Catalytic Applications for Emissions Mitigation: From Combustion Systems to Chemical Synthesis

Presentation to:

ASME TecTalk October 21, 2026 - Virtual



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Energy, Environment, and Sustainable Waste Management (EESWM)

Combustion & Catalysis Laboratory

Earth Engineering Center
CITY COLLEGE of NEW YORK

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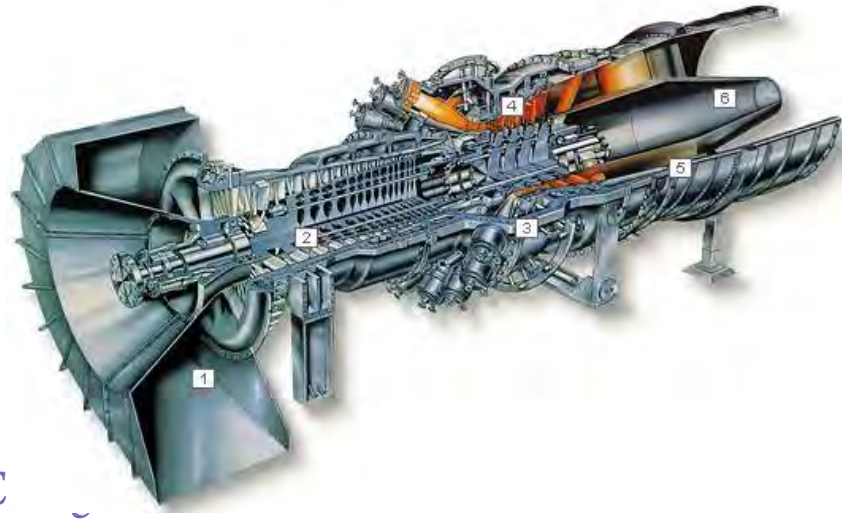
Presentation Overview

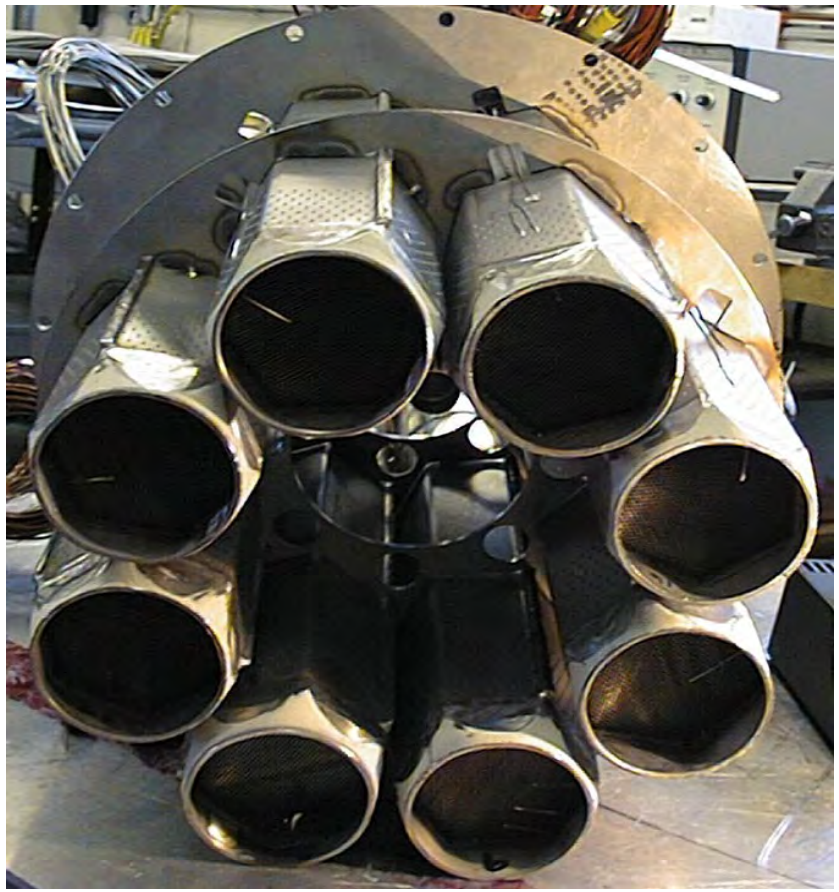
- Combustion & Catalysis Laboratory Overview
- Catalysis & Combustion → Emissions focus
  - RCL & LFGTE
- Chemical Production
  - Selectivity, H_2 production (E.A.R.) & upgrading via FCC
- Reaction Sequence Understanding ("mechanistic")
  - Isotopes to Shock Tube

Combustion & Catalysis Laboratory Overview

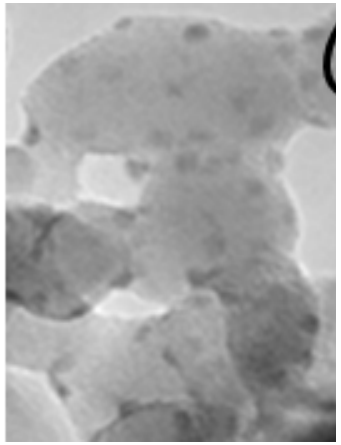
Large Scale Catalytic Reactor Experience



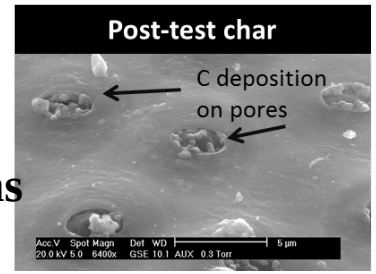




Fundamental Catalytic Research

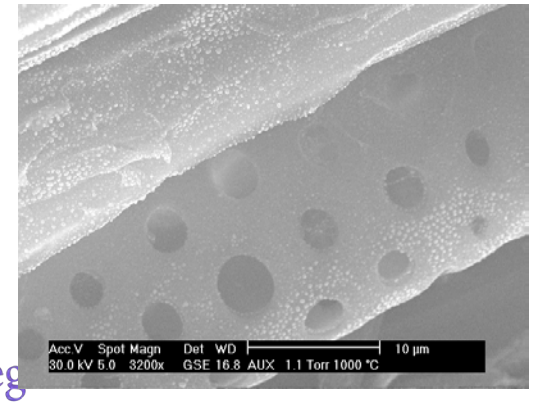


Catalysis
TEM, etc

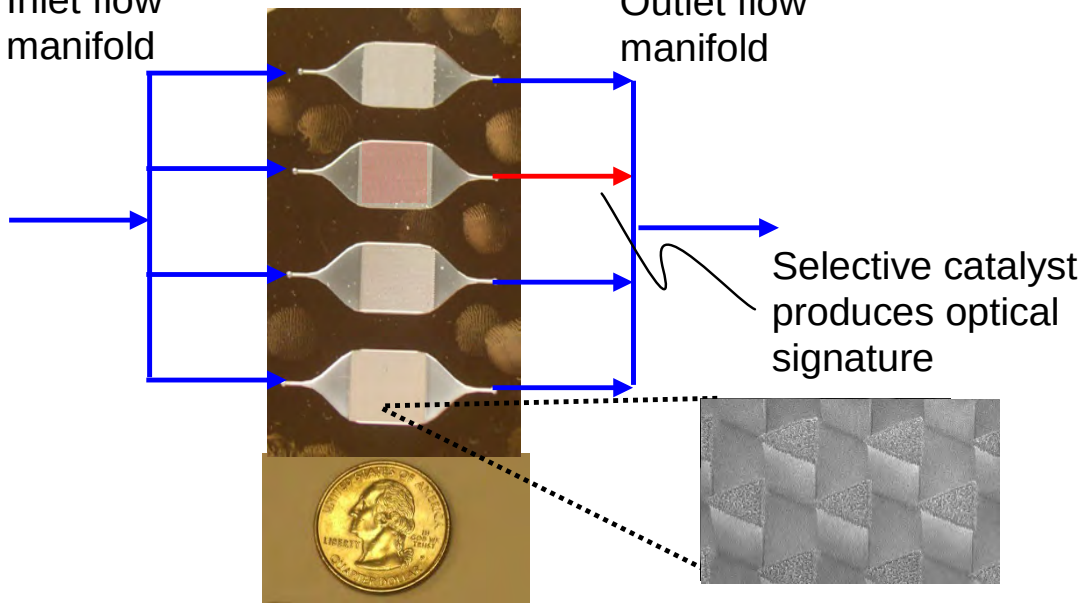


Operando reactions

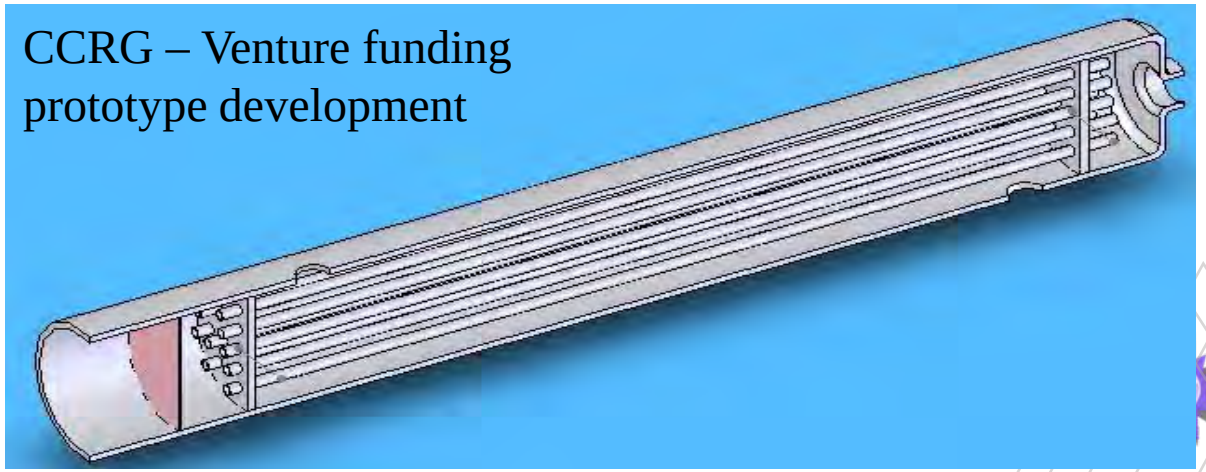
Environmental SEM



Future Products



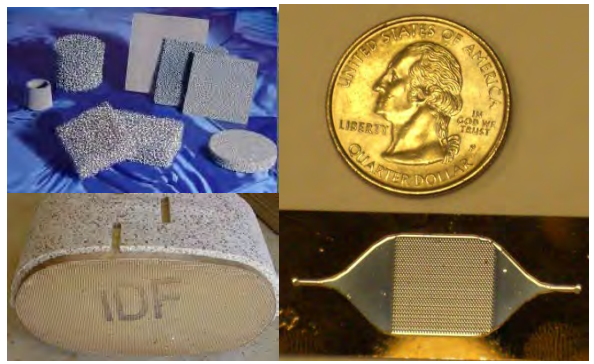
CCRG – Venture funding
prototype development

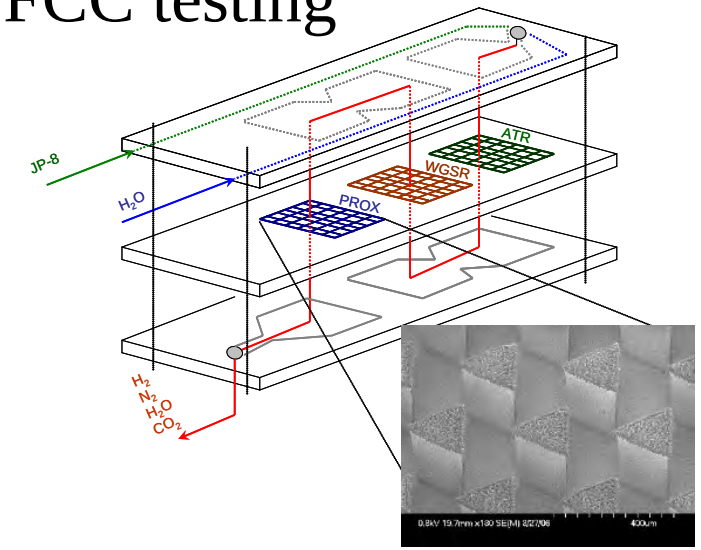


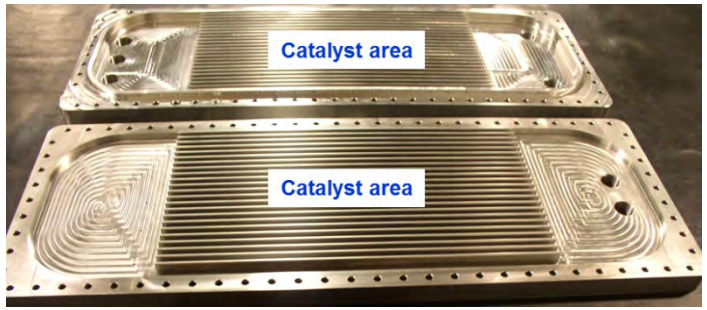
Catalytic Testbed Capabilities

Catalytic Reactor Testbeds

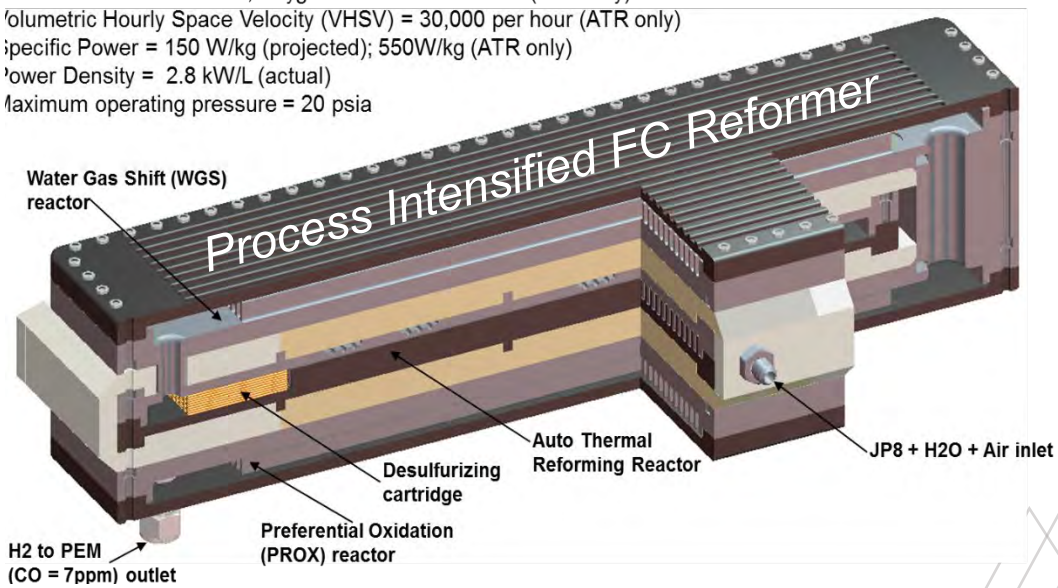
- microCatalytic to industrial Scale
- Process Intensified Units(e.g. FC reformers)
- FCC testing







TR output: 37 SLPM of H2
team-to-Carbon ratio = 2; Oxygen-to-Carbon ratio = 1 (ATR only)
olumetric Hourly Space Velocity (VHSV) = 30,000 per hour (ATR only)
pecific Power = 150 W/kg (projected); 550W/kg (ATR only)
ower Density = 2.8 kW/L (actual)
laximum operating pressure = 20 psia



Catalysis & Combustion

1) Smith, L. L., Karim, Hasan, Castaldi, Marco J., Etemad, S., Pfefferle, W. C., Khanna, V. K., Smith, K.O., “Rich-Catalytic Lean-Burn Combustion for Low-Single-Digit NOx Gas Turbines.” ASME Turbo Expo: Power for Land, Sea & Air; 2003. *(equal)*
2) Lyubovsky, M.; Smith, L. L.; Castaldi, M.; Karim, H.; Nentwick, B.; Etemad, S.; LaPierre, R.; Pfefferle, W. C., “Catalytic combustion over platinum group catalysts: fuel-lean versus fuel-rich operation.” Catalysis Today 2003, 83, (1-4), 71-84.
3) Smith, L. L.; Karim, H.; Castaldi, M. J.; Etemad, S.; Pfefferle, W. C.; Khanna, V.; Smith, K. O., Rich-Catalytic Lean-Burn Combustion for Low-Single-Digit NOx Gas Turbines. J. Eng. Gas Turbines Power 2005, 127, (1), 27-35.
4) Smith, L. L.; Karim, H.; Castaldi, M.J; Etemad, S.; Pfefferle, W. C., “Rich-Catalytic Lean-burn combustion for fuel-flexible operation with ultra low emissions.” Catalysis Today 2006, 117, (4), 438-446.
5) Kohn, M; Lee, J; Basinger, M.L; **Castaldi**, M.J., Performance of an Internal Combustion Engine Operating on Landfill Gas and the Effect of Syngas Addition, Ind. Eng. Chem. Res. 2011, 50 (6): 3570–3579
6) Kohn, M. P.; **Castaldi,** M. J.; Farrauto, R. J., Biogas reforming for syngas production: The effect of methyl chloride. Applied Catalysis B: Environmental 2014, 144, 353-361
7) Kohn, M., Castaldi M.J., and Farrauto, R.J., “Auto-thermal and Dry Reforming of landfill gas over a Rh/γAl2O3 monolith catalyst.” App. Catal. B: Environ, (94), 2010, 125-133.

Combustion & Catalysis Laboratory

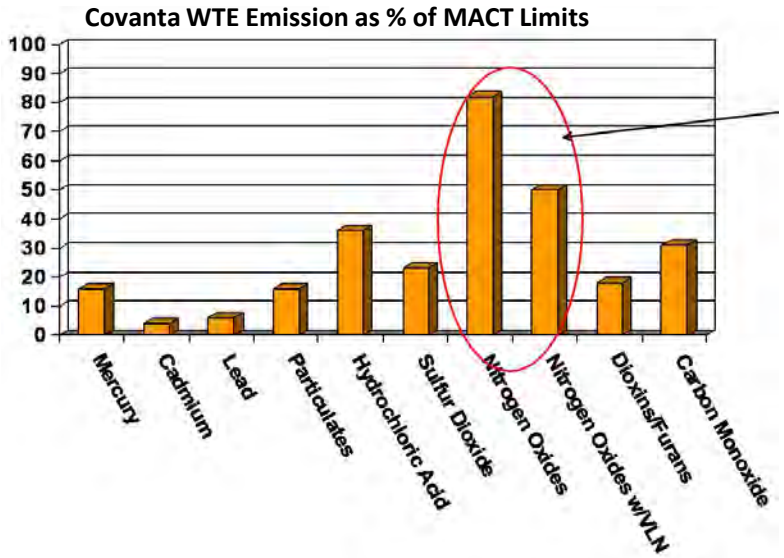
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BLUF (Bottom Line Up Front) on Catalysis & Combustion

- **Catalytic Combustion for Gas Turbine (CH_4 + air $\xrightarrow{cat}$ CO_2 + H_2O)**
  - Catalytic combustion enables ultra low emissions at high temperatures/efficiencies
  - Unstable operation led to in-situ fuel reforming development
- **In-situ fuel reforming enables new applications (Improvements from H_2 addition)**
  - Landfill gas to energy (LFGTE) → fuel upgrading

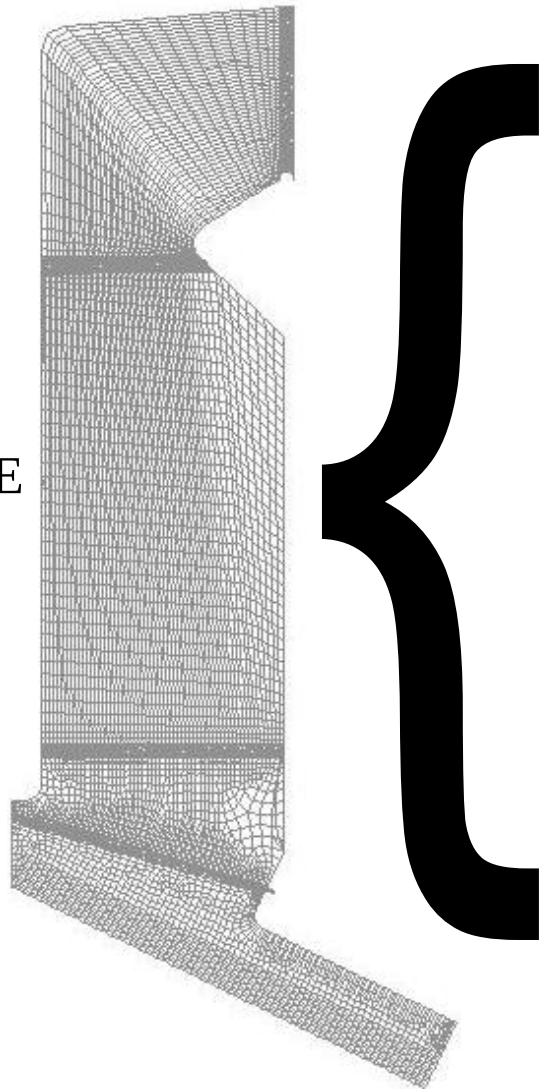
– **Overall: In-situ fuel conditioning has wide applications**

WTE: Mechanistic Analysis to Predict NO_x



- 3-D CFD to understand flow characteristics of chemical species in WTE boilers
- Inlet boundary condition to CFD model is "***above bed***" gas phase
- Solid phase not modeled
- (DCKM) to predict combustion products

GRI 3.0*-309 reaction step DCKM contains 50 species and is used in conjunction with Eddy Dissipation Concept Model for turbulent-chemistry reaction in the boiler.

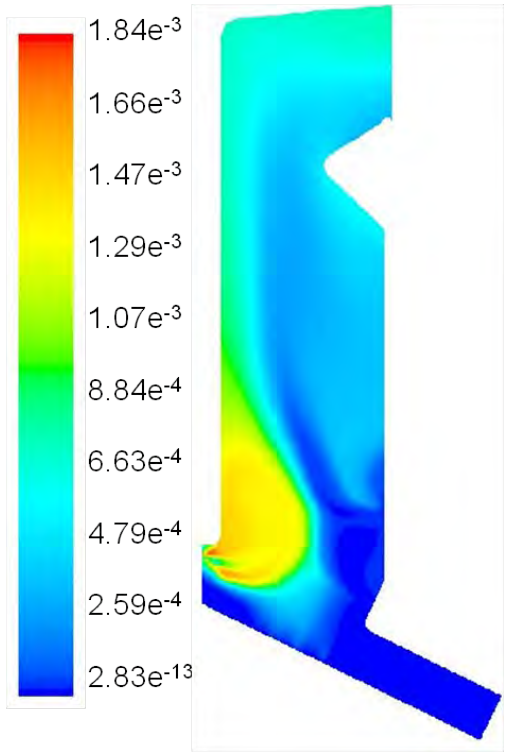


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REACTIONS
2O+M<=>O2+M                                1.200E+17   -1.000        .00
H2/ 2.40/ H2O/15.40/ CH4/ 2.00/ CO/ 1.75/ CO2/ 3.60/ C2H6/ 3.00/ AR/  .83/
O+H+M<=>OH+M                               5.000E+17   -1.000        .00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
O+H2<=>H+OH                                3.870E+04    2.700     6260.00
O+HO2<=>OH+O2                              2.000E+13     .000        .00
O+H2O2<=>OH+HO2                            9.630E+06    2.000     4000.00
O+CH<=>H+CO                                5.700E+13     .000        .00
O+CH2<=>H+HCO                              8.000E+13     .000        .00
O+CH2(S)<=>H2+CO                           1.500E+13     .000        .00
O+CH2(S)<=>H+HCO                           1.500E+13     .000        .00
O+CH3<=>H+CH2O                             5.060E+13     .000        .00
O+CH4<=>OH+CH3                             1.020E+09    1.500     8600.00
O+CO(+M)<=>CO2(+M)                         1.800E+10     .000     2385.00
   LOW/ 6.020E+14     .000    3000.00/
H2/2.00/ O2/6.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/3.50/ C2H6/3.00/ AR/ .50/
O+HCO<=>OH+CO                              3.000E+13     .000        .00
O+HCO<=>H+CO2                              3.000E+13     .000        .00
O+CH2O<=>OH+HCO                            3.900E+13     .000     3540.00
O+CH2OH<=>OH+CH2O                          1.000E+13     .000        .00
O+CH3O<=>OH+CH2O                           1.000E+13     .000        .00
O+CH3OH<=>OH+CH2OH                         3.880E+05    2.500     3100.00
O+CH3OH<=>OH+CH3O                          1.300E+05    2.500     5000.00
O+C2H<=>CH+CO                              5.000E+13     .000        .00
O+C2H2<=>H+HCCO                            1.350E+07    2.000     1900.00
O+C2H2<=>OH+C2H                            4.600E+19   -1.410    28950.00
O+C2H2<=>CO+CH2                            6.940E+06    2.000     1900.00
O+C2H3<=>H+CH2CO                           3.000E+13     .000        .00
O+C2H4<=>CH3+HCO                           1.250E+07    1.830      220.00
O+C2H5<=>CH3+CH2O                          2.240E+13     .000        .00
O+C2H6<=>OH+C2H5                           8.980E+07    1.920     5690.00
O+HCCO<=>H+2CO                             1.000E+14     .000        .00
O+CH2CO<=>OH+HCCO                          1.000E+13     .000     8000.00
O+CH2CO<=>CH2+CO2                          1.750E+12     .000     1350.00
O2+CO<=>O+CO2                              2.500E+12     .000    47800.00
O2+CH2O<=>HO2+HCO                          1.000E+14     .000    40000.00
H+O2+M<=>HO2+M                             2.800E+18    -.860        .00
O2/ .00/ H2O/ .00/ CO/ .75/ CO2/1.50/ C2H6/1.50/ N2/ .00/ AR/ .00/
H+2O2<=>HO2+O2                             2.080E+19   -1.240        .00
H+O2+H2O<=>HO2+H2O                         11.26E+18    -.760        .00
H+O2+N2<=>HO2+N2                           2.600E+19   -1.240        .00
H+O2+AR<=>HO2+AR                           7.000E+17    -.800        .00
H+O2<=>O+OH                                2.650E+16    -.6707   17041.00
2H+M<=>H2+M                                1.000E+18   -1.000        .00
H2/ .00/ H2O/ .00/ CH4/2.00/ CO2/ .00/ C2H6/3.00/ AR/ .63/
2H+H2<=>2H2                                9.000E+16    -.600        .00
2H+H2O<=>H2+H2O                            6.000E+19   -1.250        .00
2H+CO2<=>H2+CO2                            5.500E+20   -2.000        .00
H+OH+M<=>H2O+M                             2.200E+22   -2.000        .00
H2/ .73/ H2O/3.65/ CH4/2.00/ C2H6/3.00/ AR/ .38/
H+HO2<=>O+H2O                              3.970E+12     .000      671.00
H+HO2<=>O2+H2                              4.480E+13     .000     1068.00
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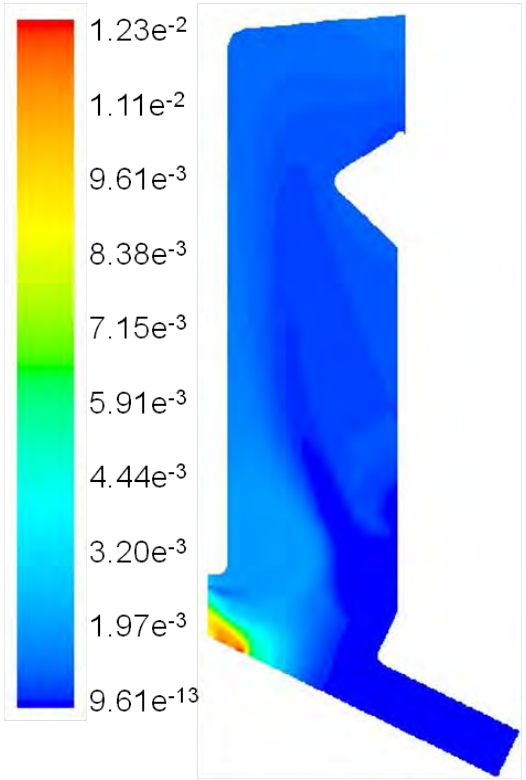
Model Results-DCKM NOx

Contours of NO (mol/mol)

Fuel-N →HCN and NH_3



Fuel-N →NO

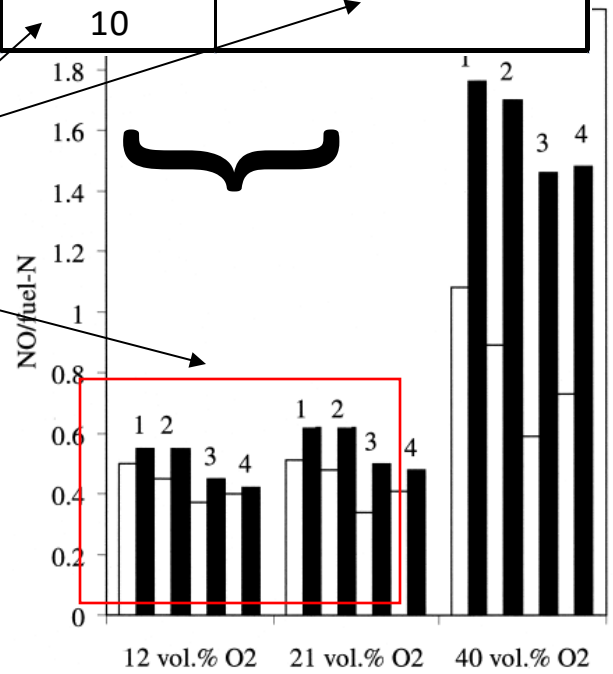


Model Results for Precursors

Fuel Nitrogen Conversion	NO (ppmdv)	Expected NO (ppmdv)
HCN	993	400[1]
NH_3	957	
NO	1036	
N_2	10	

~2X difference

Fuel-N → NO ~50%[2]



Fuel – N to HCN or NH_3 precursor: NOx formation at 2° air inlet

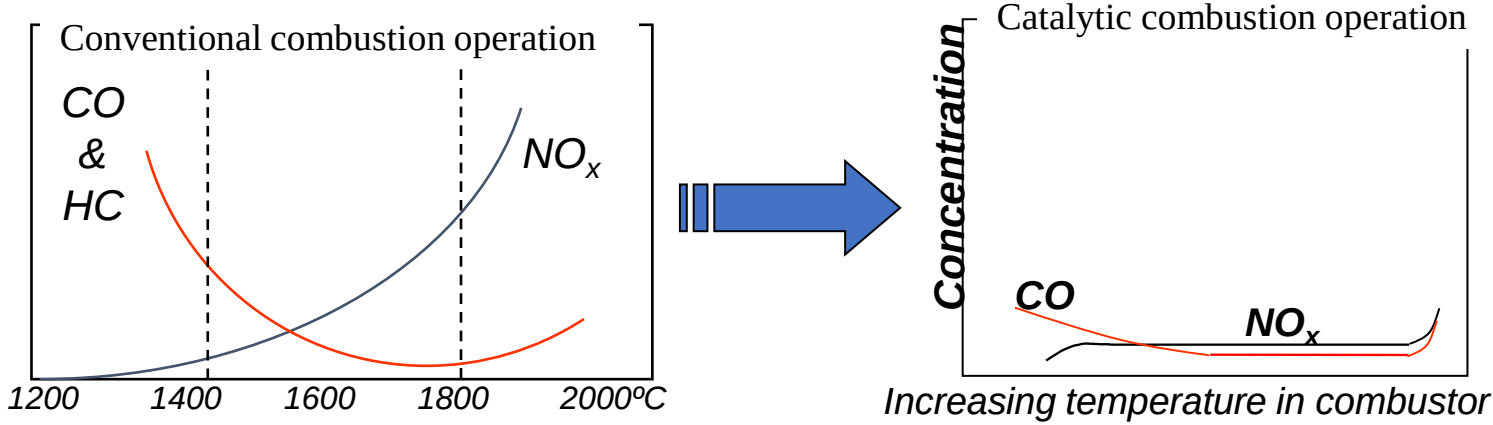
Fuel – N to NO precursor: little change in boiler

Likely Fuel – N to NO direct conversion is ~50%

1.White, M., et al., New Process for Achieving Very Low NOx2009. NAWTEC17-2372.
2. Sorum,L., et al., Formation of NO from Combustion of Volatiles from Municipal Solid Waste, Comb Flame ,123 p.195

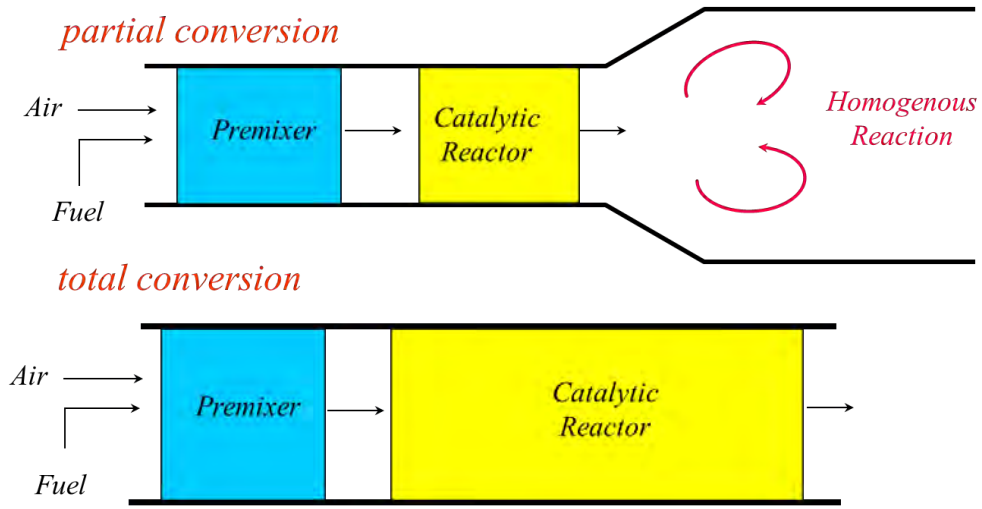
Catalyst Impact on traditional CO-NOx curve

- *Enables lower temperature operation*
- *Fuel readily converts to complete oxidation products*
- *Reactive intermediates remain on surface*
- *Achieve results long before equilibrium (e.g. CO)*



NOx prevention via Cat. Comb.

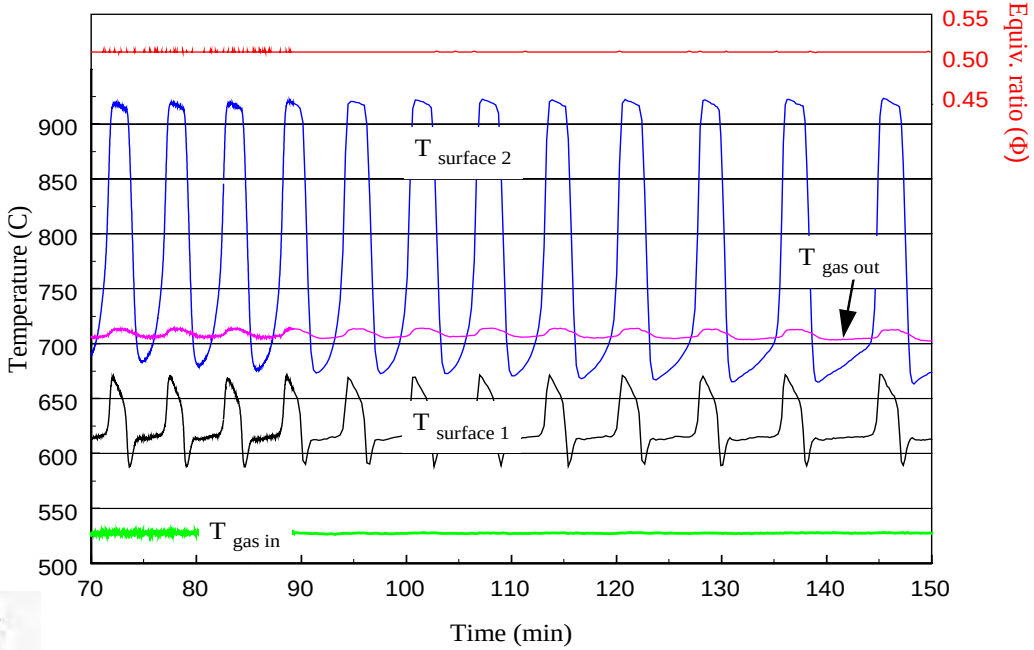
NO_x Path	Mechanism	Range of Significance	Effect of Catalytic Pre-Reaction
Thermal NO_x	$O+N_2$ --> $NO+N$ $N+O_2$ --> $NO+O$	T> 1800K	Vitiate→reduce super-equil.O-atom
Prompt NO_x	$CH+N_2$ --> $HCN+N$	ϕ >0.8	Surface rxn→reduce CH conc.
N_2O Mechanism	$O+N_2+M$-->N_2O+M (three-body rxn)	p>1atm	Vitiate→reduce super-equil.O-atom
Fuel-bound nitrogen	NH_i+O-->$NH_{i-1}+OH$ ↓ $NH+O$-->$N+OH$ $N+O_2$-->$NO+O$	~ 1:1 w/fuel-bound (negligible for NG)	Selective oxidation

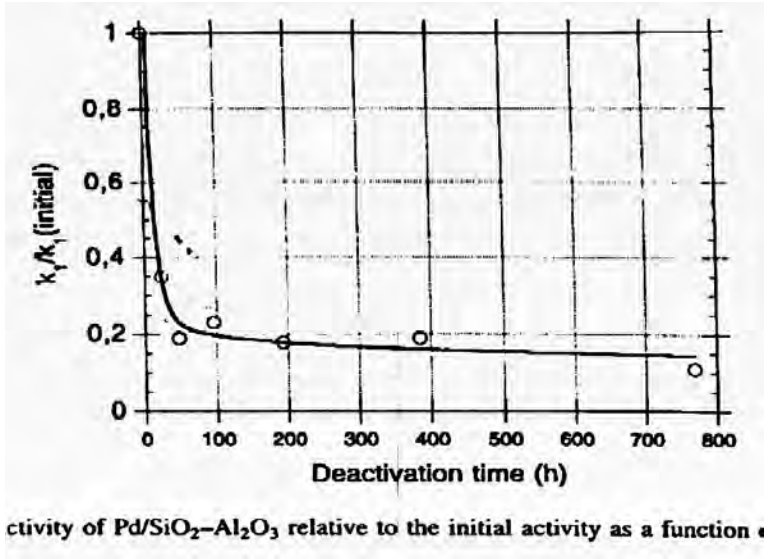


Total Catalytic Comb System - Drawbacks

$$(CH_4 + \text{air} \xrightarrow{cat} CO_2 + H_2O)$$

- Oscillatory catalyst behavior
  - Catalyst activity hysteresis (Pd/PdO shift)
  - Positive thermal feedback along catalyst bed
- Long-term catalyst deactivation
  - Water assisted sintering
  - CO_2 poisoning
- **Loss of Effectiveness**
- **MELTDOWN**!





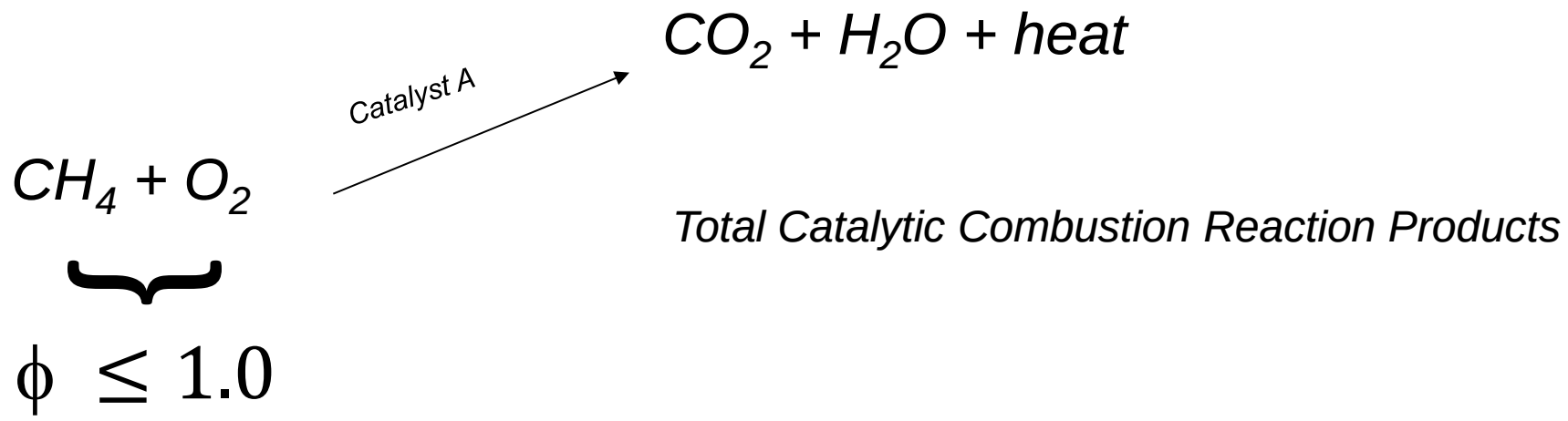
ctivity of Pd/SiO_2–Al_2O_3 relative to the initial activity as a function

Total catalytic combustion systems need to be more robust

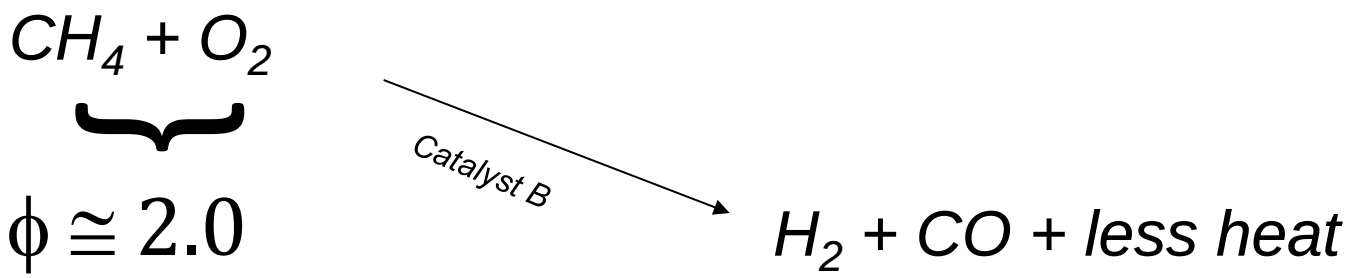
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Final product adjustment using catalyst formulation and reactor design



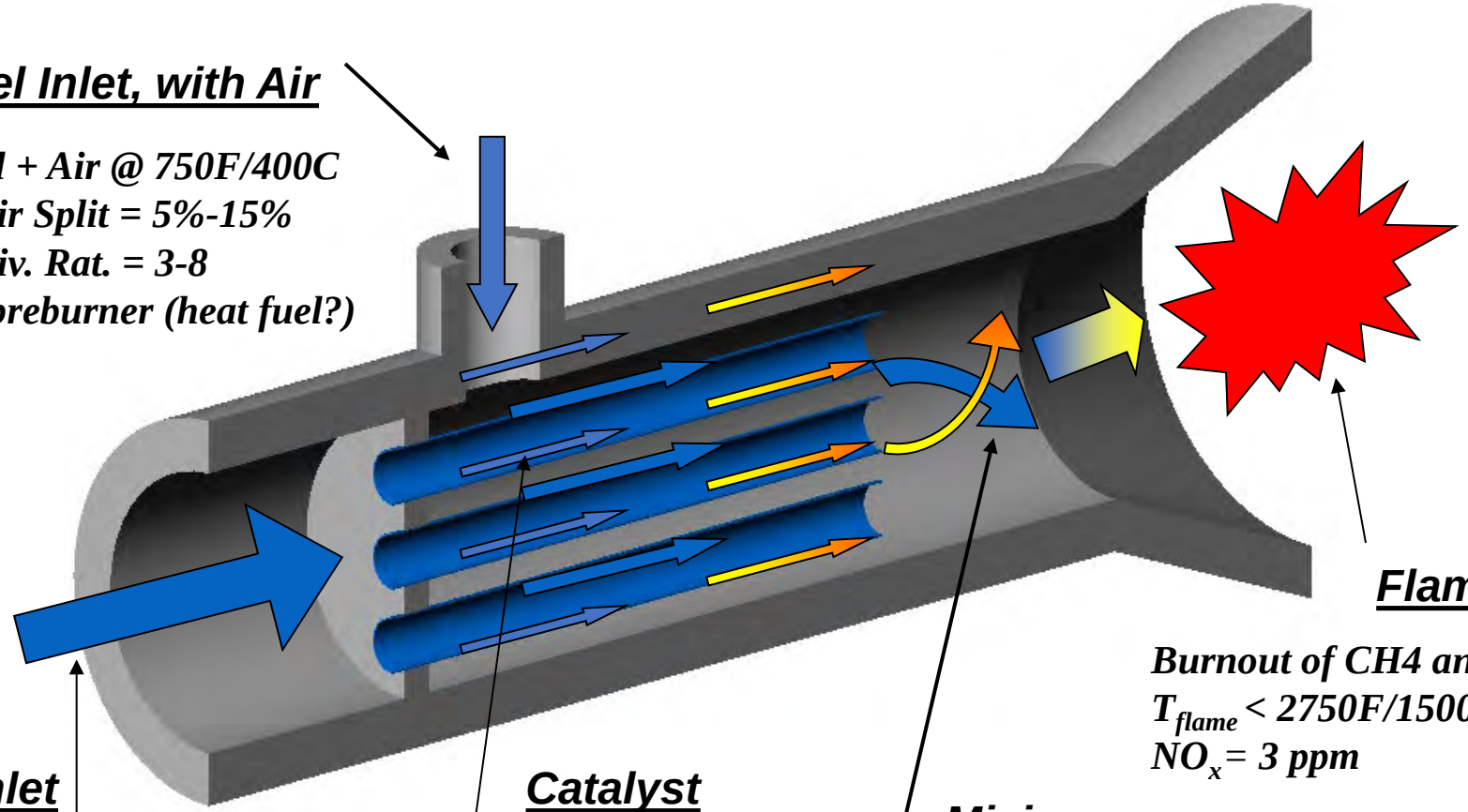
Final product adjustment using catalyst formulation and reactor design



Fuel Rich Catalytic Combustion Reaction Products

We see, if we stop at CO, H_2 will be produced as a result.

Fuel Rich Operation of Catalytic Combustion



Fuel Inlet, with Air

Fuel + Air @ 750F/400C
% Air Split = 5%-15%
Equiv. Rat. = 3-8
No preburner (heat fuel?)

Flame

Burnout of CH4 and CO
T_{flame} < 2750F/1500C
NO_x = 3 ppm

Air Inlet

Air @ 750F/400C
No preburner
ΔP/P < 5 %

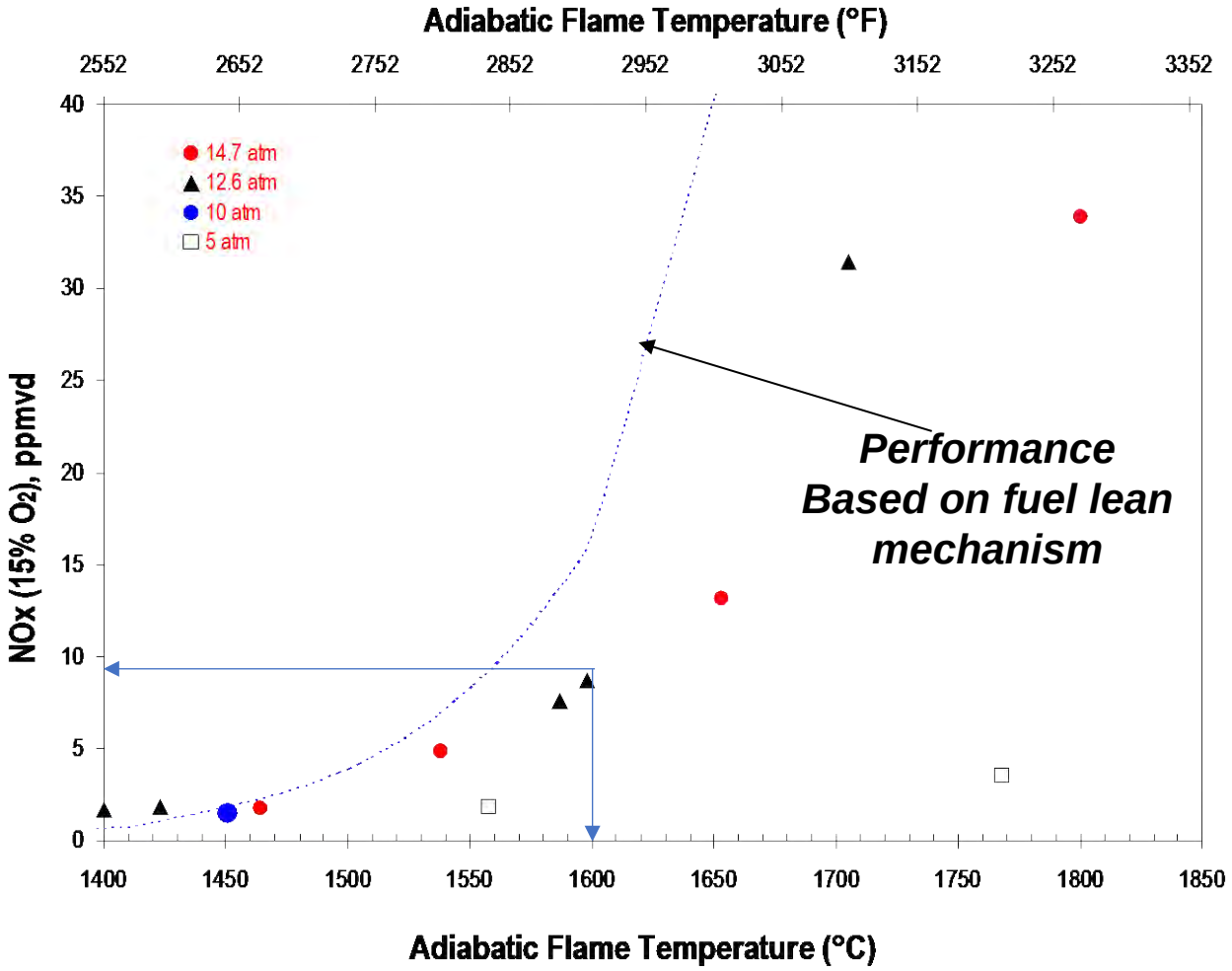
Catalyst

Air-Cooled Catalytic Reactor
T_{wall} <1650-1750F/950C
Durability ≈8000 hr
Stress<5ski@1800F (1000C)

Mixing

Mix Air w/ Partially Reacted Fuel/Air
T_{mix} = 1290- 1380F/700-750C
τ_{mix} < 5 msec
U=150ft/s

Fuel Rich Full Combustor Performance



- *Single digit NOx*
- *Safe / robust operation at high firing temperatures*
- *Stable flame at low firing temperatures (1600°C, 2850°F)*

Landfill Gas (LFG) [or GHG Reforming]

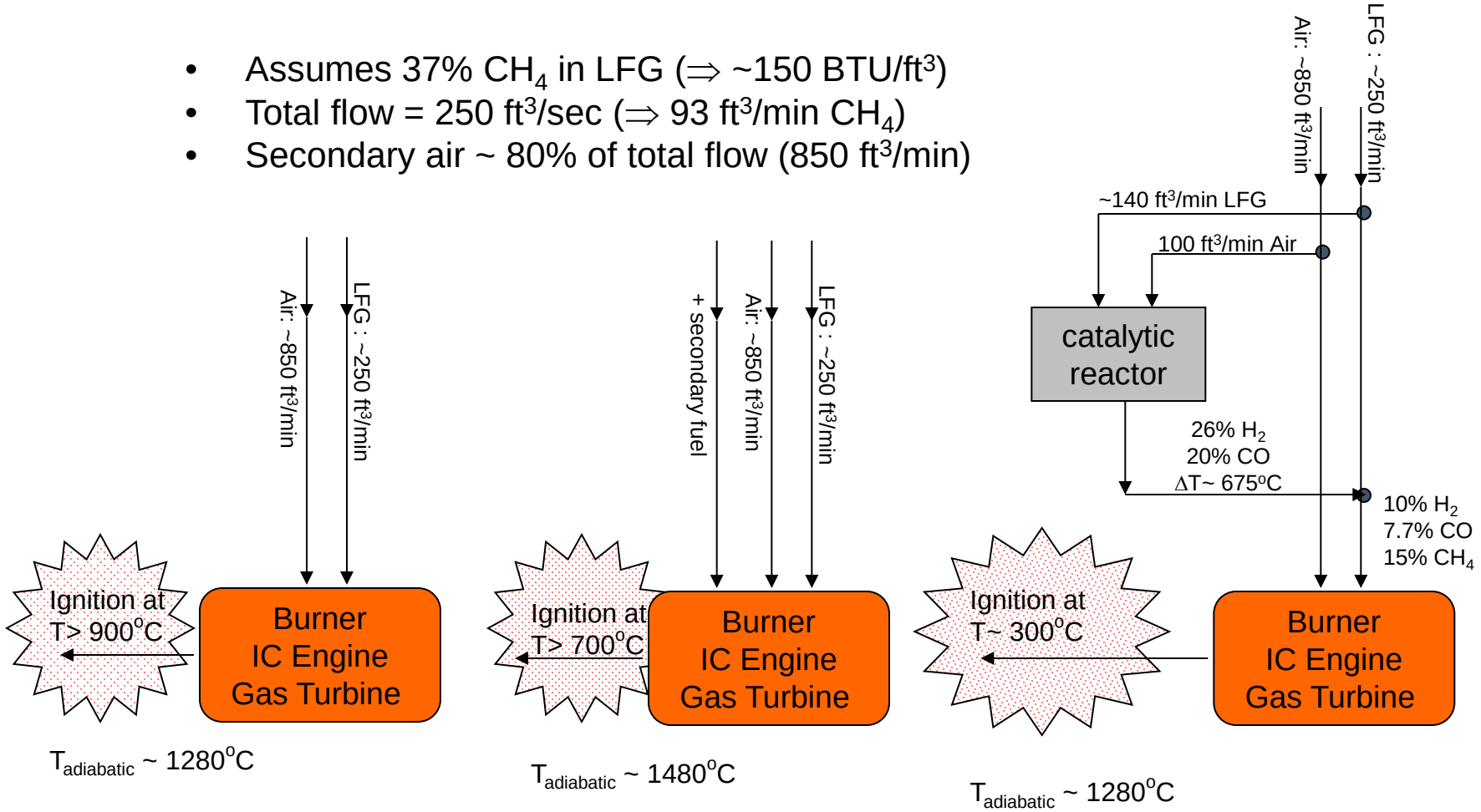
Landfill gas and landfill gas to energy (LFGTE)

- 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%).
- Landfill gas causes odors at a landfill.
- Projects help destroy methane, a potent heat-trapping gas.
- Projects generate renewable energy and offset the use of non-renewable resources such as coal, natural gas, and oil.

LFGTE Issues and Solutions

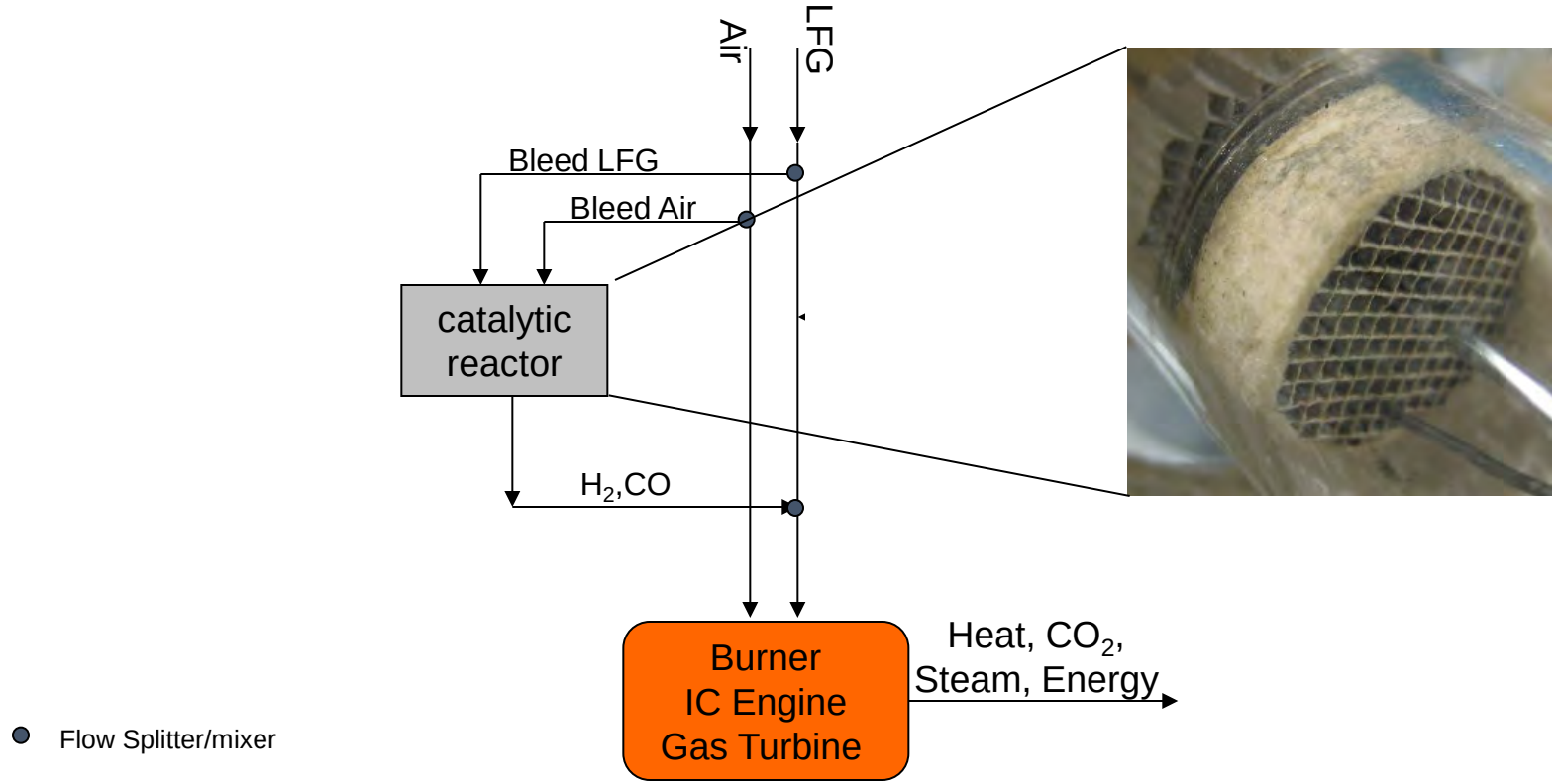
$$(CO_2/CH_4 + \text{air} \xrightarrow{cat} CO + H_2)$$

- 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)



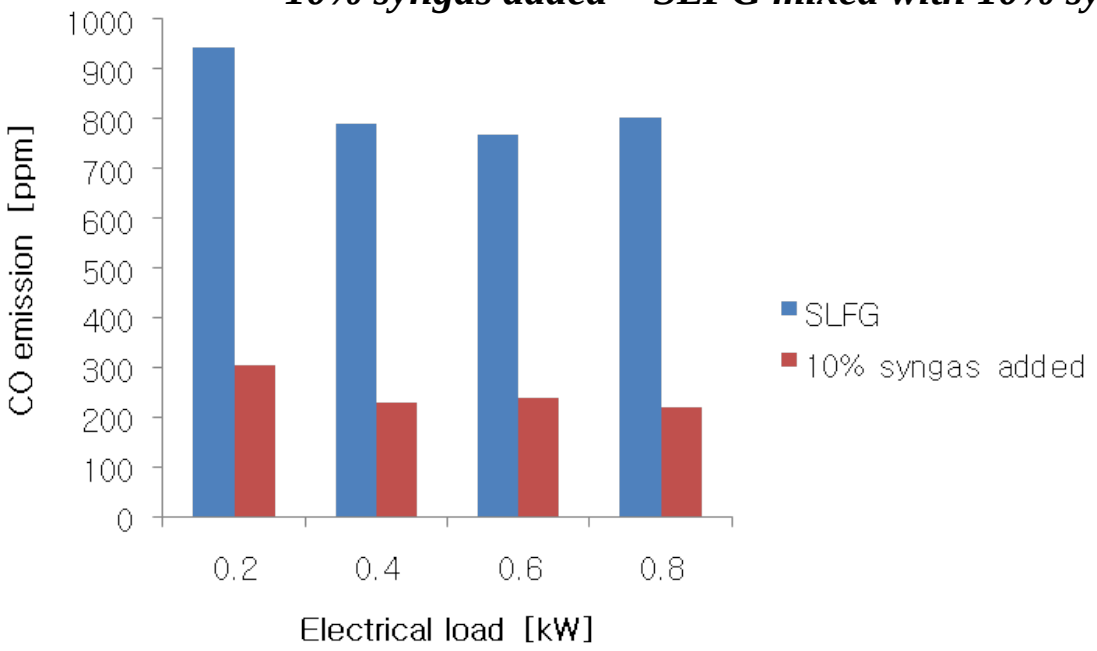
Requires lower net energy & ignition temp. CH_4 fluctuation permissible

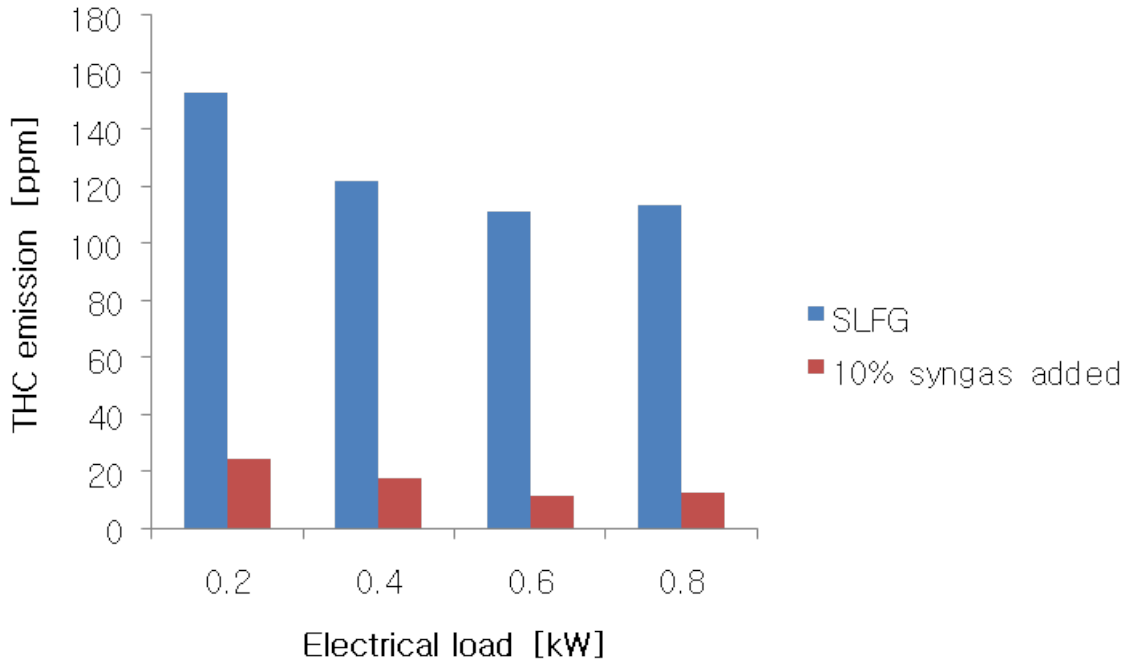
System Implementation Schematic

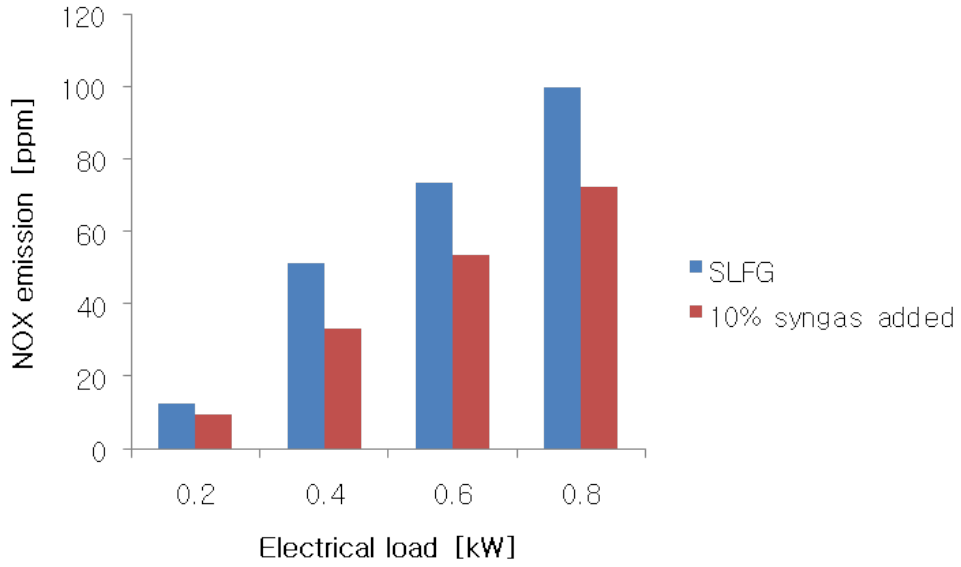


Test data @ CCL :Honda GC 160E

- ***SLFG = simulated landfill gas***
- ***10% syngas added = SLFG mixed with 10% syngas***

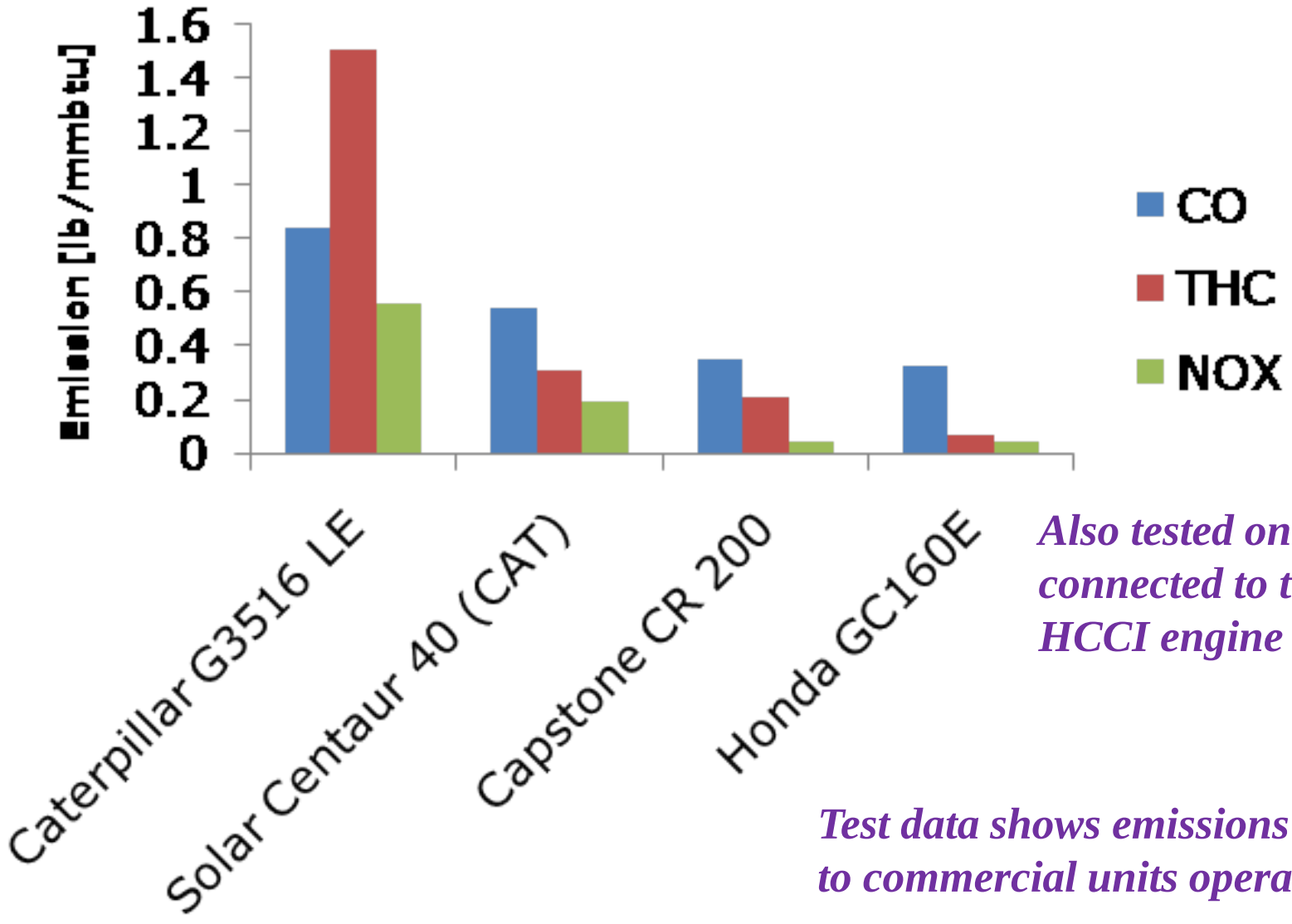






Test data shows lower emissions possible across all loads utilizing syngas produced from LFG

Comparison data of Laboratory test engine (Honda GC 160E) with commercial units



Also tested on a 30-hp dynamometer connected to the flywheel of an HCCI engine @ 1200 rpm

Test data shows emissions from test unit at CCL is comparable to commercial units operating on LFG (without 10% syngas)

Chemical Production

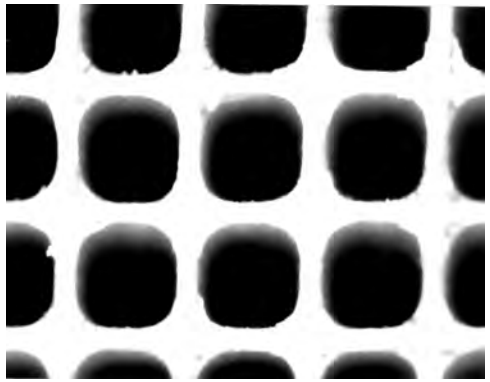
1) Roychoudhury, S.; Castaldi, M.; Lyubovsky, M.; LaPierre, R.; Ahmed, S., “Microlith catalytic reactors for reforming iso-octane-based fuels into hydrogen.” Journal of Power Sources 2005, 152, 75-86.
2) Dorazio, L., Ruettinger, W., Castaldi, M.J, Farrauto, B.F., “Deactivation, Regeneration, and Stable Performance of a Platinum-Molybdenum-Rhenium Water Gas Shift Catalyst for on-Site Hydrogen Generation,” Topics in Catalysis, 2008, 51 (1-4), pp. 68-75.
3) Duyar, M.S., Farrauto, R.J., Castaldi, M.J., **Yegulalp**, T.M., In-Situ CO2 Capture Using CaO/□-Al2O3 Washcoated Monoliths for Sorption Enhanced Water Gas Shift Reaction Ind. & Eng. Chem. Res 2013
4) Castaldi, M. J. “Method for reduced methanation.” U.S.Patent #6,746,657, 2004
5) Mastry, Melissa Clough, Lucas Dorazio, James C. Fu, Juan Pedro Gómez, Sergio Sedano, Snehesh S. Ail, Marco J. Castaldi, and Bilge Yilmaz. "Processing renewable and waste-based feedstocks with fluid catalytic cracking: Impact on catalytic performance and considerations for improved catalyst design." *Frontiers in Chemistry* 11 (2023): 1067488.
6) Ail, Snehesh Shivananda, Marco J. Castaldi, Anthony Vallace, Charles Coe, and Michael Smith. "Investigations to intensified hydrogen production via sorption enhanced water gas shift reaction." *Applied Catalysis A: General* 678 (2024): 119709.

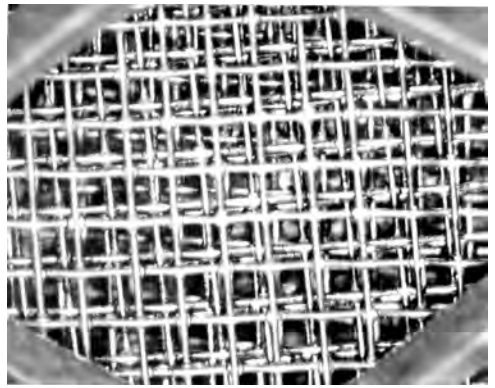
BLUF on Chemical Production

- **Rector geometry can impact selectivity (WGS with reduced methanation)**
  - Short contact time (SCT) permits fast transport
  - Mixing regions eliminate channeling issues
- **In-situ fuel product capture = equilibrium adjustment reactors (EARs) (enhanced H_2 production**
  - Li_4SiO_4 demonstrate reversibly, and isothermally adsorbs CO_2 with a working capacity of 36.7 wt%
- **Upgrading potential for bio- & pyoil from wastes using existing FCC infrastructure (~50 olefin recycle)**
  - Demonstrated potential to convert ~50% of plastic pyoils to olefins

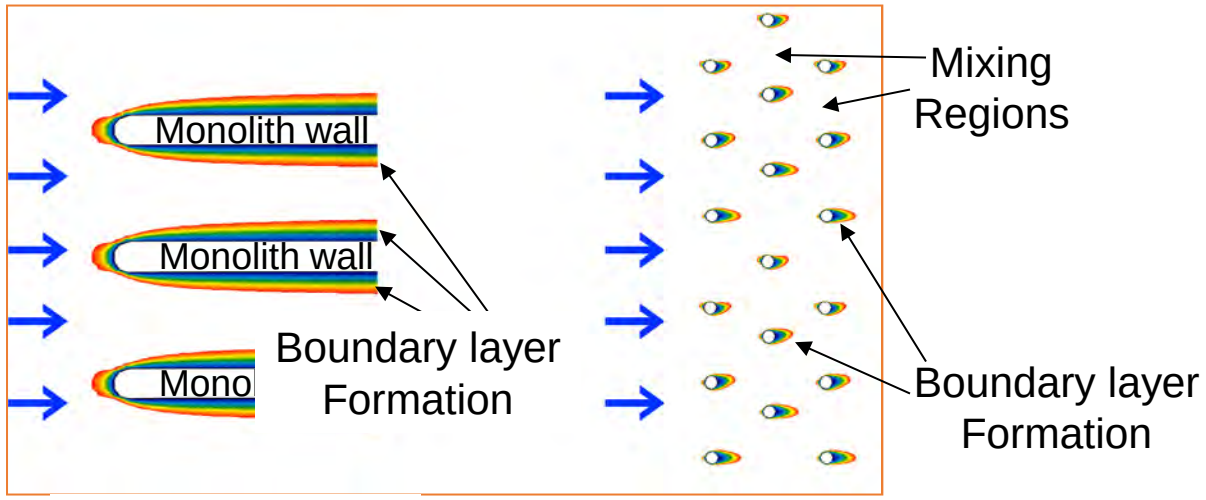
– **Overall: Requires appropriate reactor AND catalyst design integration**

Reactor Comparison





400	Cells/in^2	2500
2.64	Geometric Surface Area (m^2/l)	6.3
3.0 - 5.0	Channel Length (in)	0.003
70 - 120	Channel Length to Diameter Ratio (L/d)	0.3
< 1200	Operating Temperature (C)	< 1200
70	Frontal Open Area	72



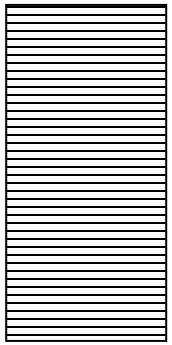
Short Contact Time (SCT)

- Higher cell density
- Increased SSA
- High transport prop.
- Low pressure drop

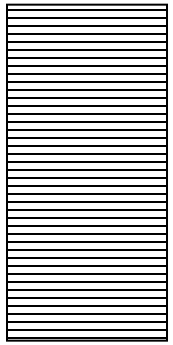
Performance Comparison

$$(CO + H_2O \xrightarrow{cat} CO_2 + H_2 + CH_4)$$

400 cpsi Monolith



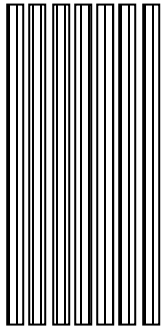
CO Conversion	Equilibrium
methanation	**4000 ppm**
Space Velocity	110,000 hr^{-1}
Volume	1.00



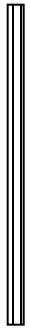
CO Conversion	87%
CO Selectivity	49%
Space Velocity	**44,000 hr^{-1}**
Volume	**1.00**

selectivity

SCT Substrate



CO Conversion	Equilibrium
methanation	**400 ppm**
Space Velocity	110,000 hr^{-1}
Volume	1.00



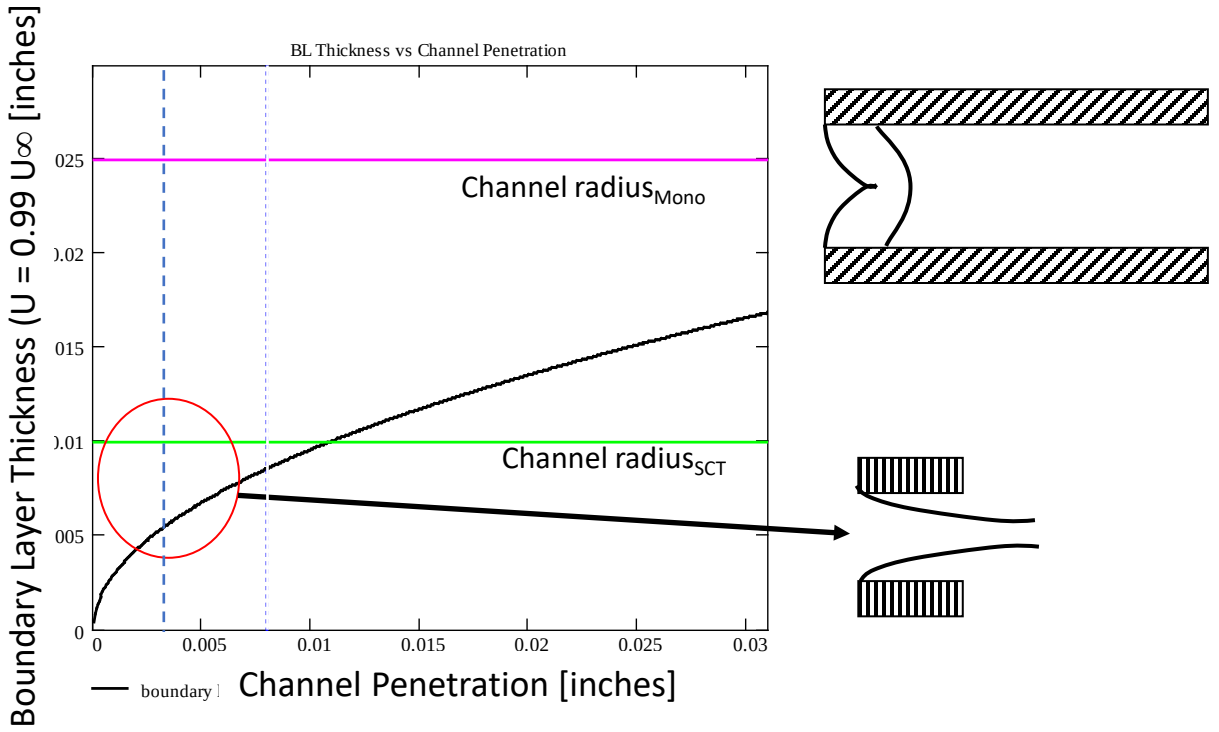
CO Conversion	87%
CO Selectivity	50%
Space Velocity	**440,000 hr^{-1}**
Volume	**0.10**

Gauze reactors result in similar performance @ 1/10th the volume compared to monoliths

Explanation for Selectivity

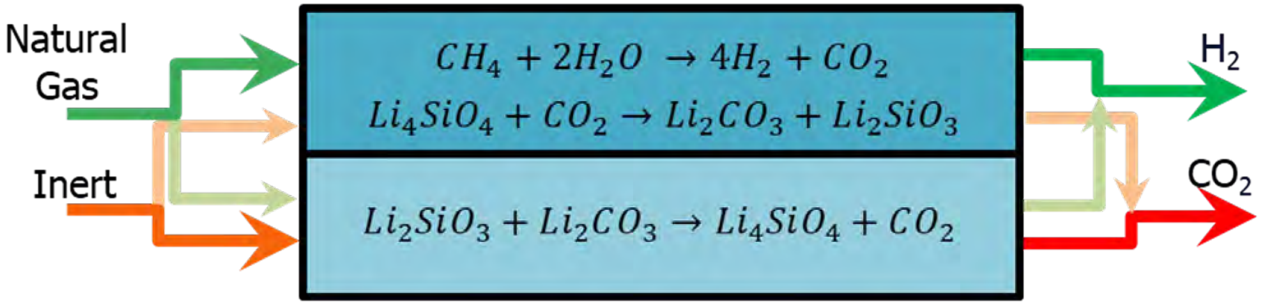
$$(CO + H_2O \xrightarrow{cat} CO_2 + H_2 + CH_4)$$

- Boundary layer is resistance to heat transfer – Higher surface temperature
- CH_4 production is increased at higher temperature
- Products are removed from surface before reacting further

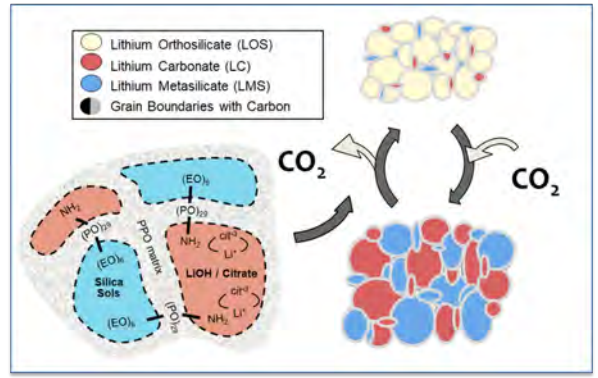


Equilibrium Adjustment Reactor (EAR)

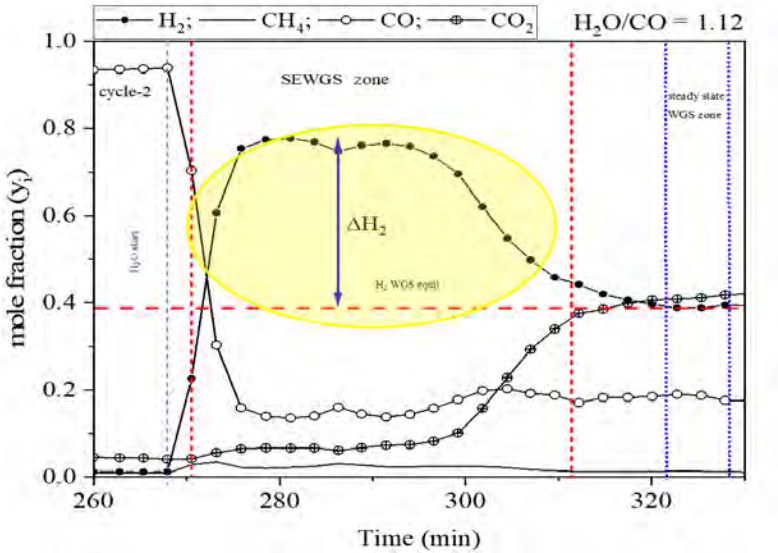
$$(CH_4 + H_2O \xrightarrow{cat} CO_2 + H_2)$$



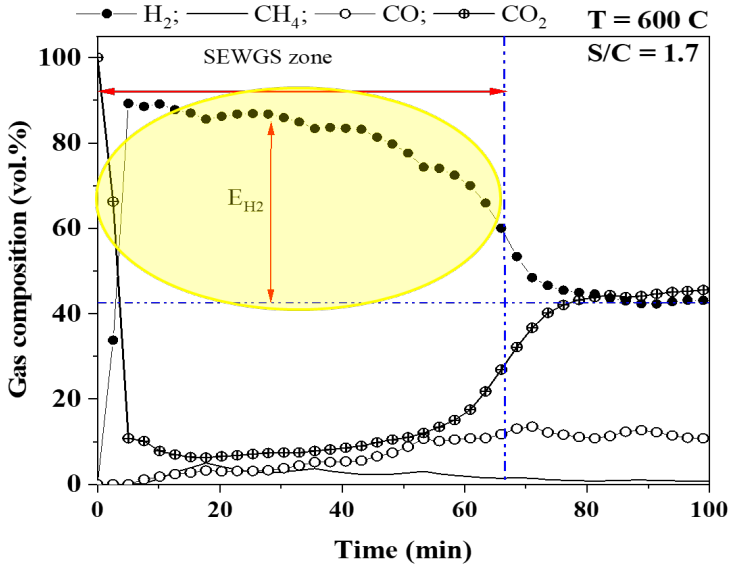
Dual-bed scheme requires only gas switching.
Li_4SiO_4 operates at constant temperature



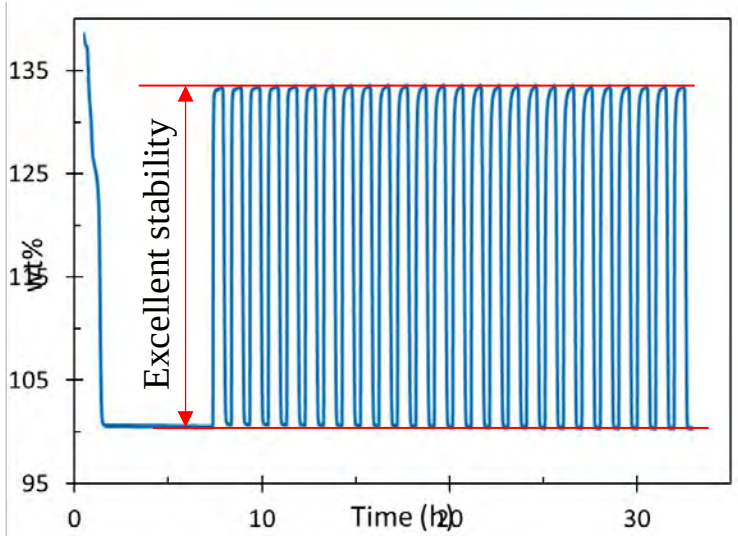
Fast kinetic uptake due to carbonate and metasilicate domains mediated by surfactant during gel stage.



WGS conditions with **H_2O/CO** = 1.12;
T = 600° C; catalyst: 5% Pt/g-Al_2O_3.



Steam-methane reforming with **H_2O/CH_4** = 1.7:1;
T = 600° C; catalyst: 5% Pt/g-Al_2O_3.



Cyclic stability for 80 30-minute cycles @ 50% CO_2 with 10 % steam (balance N_2).

The City College of New York

Single-step technology enables transition from grey to blue hydrogen

Combustion & Catalysis Laboratory

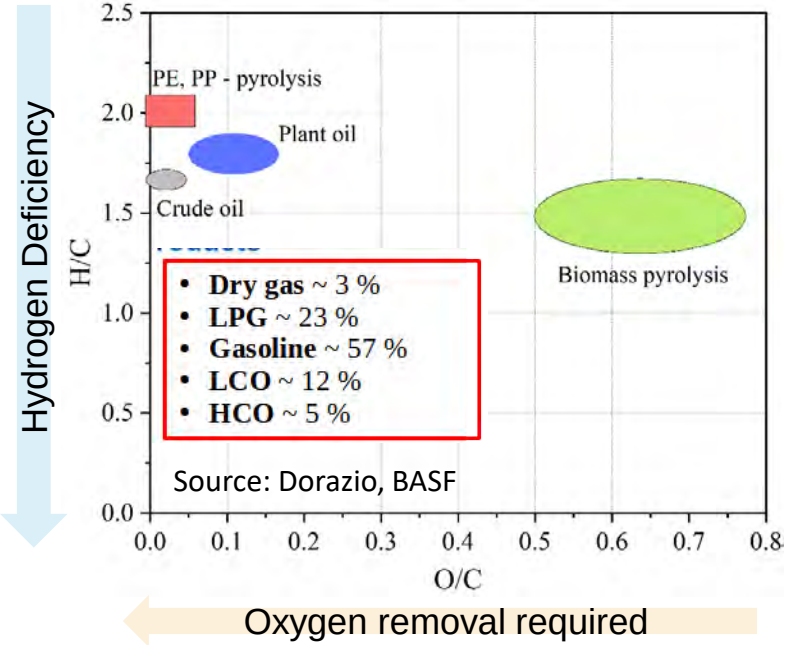
FCC catalysis for conversion of waste biomass & plastic

Biomass  or Plastic 

pyrolysis → 

Ballistic Heating @ ~500°C min^{-1}

$\xrightarrow{cat}$ C_2H_2, C_3H_6, C_4H_8



- FCC → production of transportation fuels and commodity chemicals
- FCC units process a variety of gasoil feedstock with varying contaminant levels
- Waste biomass & plastics can provide **renewable and recyclable pyoils** for upgrading

Bio-based pyrolysis oils present challenges:

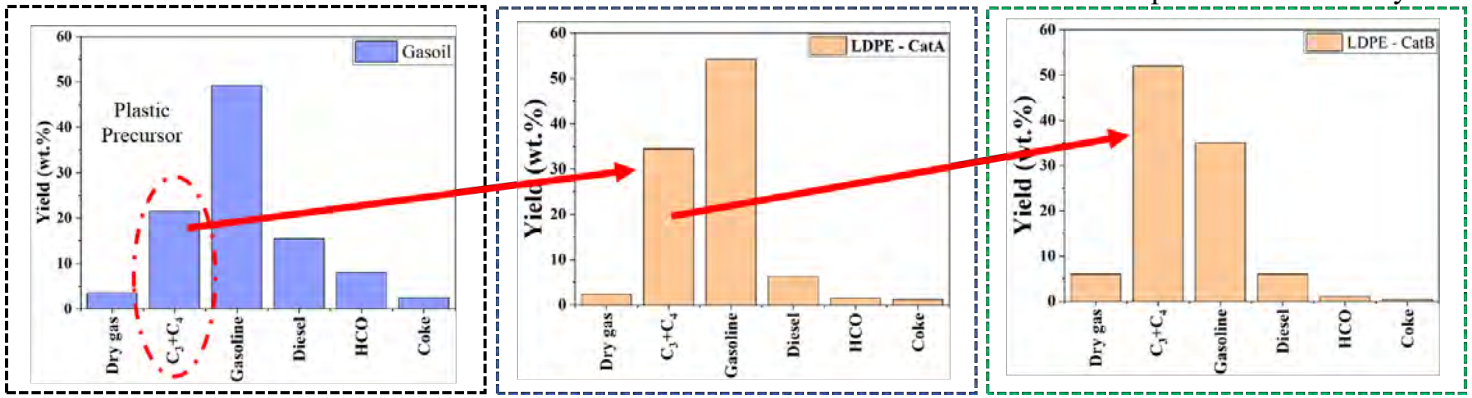
High oxygen content

Metals → catalyst fouling

Catalyst A yields for conventional gasoil

BASF catalyst designed for transportation fuel production – Catalyst A

BASF catalyst designed for C_3-C_4 chemicals production – Catalyst B



Catalyst design enables selective olefin production

Summary

- Fundamental understanding of combustion and catalysis processes enables technologies mitigating environmental burdens.
- Processes must be field tested or at relevant conditions
  - RCL → H-frame GT conditions
  - LFGTE → relevant scale engine matching BSE
- Requires coupling Reaction kinetics, heat and mass transfer
  - Selectivity, H_2 production (E.A.R.) & upgrading via FCC

Acknowledgements



Combustion & Catalysis Laboratory

ASME EESWM for Opportunity
Past & present CCL students & Post-docs
Collaborators & sponsors

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