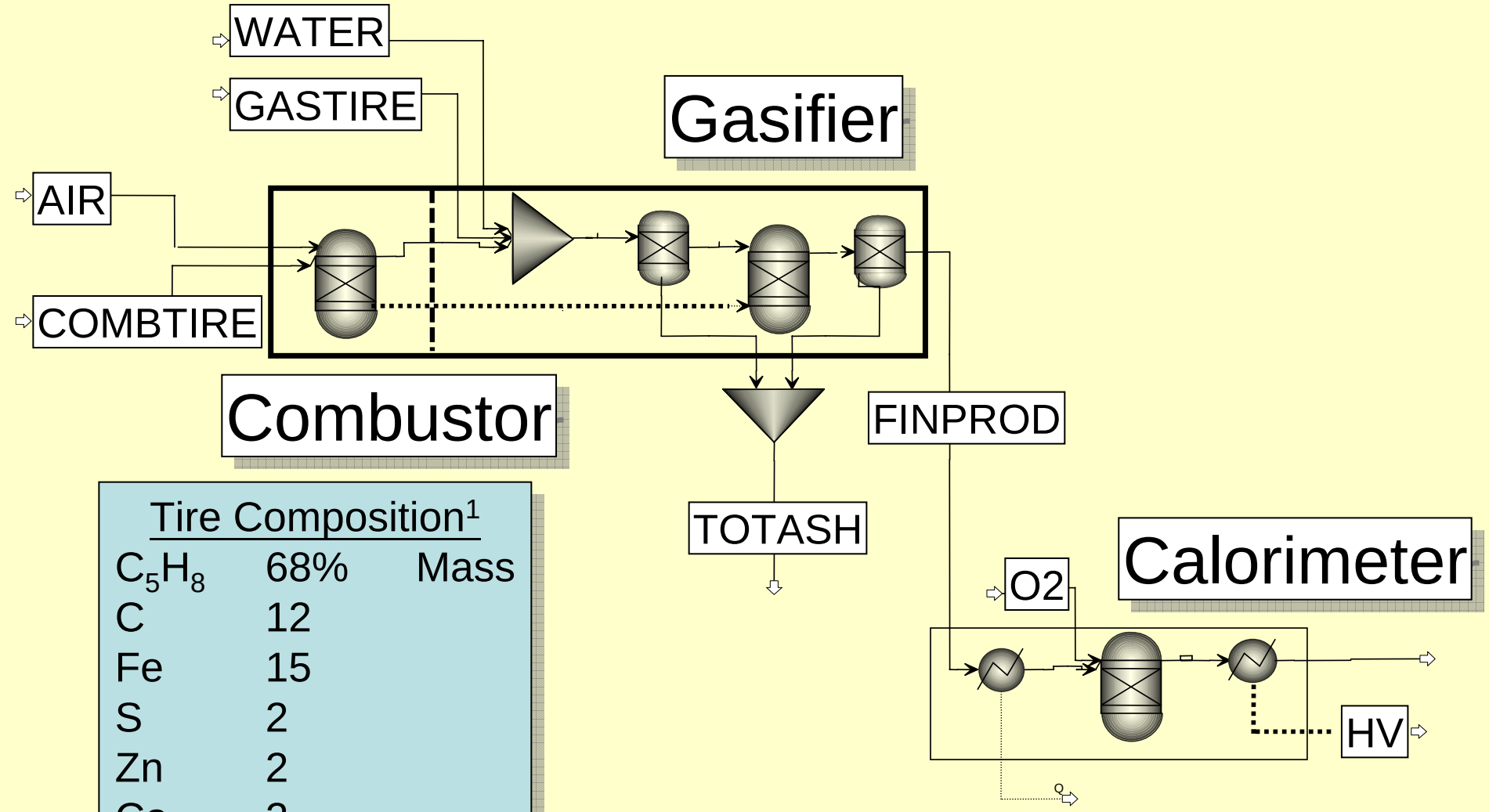
Steam reforming[3]

$C_{(s)} + H_2O \rightarrow CO + H_2$ $\Delta H_r = 14$ MJ/kg

Water-gas shift[3]

$CO + H_2O \rightarrow CO_2 + H_2O$ $\Delta H_r = -1.5$ MJ/kg

Aspen™ System Simulation

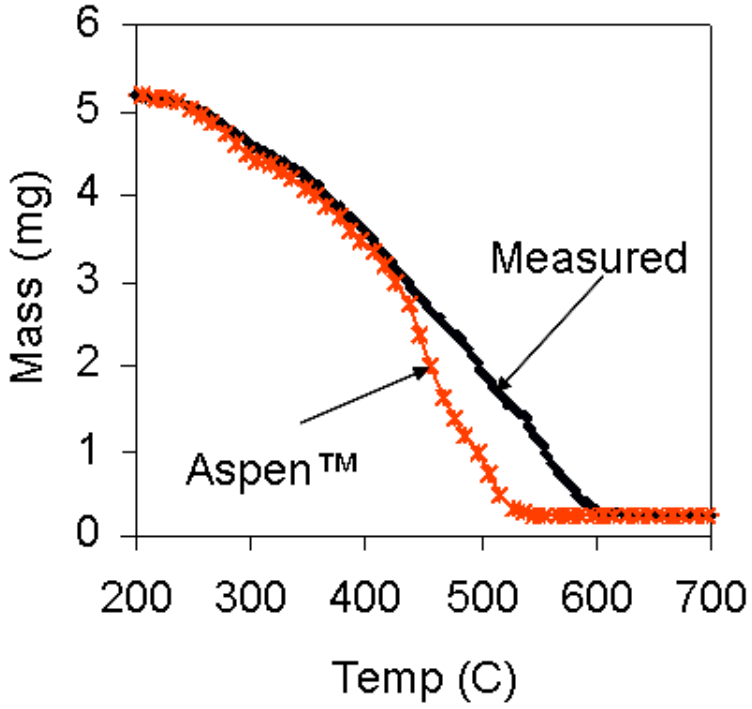


Tire Composition[1]		
C_5H_8	68%	Mass
C	12	
Fe	15	
S	2	
Zn	2	
Ca	2	

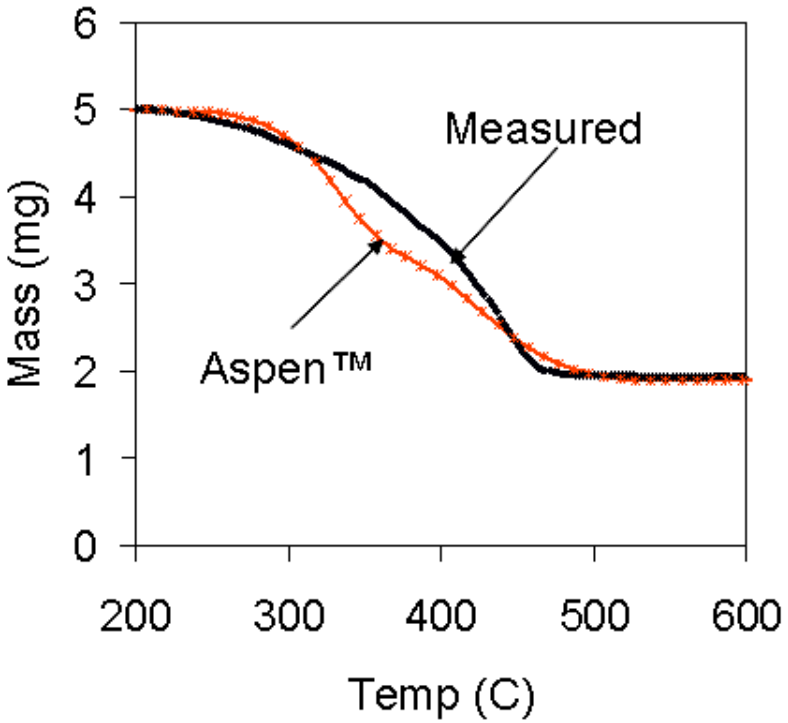
1 Reisman JI, Lemieux PM. "Air emissions from scrap tire combustion". *Clean Air Technology Center* EPA, 1997.

Simulation Results

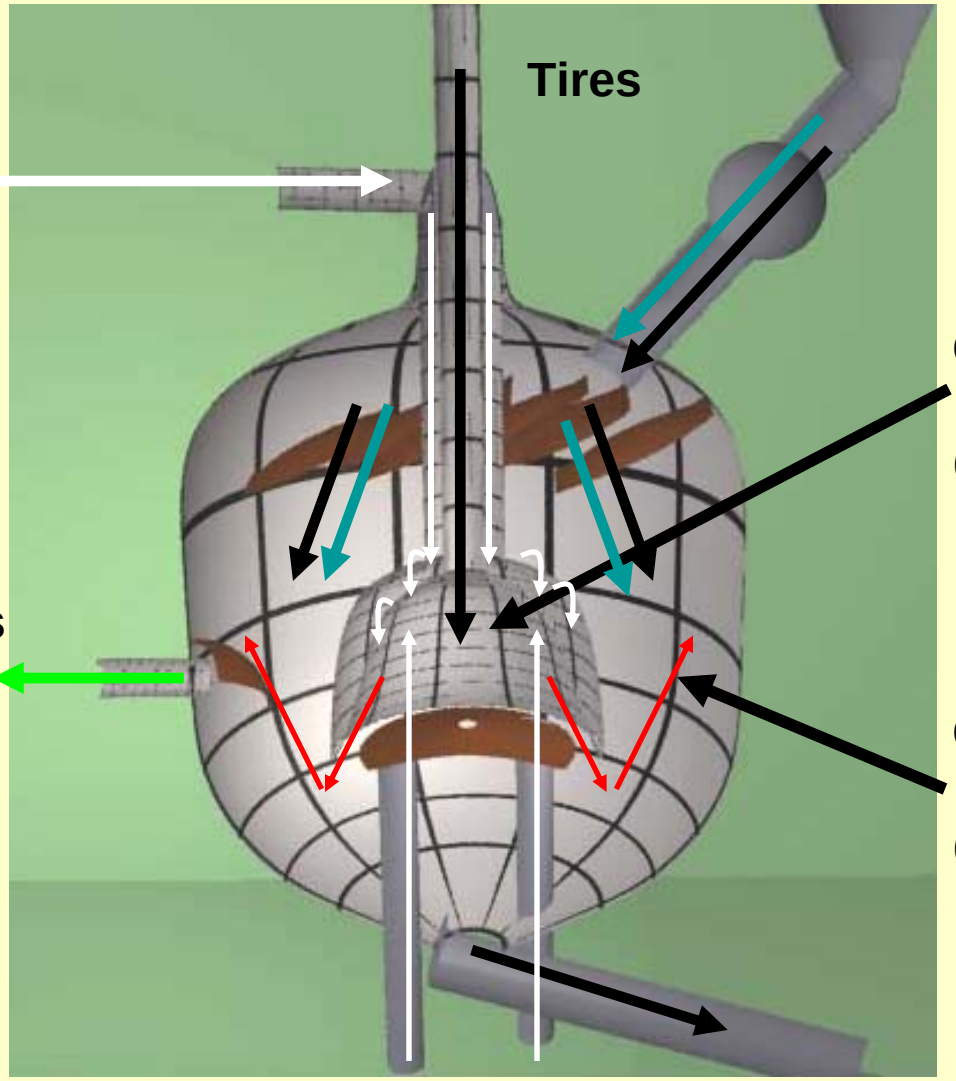
Combustion

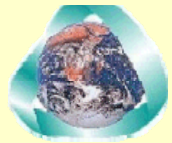


Gasification



Combustion-Gasification System

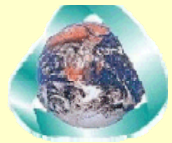




MSW Particles

- Investigate MSW particle decomposition (TGA)
  - Size dependency
  - Shape dependency
  - Waste mixture effects
- Determine kinetic parameters governing MSW decomposition
- Develop mechanistic understanding
- Develop predictive (model) capability

GHG Reforming: LFG



Research initiatives

- Understand catalyst activity
  - Kinetics (reactions, deactivation, poisons)
  - Mechanisms
- Investigate promising reactions
  - Hydrogen generation
    - Combustion improvements- emissions/efficiency
  - Chemical synthesis
- Reactor design

CO_2 as a potential feedstock.

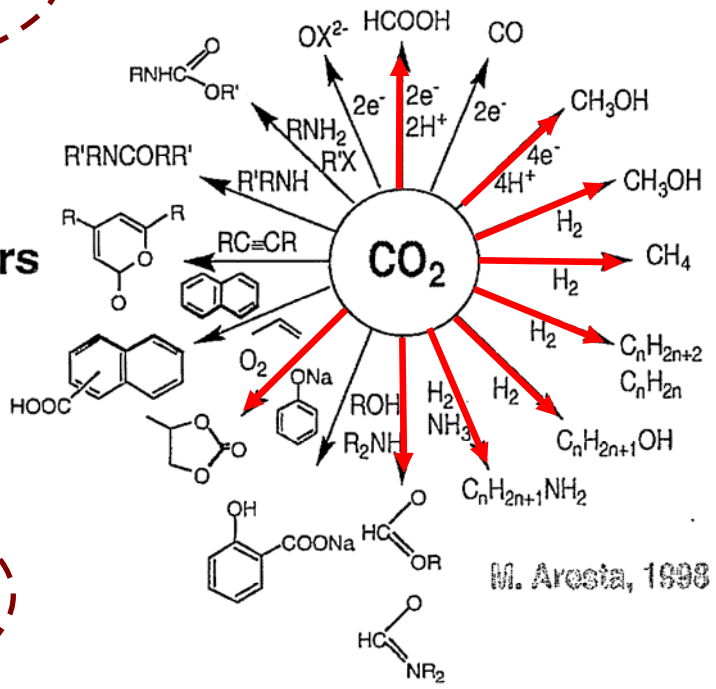
Intermediates or fine chemicals for the chemical industry

- -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



Plug Flow Reactor Calc

(Gas Research Institute – 3.0 mechansim)

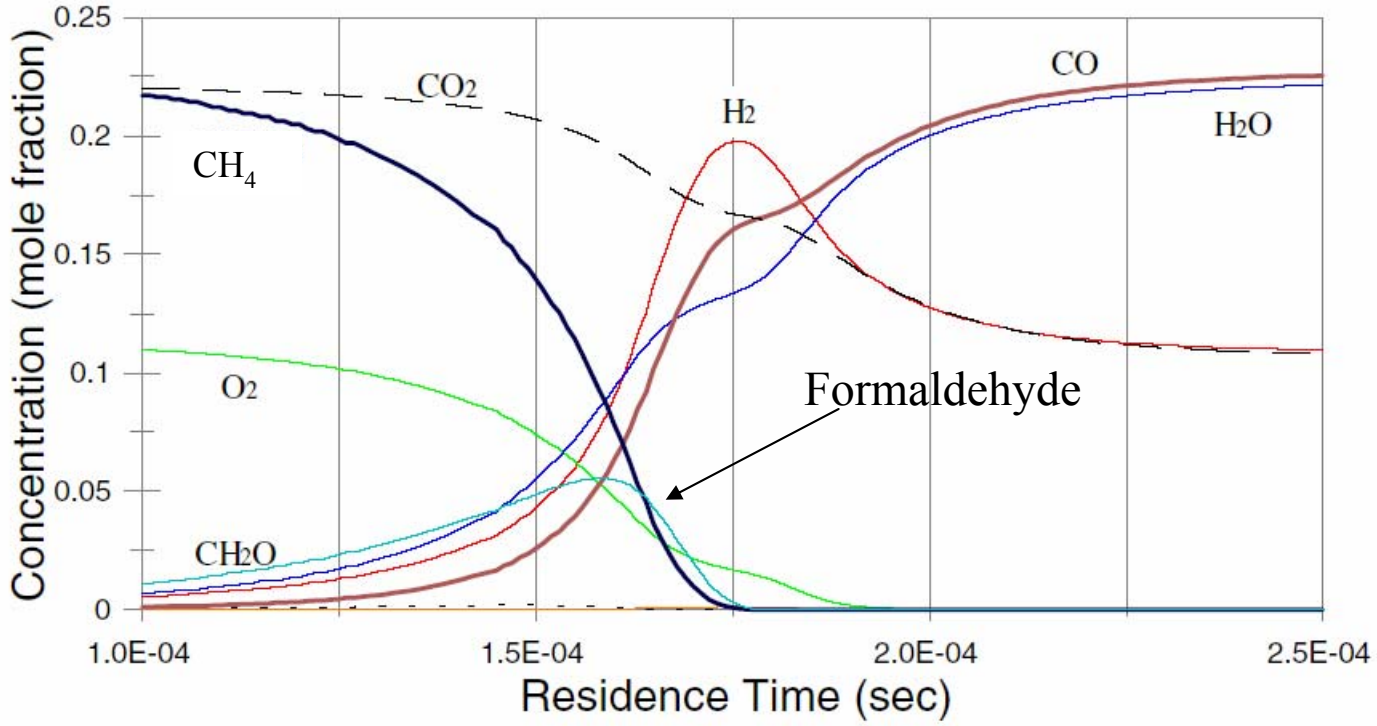
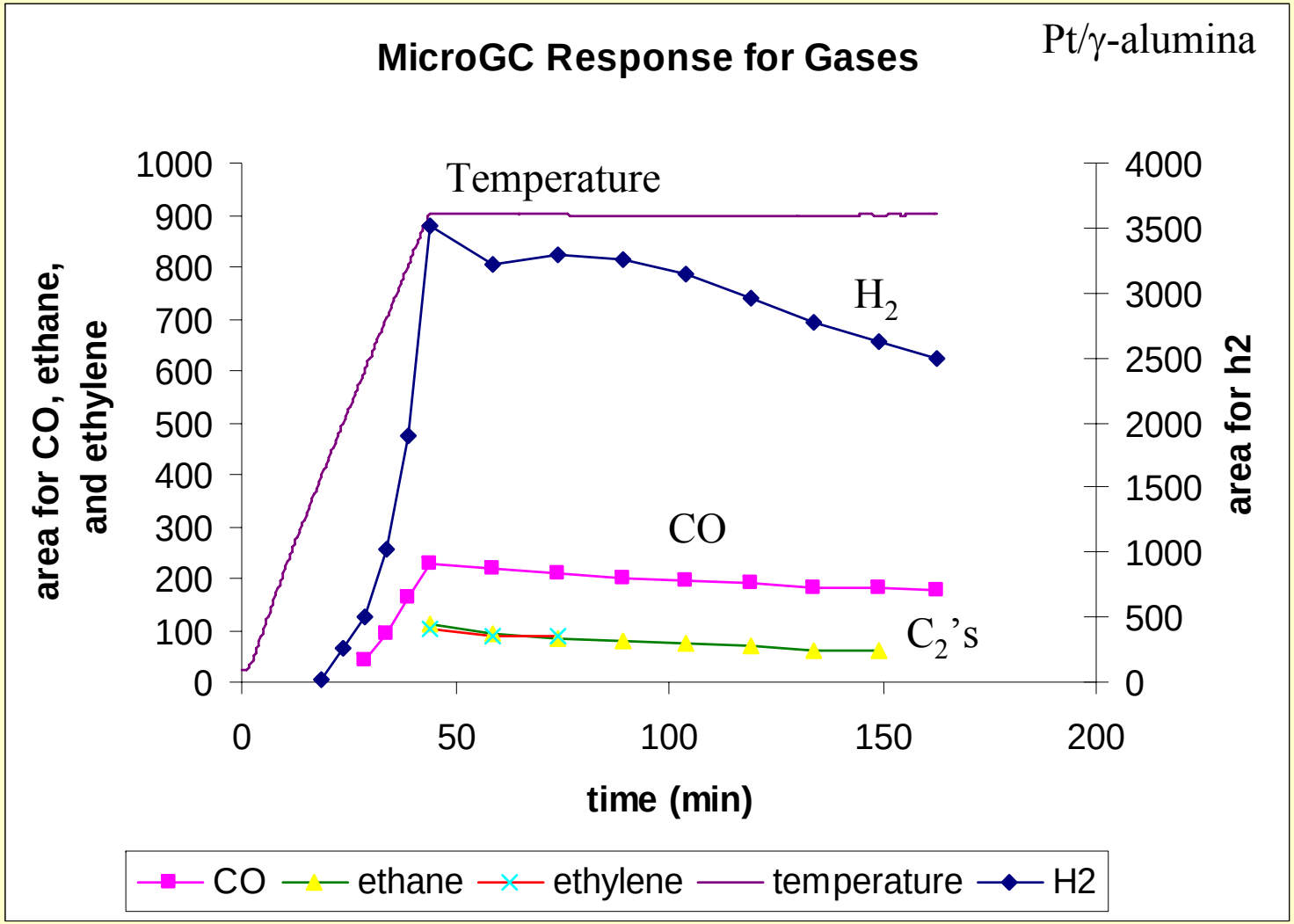


Figure 1. Concentration profiles for a plug flow CH_4 /CO_2 reforming system

TGA Data: C_2H_2 formation

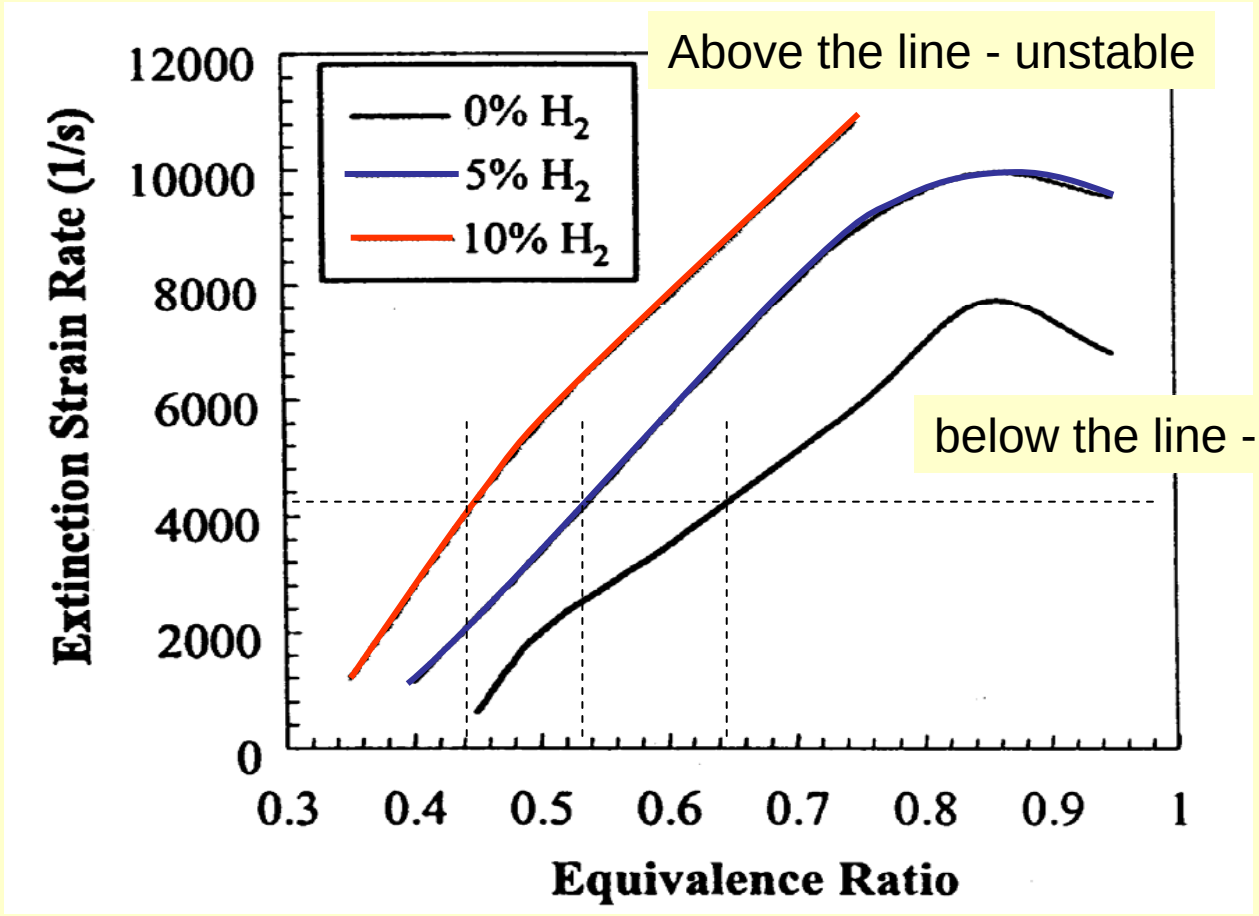


Combustion Enhancements

- 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

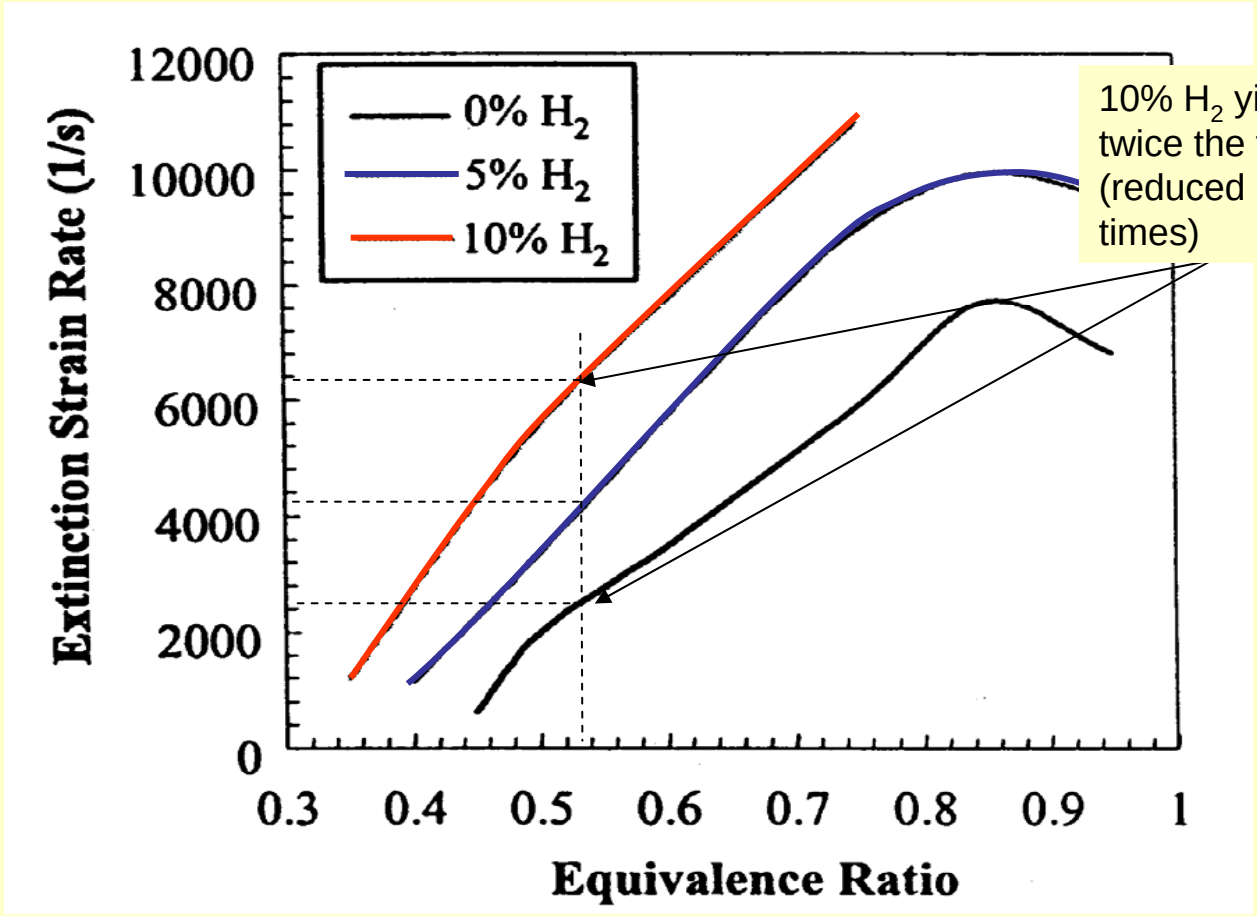
Combustion Benefits from H_2



H_2 addition increases reactivity, extending stability/blowout limits

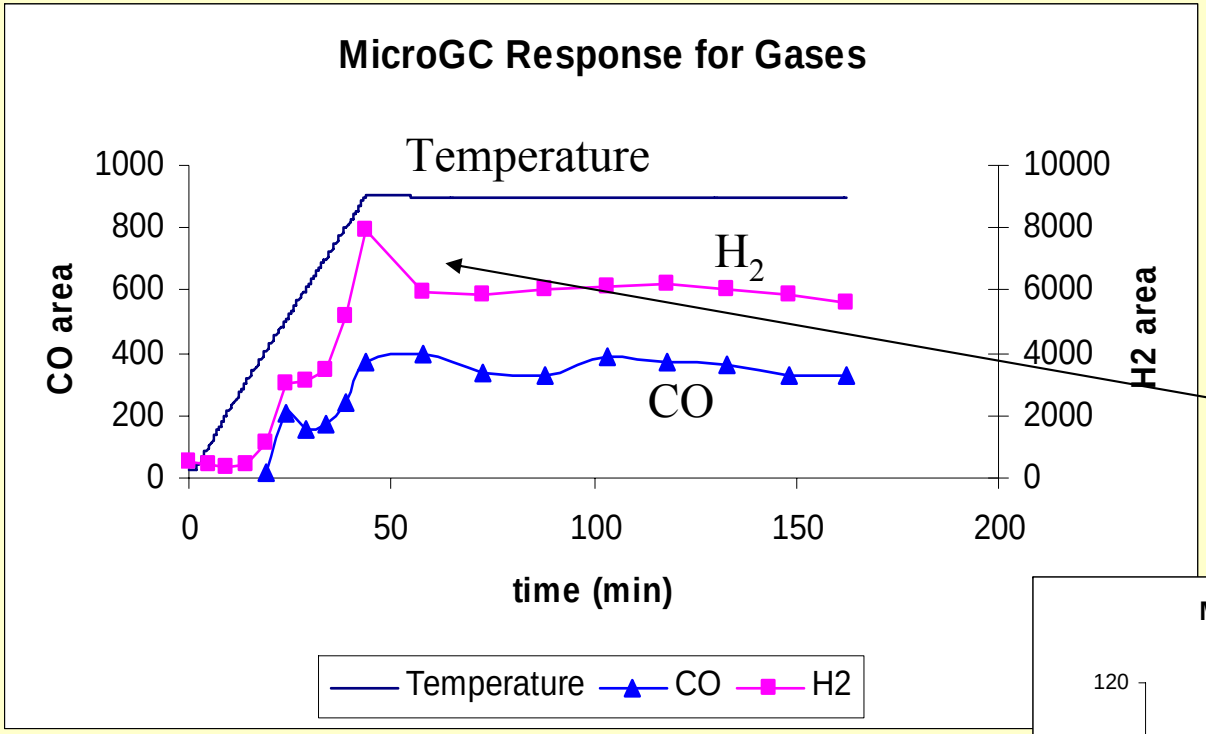
Calculation, GRI 2.1 mechanism for CH_4 @ 1 atm, 400 C inlet; Cong & Jackson (1999)

Combustion Benefits from H_2

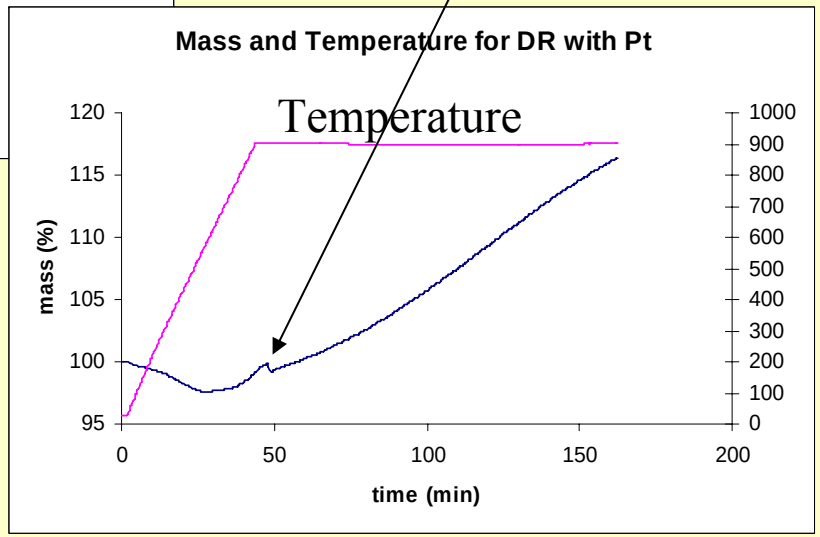


10% H_2 yields stability at twice the turbulence levels (reduced ignition delay times)

TGA Data – Syngas formation



Competitive Carbon deposition corresponds with loss in activity



EDX results:

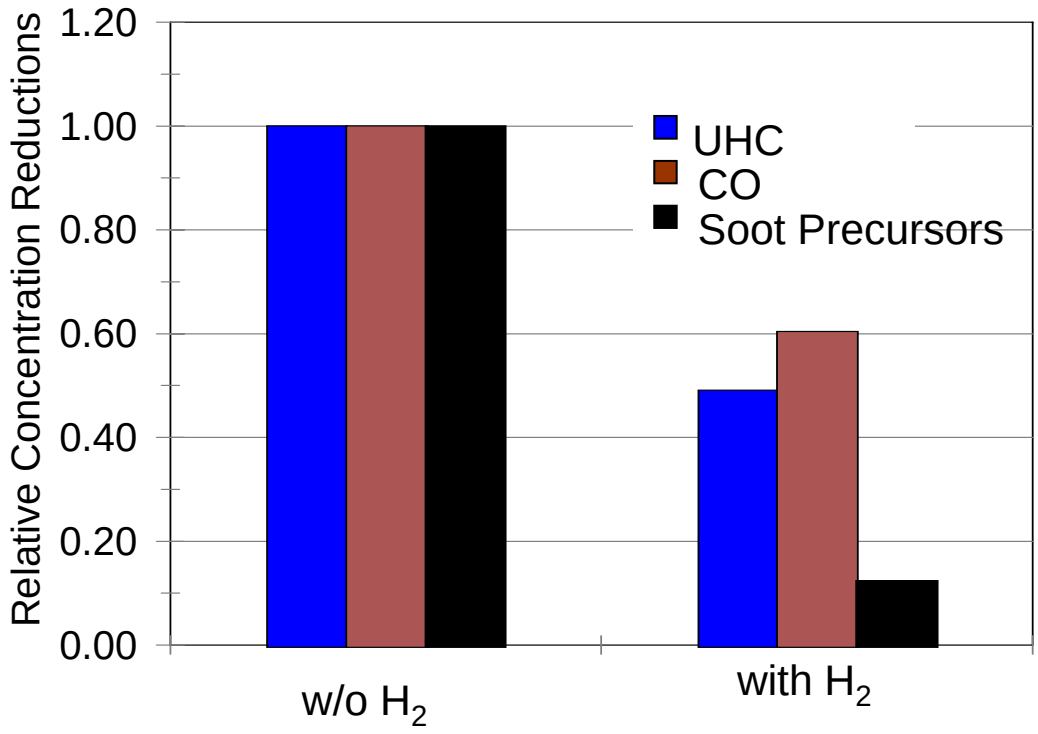
71.7 % Al

4 % Pt

24.3 % C

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

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

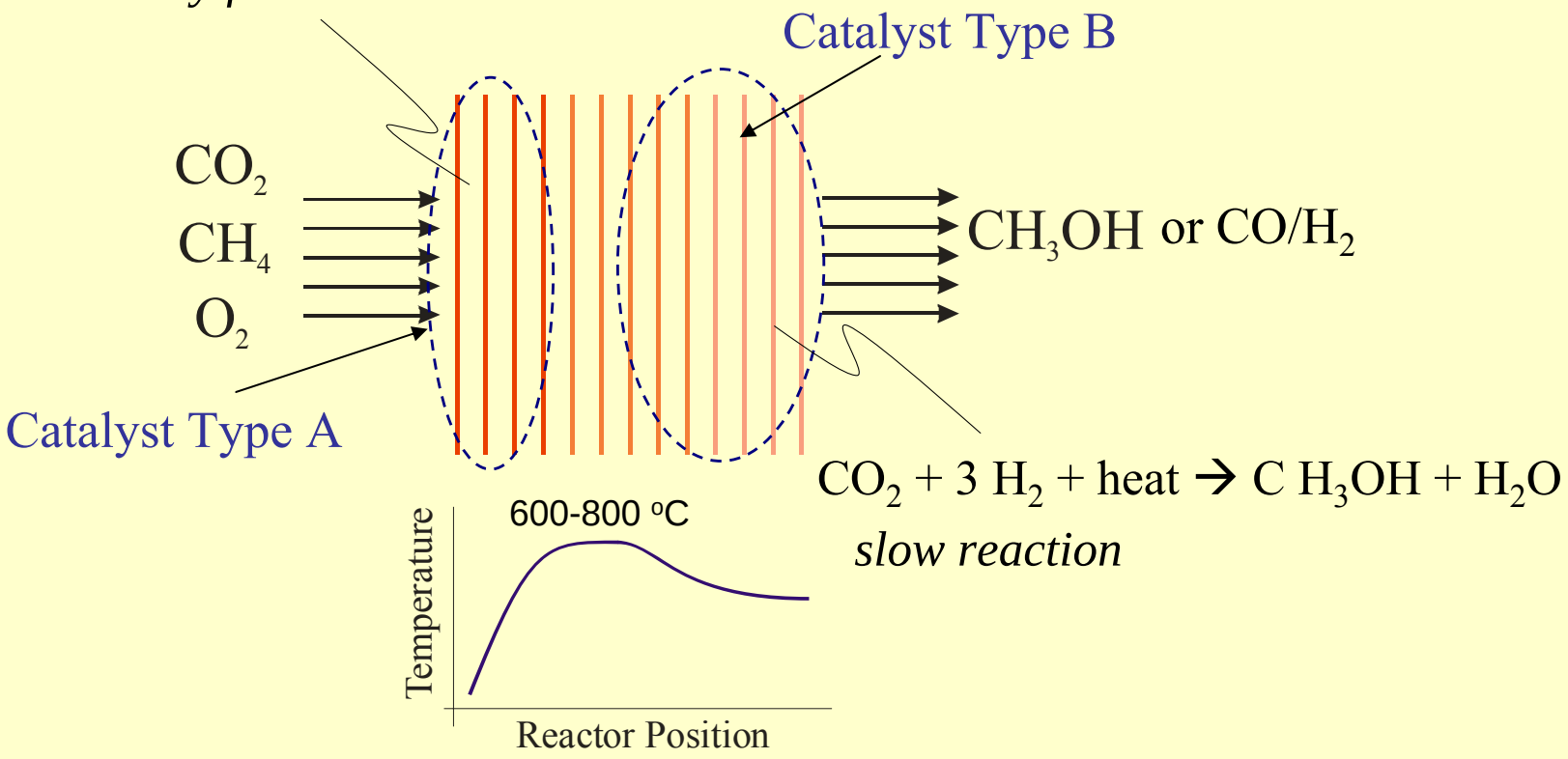
– Hydrogen Consultants, Inc. of Littleton, Colorado, has also demonstrated that methane blended with only 5% hydrogen (Hythane®) can result in NOx and CO reduction of up to 50%.

CO_2/CH_4 Reforming

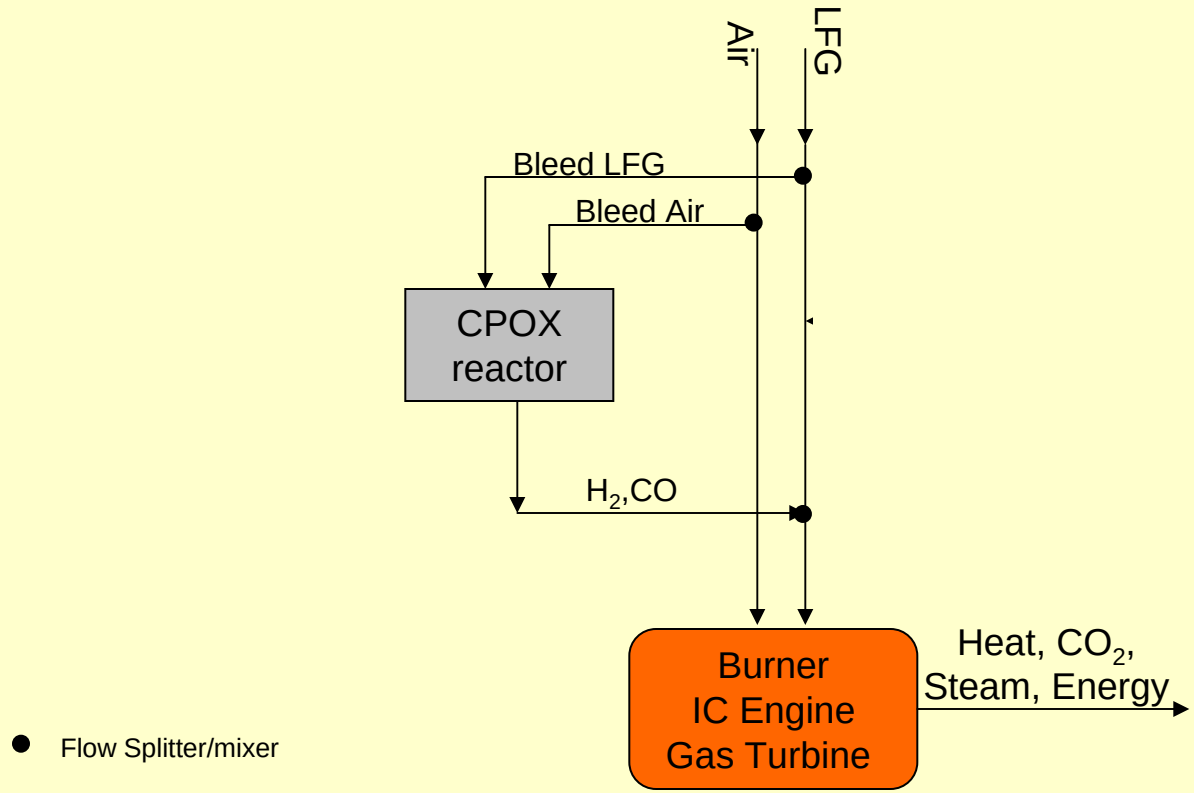
$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O + heat$

$CH_4 + ½\ O_2 \rightarrow CO + 2H_2 + heat$

very fast reaction



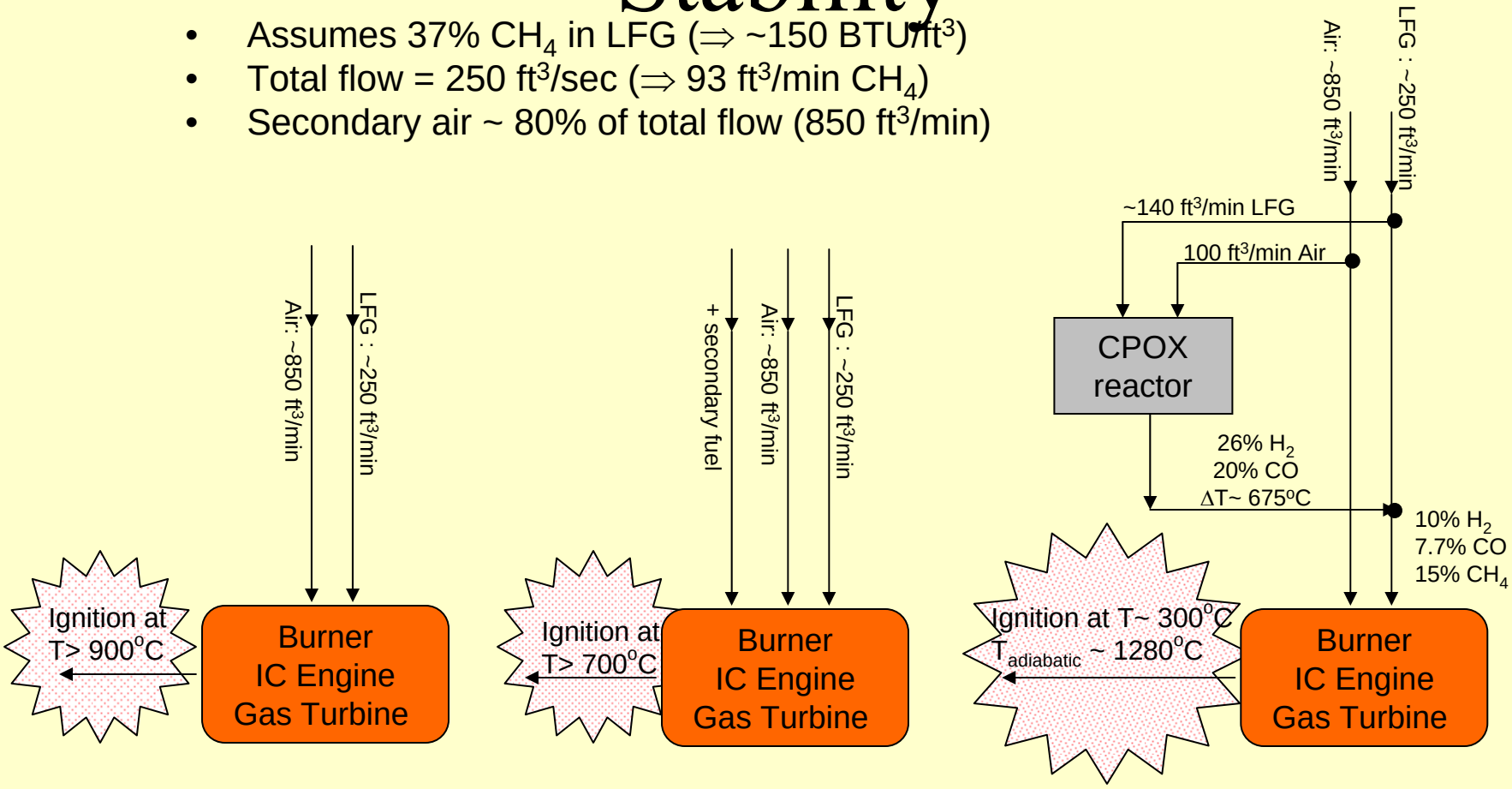
System Implementation Schematic



More reactive system; Reduce/eliminate secondary fuel usage

Lower Ignition Temperature for Stability

- Assumes 37% CH_4 in LFG ($\Rightarrow$ ~150 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

H_2 from Waste (carbon)

- CO_2 separation
  - The need for separating carbon dioxide from the product gases and plant effluent in order to prevent it from entering the atmosphere.
- Clean H_2 Production.
- Zero emissions from fossil fuel power plants in the near future.
- Reduce the dependence on imported oil
- Power and hydrogen produced from waste must be economically attractive as compared to oil.

Reactions Considered

1)Devolatilization = CH_4 + CO + CO_2 + Oils + Tars + C (Char)

2) C + O_2 = CO_2 + 393,522kJ/kmol

3) C + 1/2O_2 = CO + 110,521 kJ/kmol

4) CO + 1/2O_2 = CO_2 + 283,001 kJ/kmol

5) H_2 + 1/2O_2 = H_2O + 285,513 kJ/kmol

6) C + H2O = CO + H_2 - 131,453 kJ/kmol

7) C + 2H_2O = CO_2+ 2H_2 - 90,426 kJ/kmol

8) C + CO_2 = 2CO - 172, 898 kJ/kmol

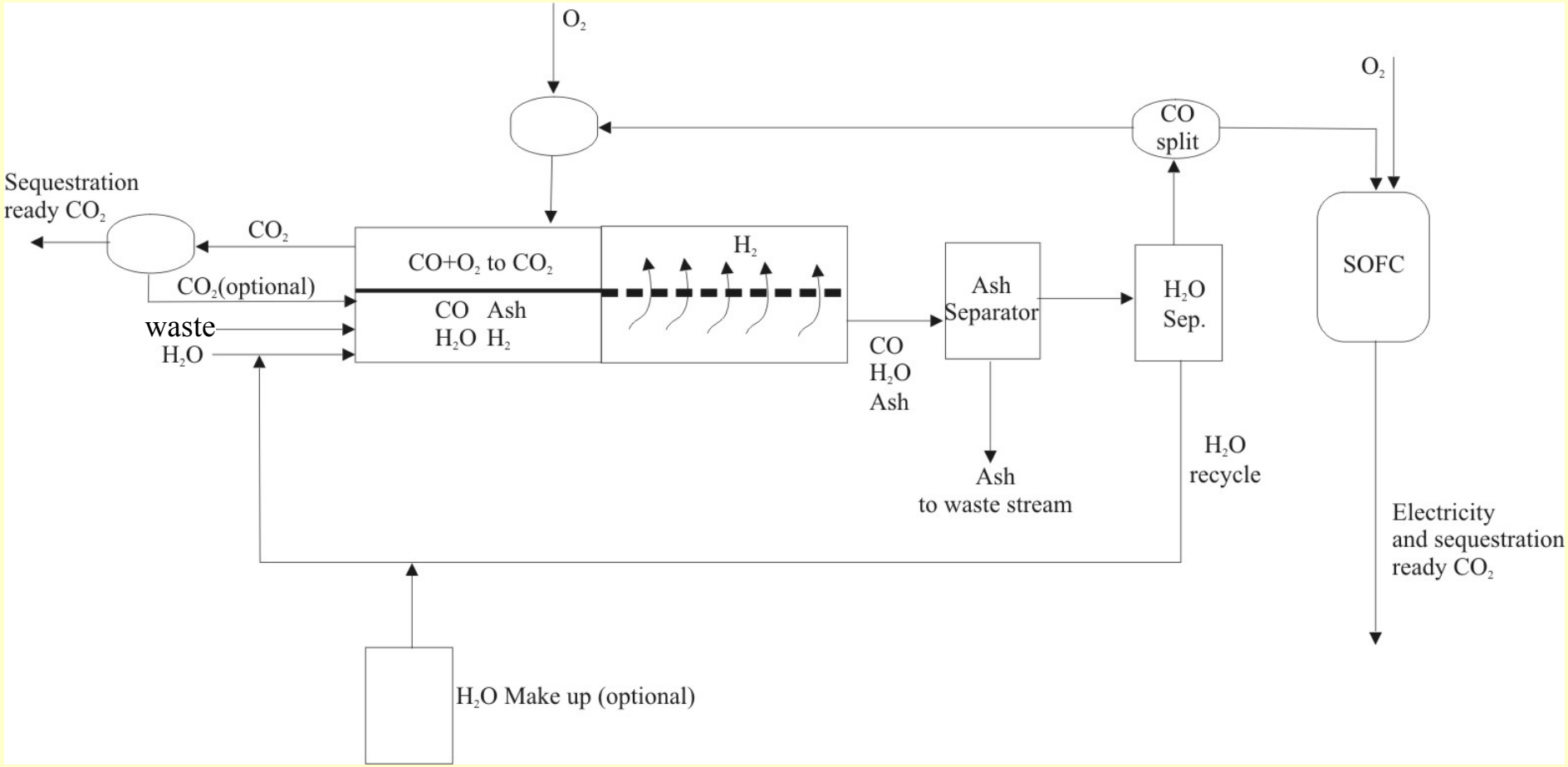
9) CO + H_2O = CO_2 + H_2 + 41,027 kJ/kmol

10) CO + 3H_2 = CH_4 + H_2O + 206,172 kJ/kmol

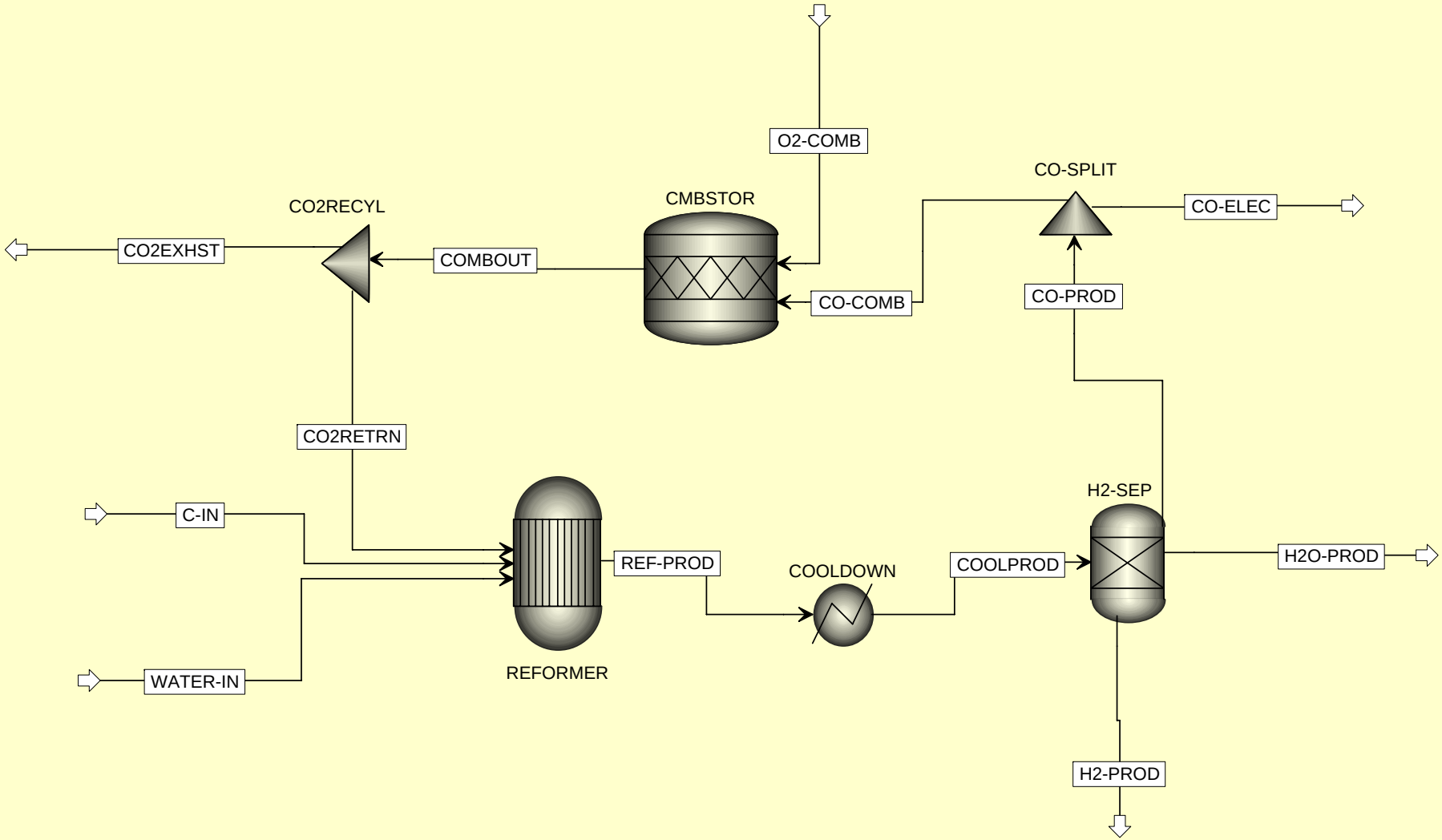
11) C + 2H_2 = CH_4 + 74, 873 kJ/kmol

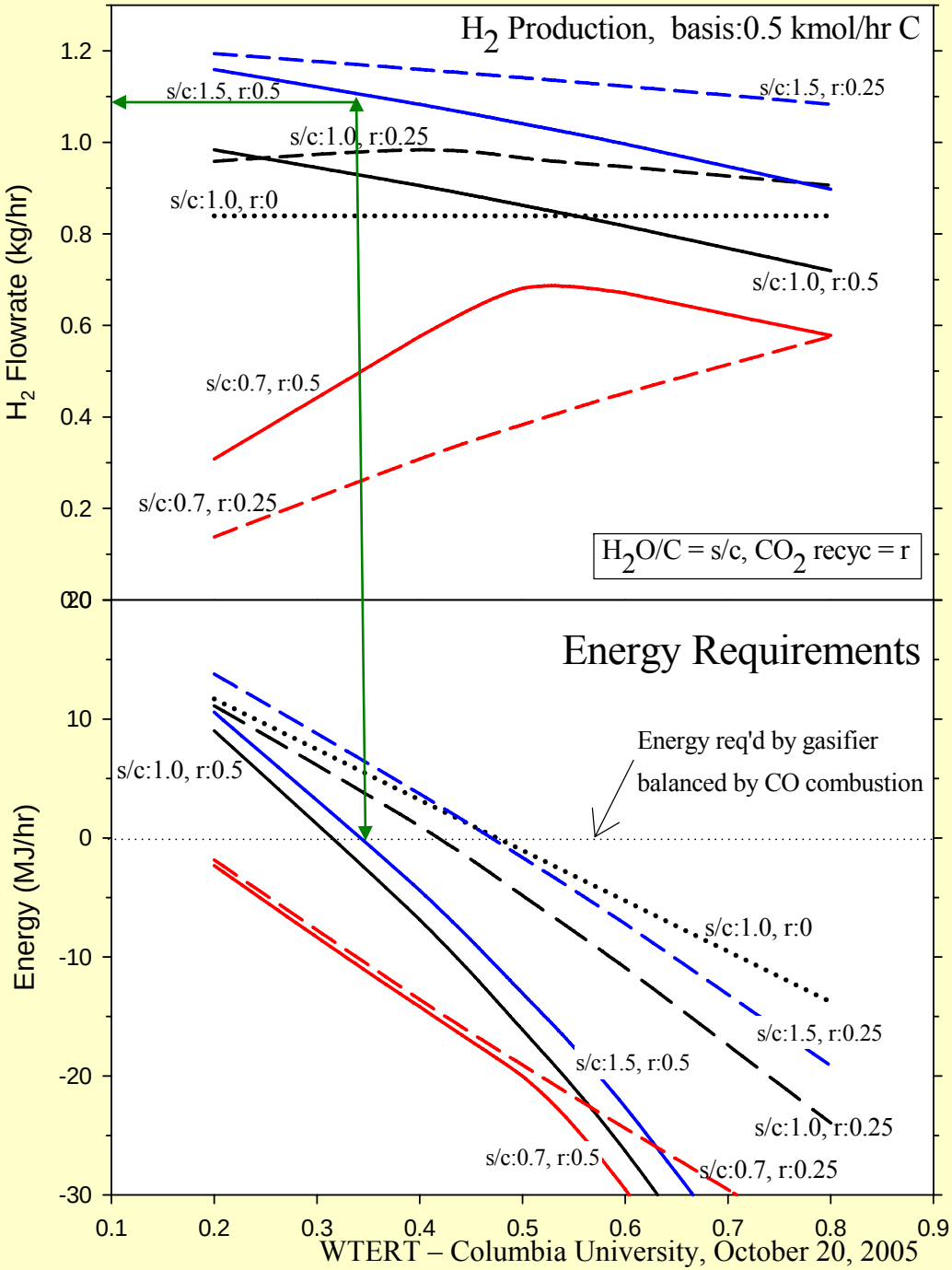
12) CH_4 + 2O_2 = CO_2 + H_2O + 560,475 kJ/kmol

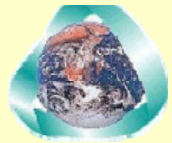
Catalytically Controlled Reaction Gasifier (CRG Process)



Waste to H2 Aspen™ Simulation




H2 Production, basis:0.5 kmol/hr C
H2 Flowrate (kg/hr)
s/c:1.5, r:0.5
s/c:1.5, r:0.25
s/c:1.0, r:0.25
s/c:1.0, r:0
s/c:1.0, r:0.5
s/c:0.7, r:0.5
s/c:0.7, r:0.25
H2O/C = s/c, CO2 recyc = r
Energy Requirements
Energy (MJ/hr)
Energy req'd by gasifier
balanced by CO combustion
s/c:1.0, r:0.5
s/c:1.0, r:0
s/c:1.5, r:0.25
s/c:1.5, r:0.5
s/c:1.0, r:0.25
s/c:0.7, r:0.5
s/c:0.7, r:0.25
1.2
1.0
0.8
0.6
0.4
0.2
0
10
0
-10
-20
-30
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9

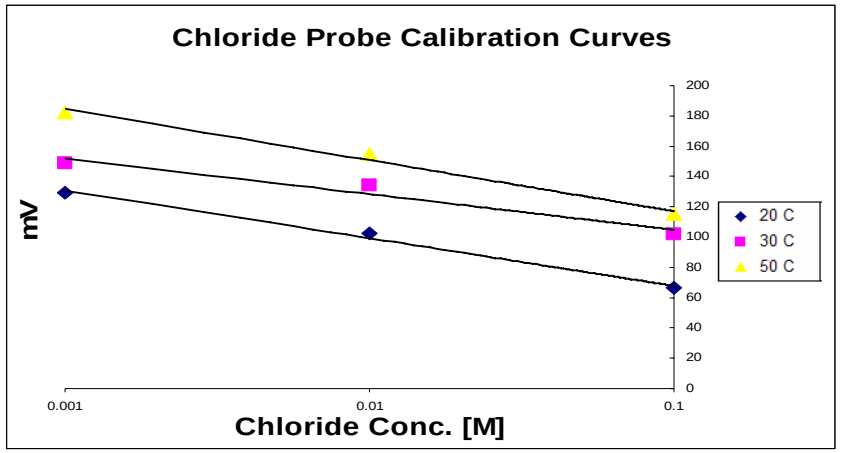


Ash

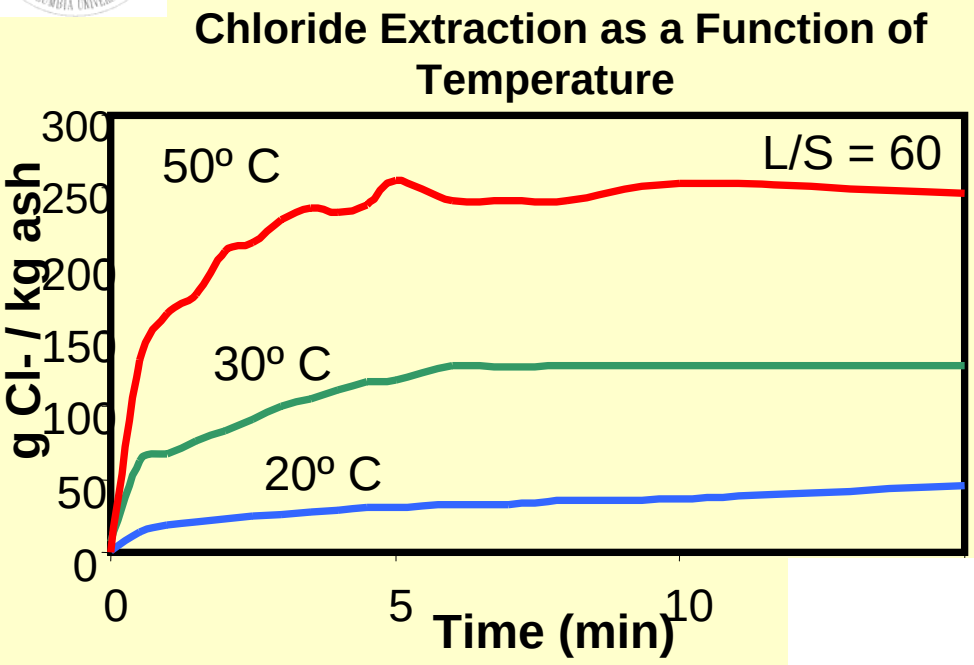
- Investigate treatment methods to remove or fix leachable contaminants
- Identify novel beneficial uses
  - Catalysis
  - scrubbing
- Understand contaminant partitioning

Method

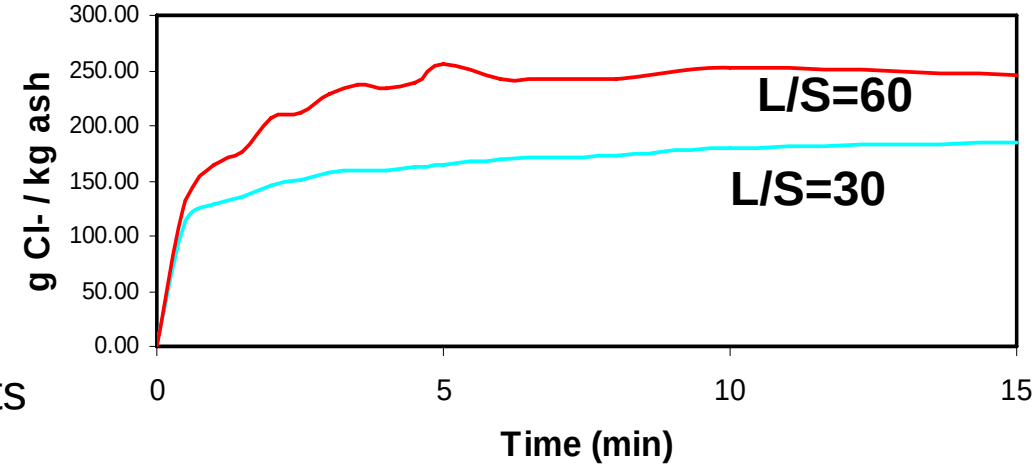
- Chloride extraction was done in a batch method.
- Glass beaker - reactor.
- A motorized mixer for agitation.
- Temperature was controlled by a circulating water bath.
- Chloride concentrations were measured using a chloride electrode.
- Chloride probe calibrations were prepared for each extraction temperature to account for temperature effects on the probe.



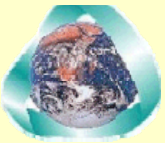
Initial Results



•Determination of optimal temperature
•understand rate limiting step



•Liquid to solid extraction ratio
•Understand saturation constraints



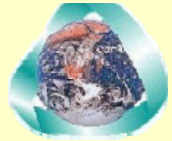
Corrosion

- Investigate and understand corrosion parameters
  - Temperature
  - Time
  - Atmosphere
- Determine kinetics of corrosion for various alloys
  - Enable a mechanistic development for prediction

Experimental Goal

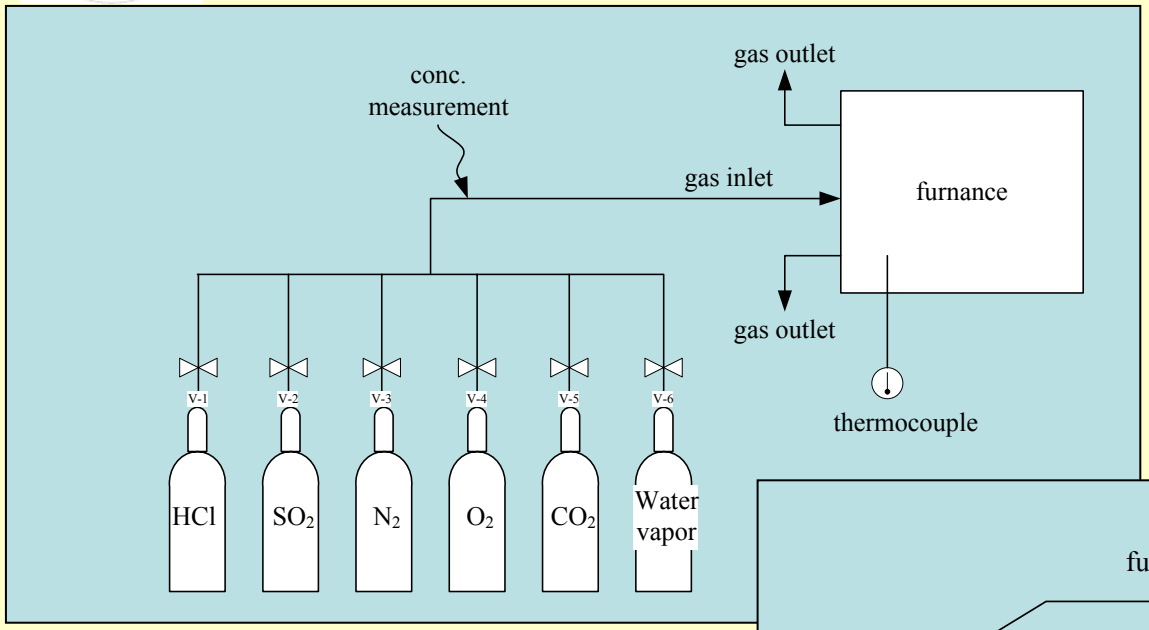
- **Determine corrosion rate of various metals under controlled conditions**
- **Characterization of corrosion products**
- **Corrosion abatement test**
  - Temperature
    - waterwall: 300℃
    - superheater: 450℃
  - Atmosphere
    - HCl: 400-600ppmv
    - SO_2: 50-150ppmv
    - O_2: 8-10%
    - CO_2: 8%
    - Water vapor: 15%
    - N_2: bal.
  - Molten salt deposit
    - no deposit
    - alkali surlfate
    - alkali chloride
    - mix
  - Chemical additive
    - $Ca(OH)_2$
    - $Mg(OH)_2$
    - mix

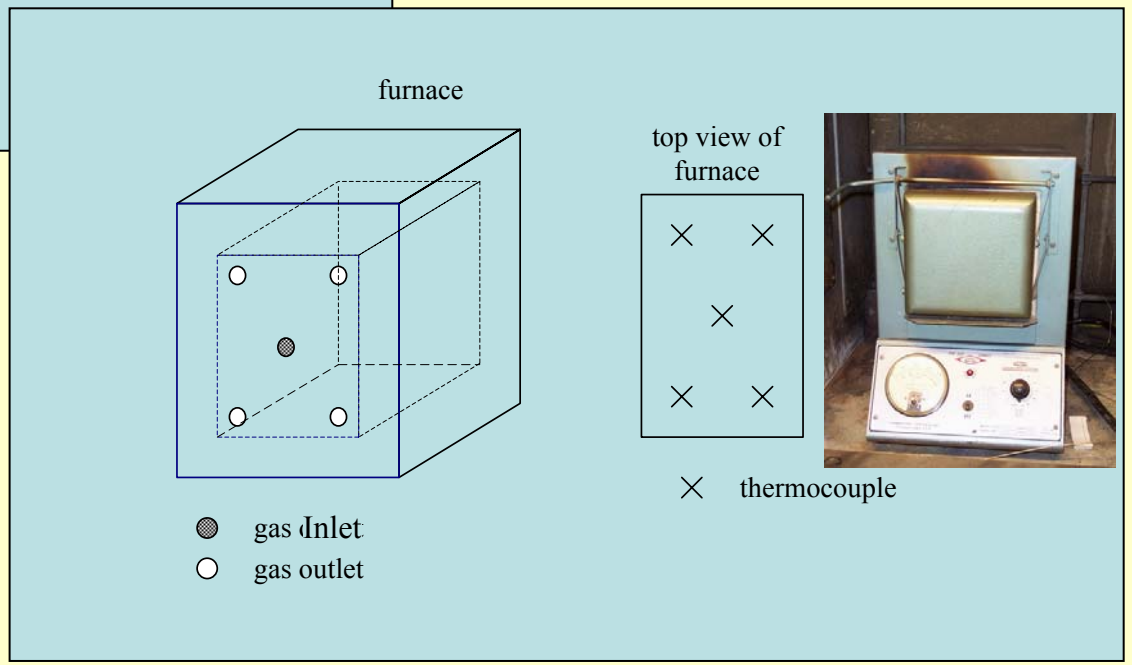
Chemical Composition of Alloys (wt.%)



Alloy	C	Si	Mn	P	S	Ni	Cr	Mo	Fe	Nb+Ta	Others
SA178A	0.07	0.06	0.47	0.01	0.004	0.054	0.016	0.01	balance	0.002	Cu = 0.119 Al = 0.026 Ca = 0.001 N = 0.008 Ti = 0.003 V = 0.002
SA213-T12	0.08	0.28	0.43	0.014	0.002	-	1.05	0.52	balance	-	-
SA213-T22	0.10	0.32	0.49	0.017	0.002	-	2.21	0.95	balance	-	-
QSX5 (from Japan)	<0.03	2.50-3.50	<1.00	-	-	22.00 -25.00	24.00 -26.00	1.00 -2.00	balance	Nb added	-
NSSER-4 (from Japan)	0.04	2.5	0.8	-	-	13.1	17.3	2.5	balance	-	-
Inconel 625	0.03	0.19	0.24	0.001	0.001	64.3	21.1	8.5	1.5	3.44	Al = 0.28 Ti = 0.28 Co < 0.1

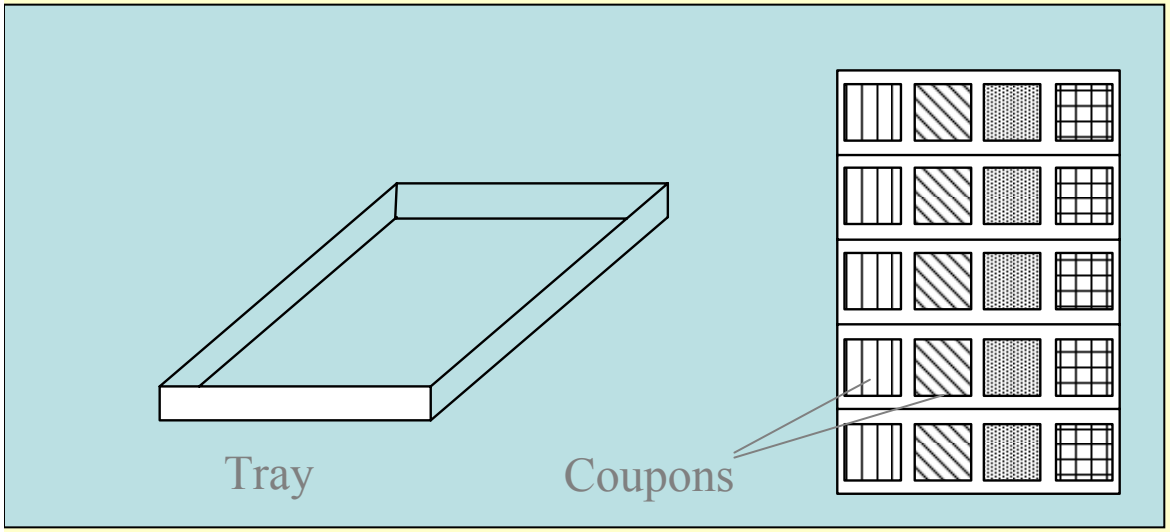
Experimental Setup

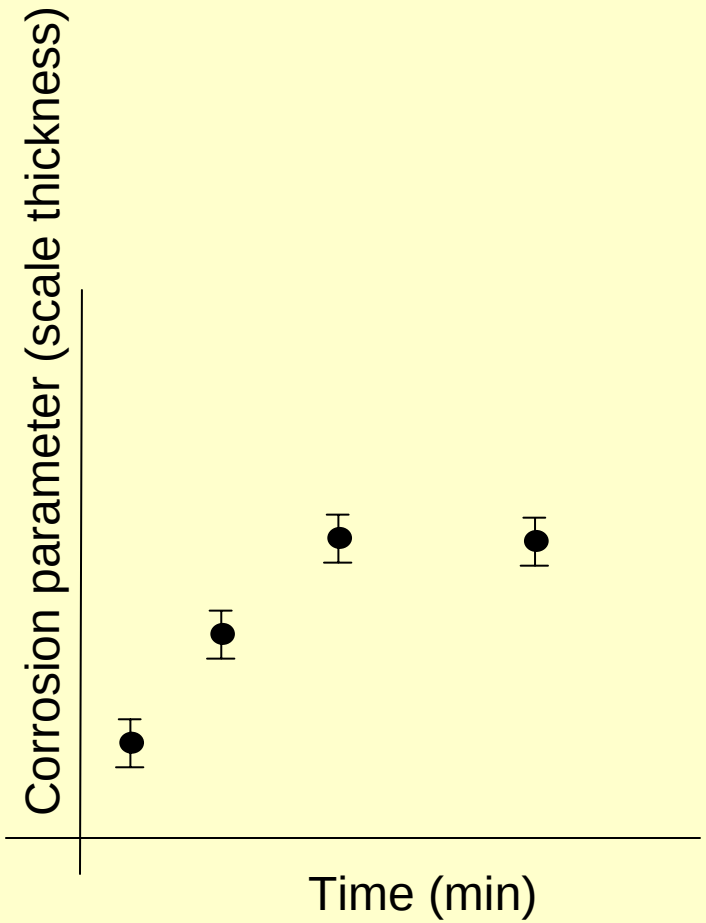




Experimental Approach

- Running time
  - 60 hrs (sample every 12 hrs)
  - Provide time dependant data





Conclusion

- Applying combustion and catalysis understanding leads toward WTE improvements technologies.
- Fundamental investigations can lead to novel technologies.
- There is no “one-solution” to the energy problem.

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