Hydrogen from Renewable Fuels by Autothermal Reforming: Alcohols, Carbohydrates, and Biodiesel

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Producing Hydrogen

Steam reforming

$\text{Fuel} + H_2O \rightarrow H_2 + CO$

Water Gas Shift

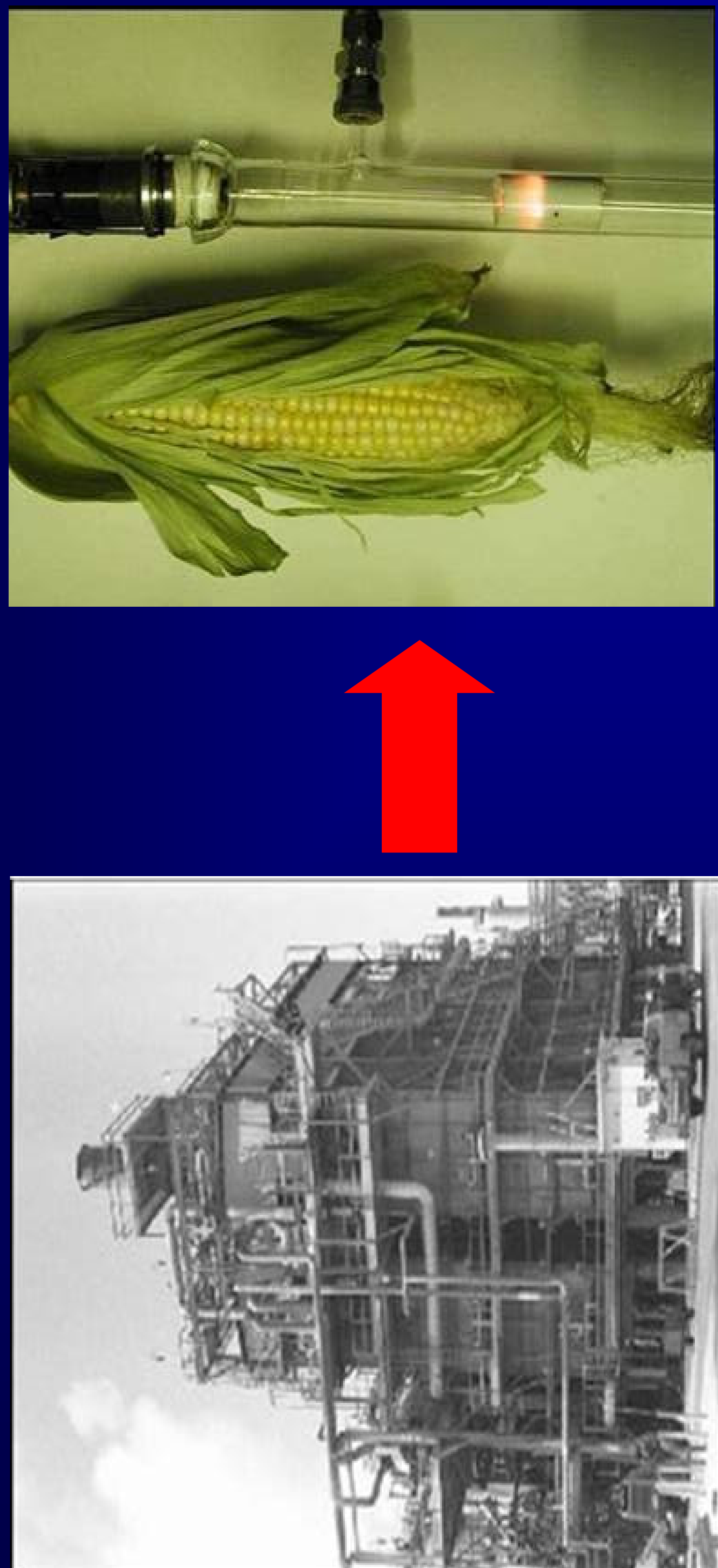
$CO + H_2O \rightarrow CO_2 + H_2$

95% of H_2 is made by this process
Endothermic process
Requires tube furnace
Does not scale down

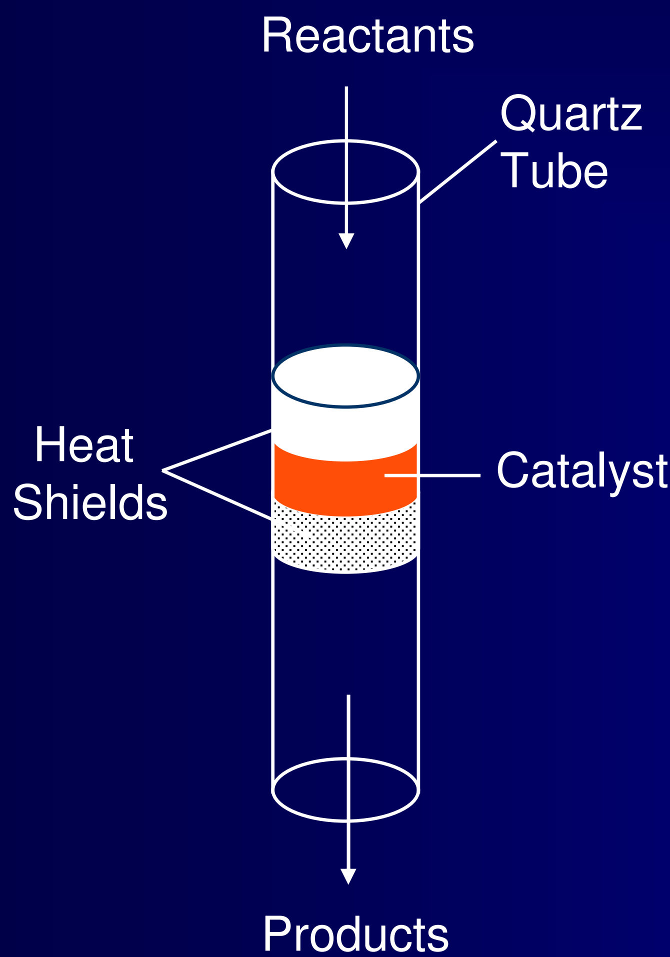
Catalytic Partial Oxidation

$\text{Fuel} + O_2 \rightarrow H_2 + CO$

Need H_2 for large and small applications
Gas to liquids refineries
Fueling station
Portable power



Catalytic Partial Oxidation



- Converts hydrocarbons into valuable chemicals: syngas (H_2 & CO), olefins, oxygenates, etc.
- Exothermic process
- Runs autothermally
- Short contact times (Milliseconds)
- Vapor phase reactions

Hydrogen and Chemicals in Millisecond Reactors

Hydrogen Economy

Distributed power

Fuel cells

Pollution abatement

Renewable energy

Renewable chemicals

Reactions

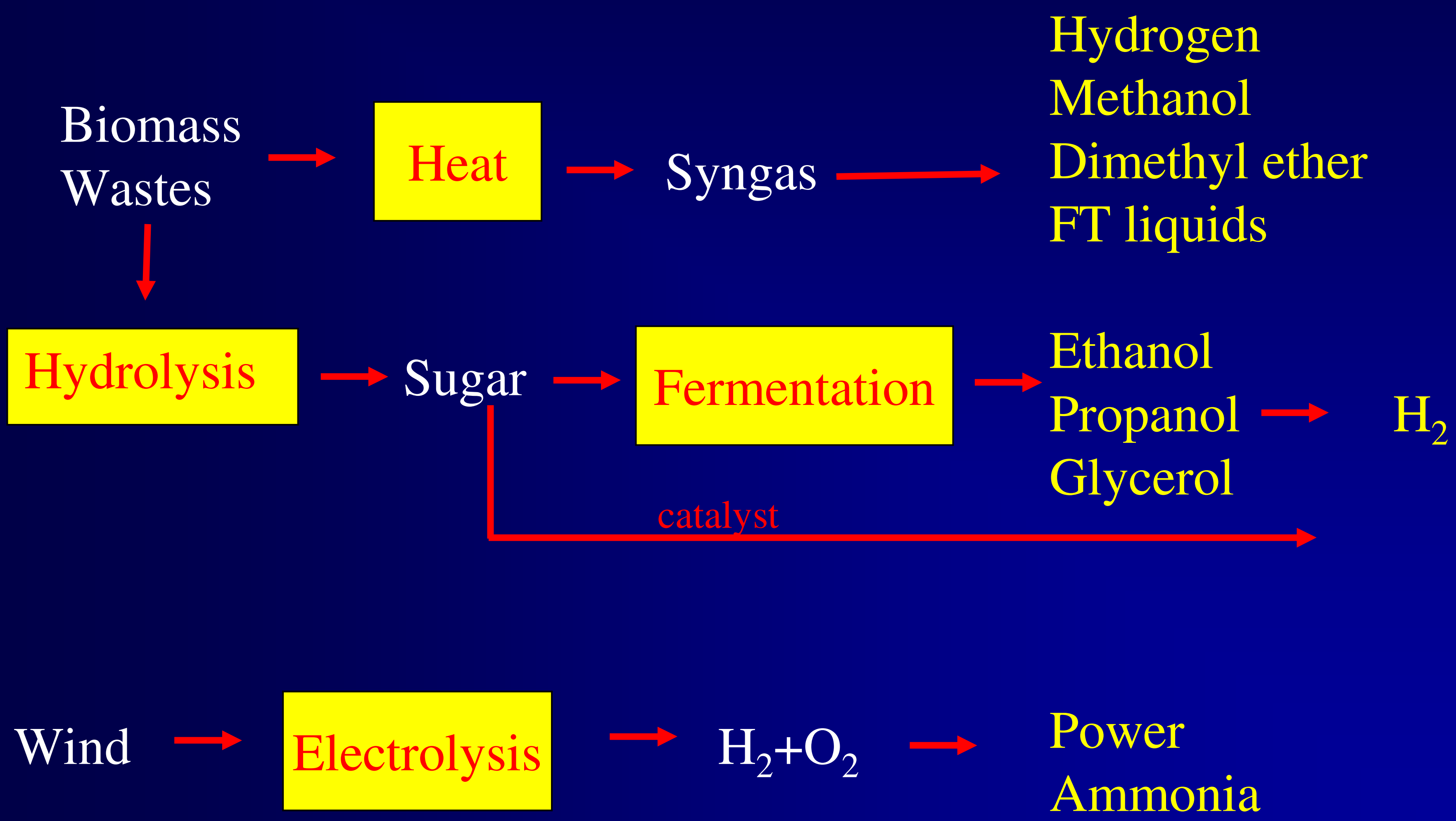
$CH_4 \rightarrow H_2 + CO \rightarrow$ synfuels
$\rightarrow$ methanol

$\rightarrow H_2$ hydrogen economy

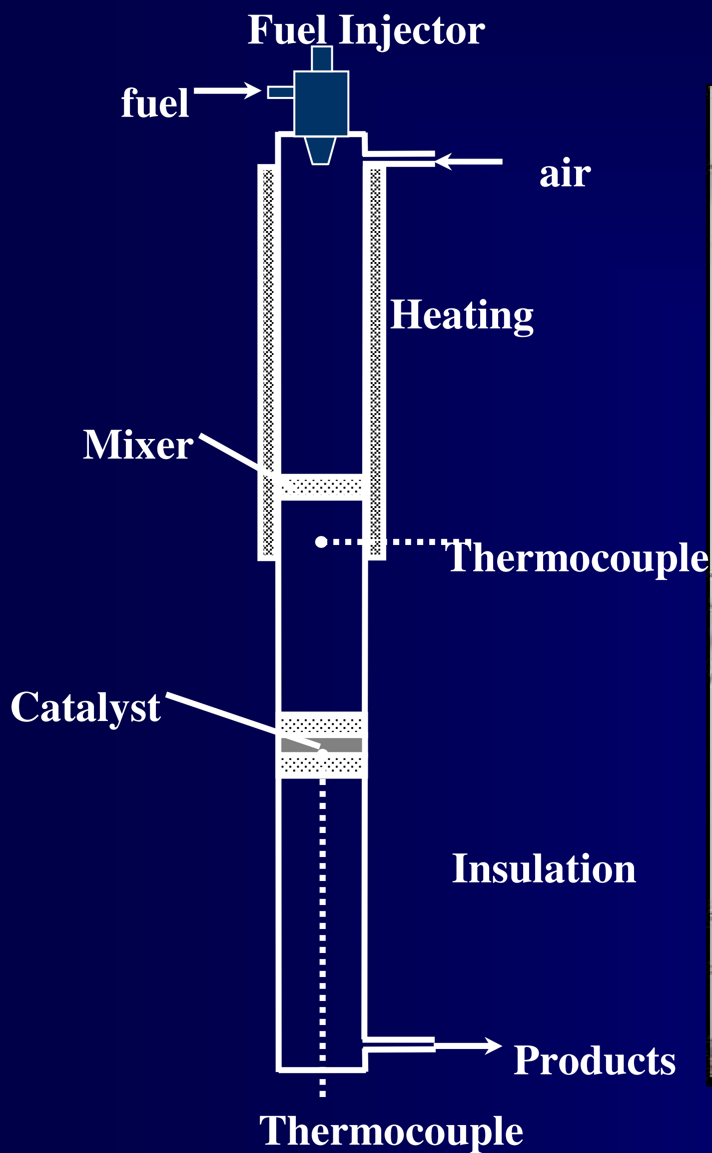
gasoline $\rightarrow H_2$ portable power
diesel $\rightarrow H_2$

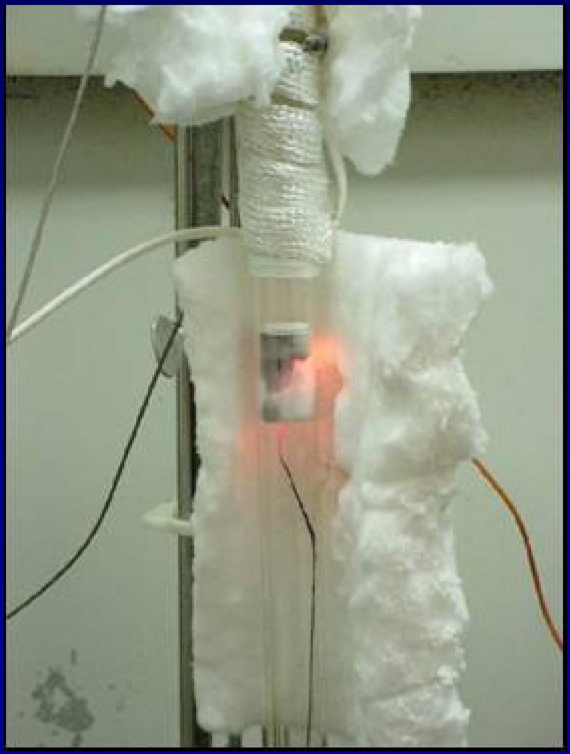
alcohols $\rightarrow H_2$ renewable energy
carbohydrates $\rightarrow H_2$
biodiesel $\rightarrow H_2$
olefins renewable chemicals

Renewable Hydrogen



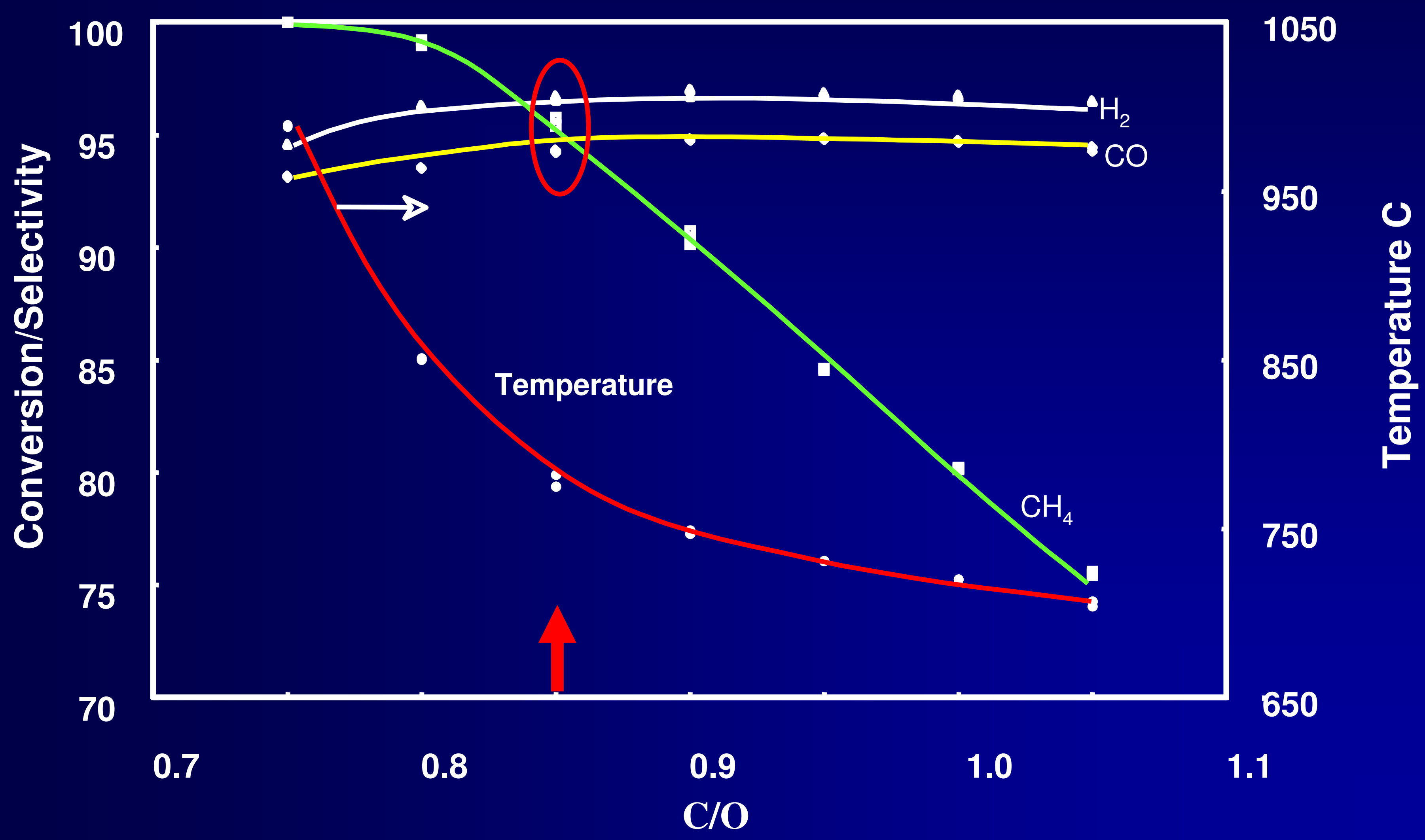
Reactor


Fuel Injector
fuel
air
Heating
Mixer
Thermocouple
Catalyst
Insulation
Products
Thermocouple



Methane to Syngas

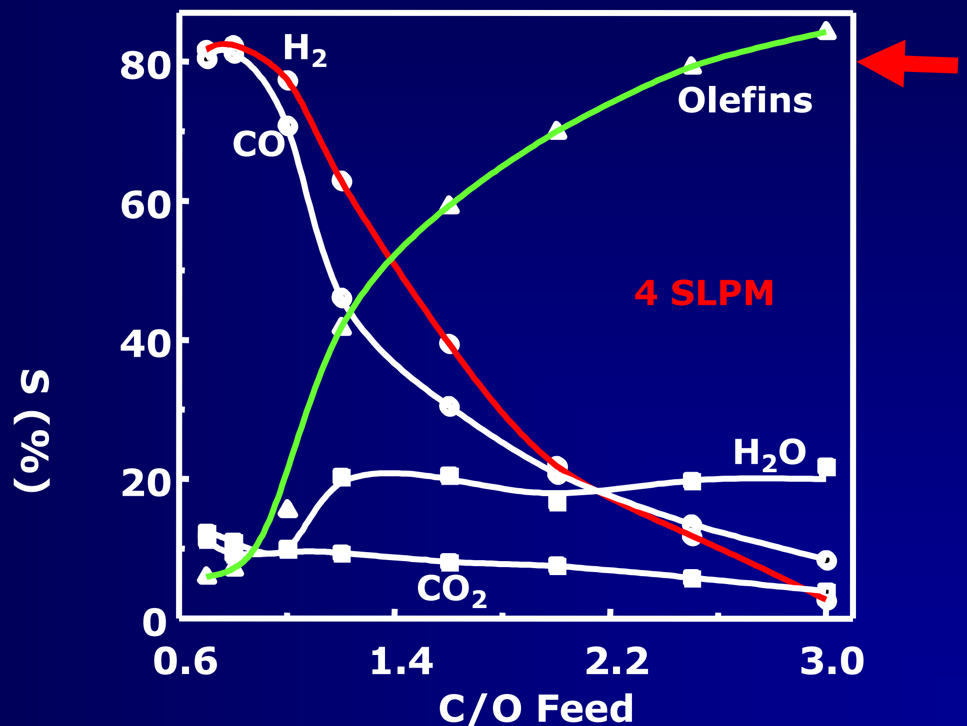
Rh Catalyst, 5 SLPM Total Flow, no preheat



Gasoline and Diesel to Syngas

- High boiling points, >300^{o}C
- Pyrolysis before vaporization
- Polycyclic aromatics
- Mixtures

Hexadecane Partial Oxidation

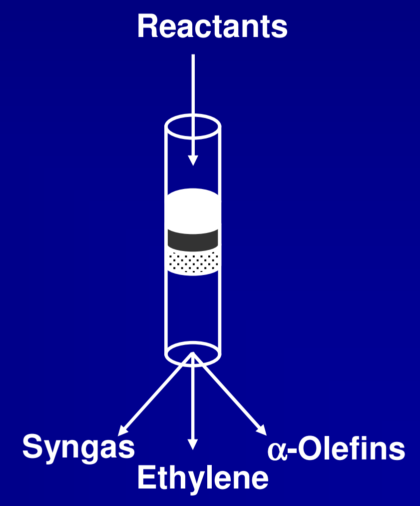


80 ppi α-Al_2O_3, ~3 wt% γ-Al_2O_3, ~3 wt% Rh

Reactor Tunability

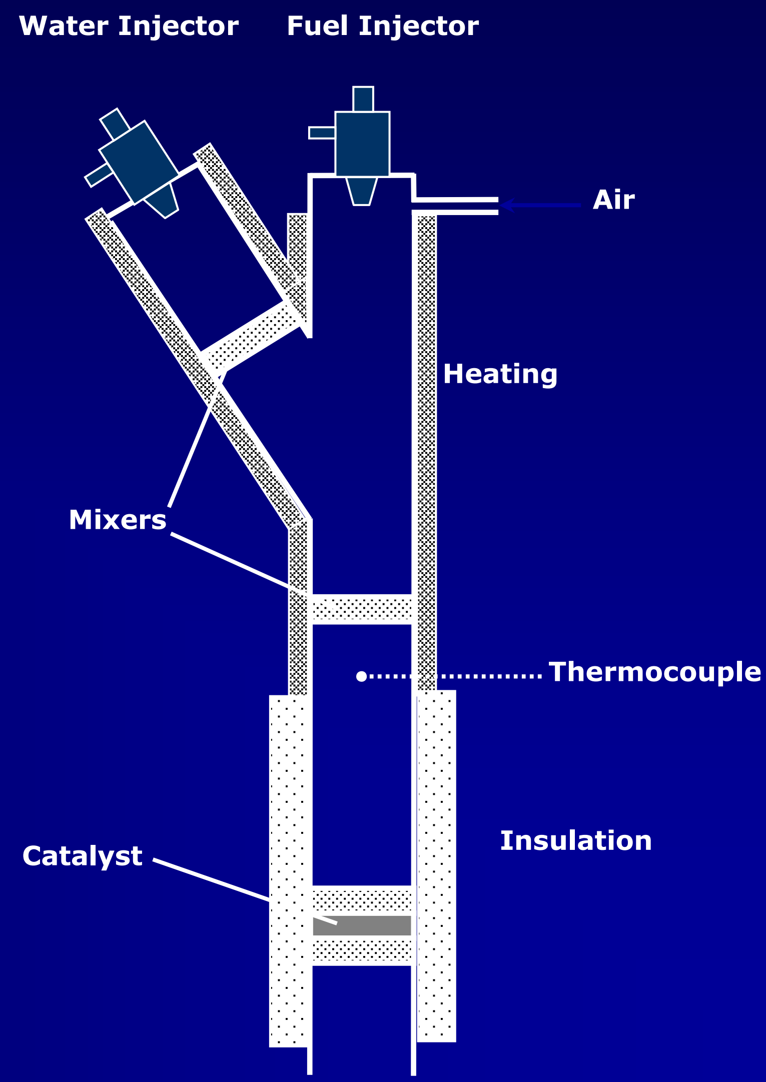
	Syngas	↔	Ethylene	↔	α-Olefins
C/O	~ 1		~ 1.3		~ 2.0
S(%)	~ 85		~ 36		~ 60

- 45 or 80 ppi α-Al_2O_3
- 0-3 wt% γ-Al_2O_3 wash-coat
- ~1-5 wt% Rh

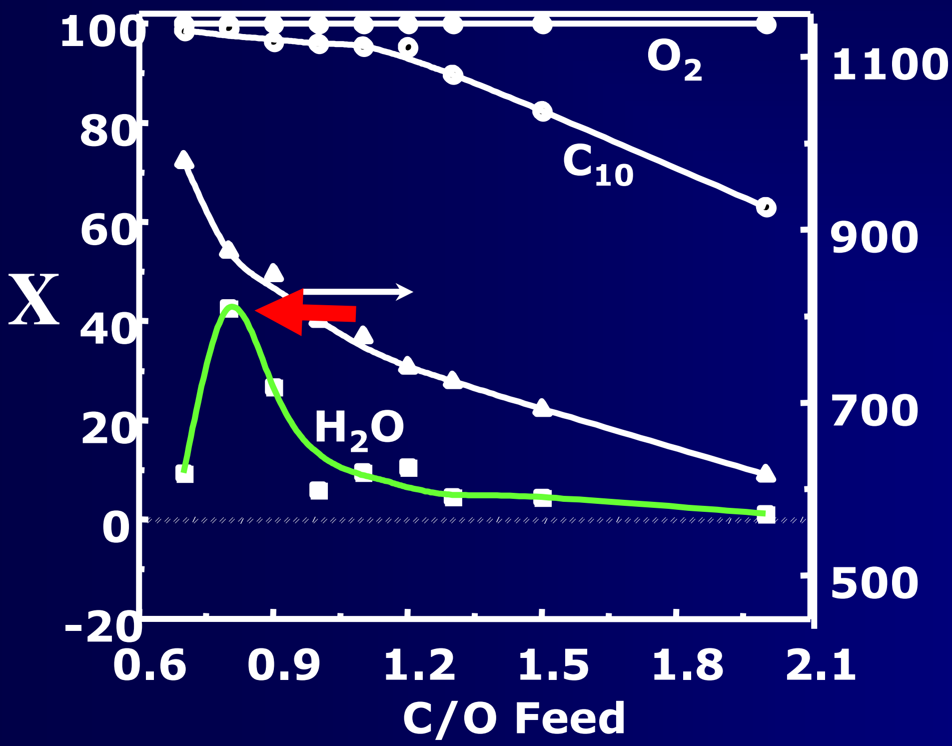


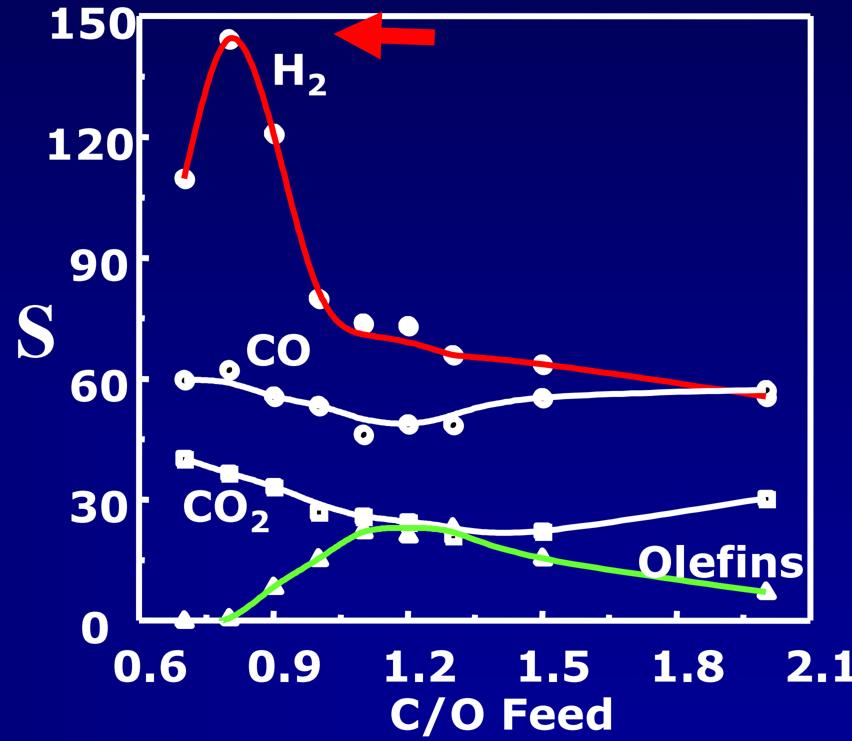
Steam Addition

- 80 ppi α-Al_2O_3 monolith
- ~4 wt% γ-Al_2O_3 wash-coat
- ~2 wt% Rh
- 4 SLPM
- Steam to Carbon ratio of 1



Steam Addition





80 ppi α-Al_2O_3, ~4 wt% γ-Al_2O_3, ~2 wt% Rh, 4 SLPM, S/C = 1

Catalysis

Surface area not important

- all ~2 m^2/g
- γ-Al_2O_3 converted to a after heating to 1000^oC
- metals form films 1 μm thick

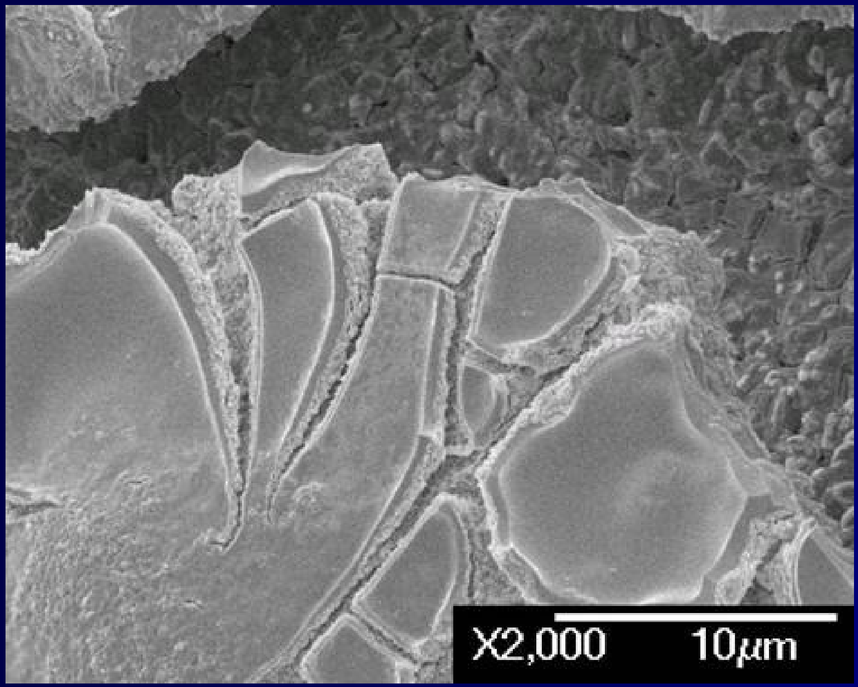
All conversions 100%

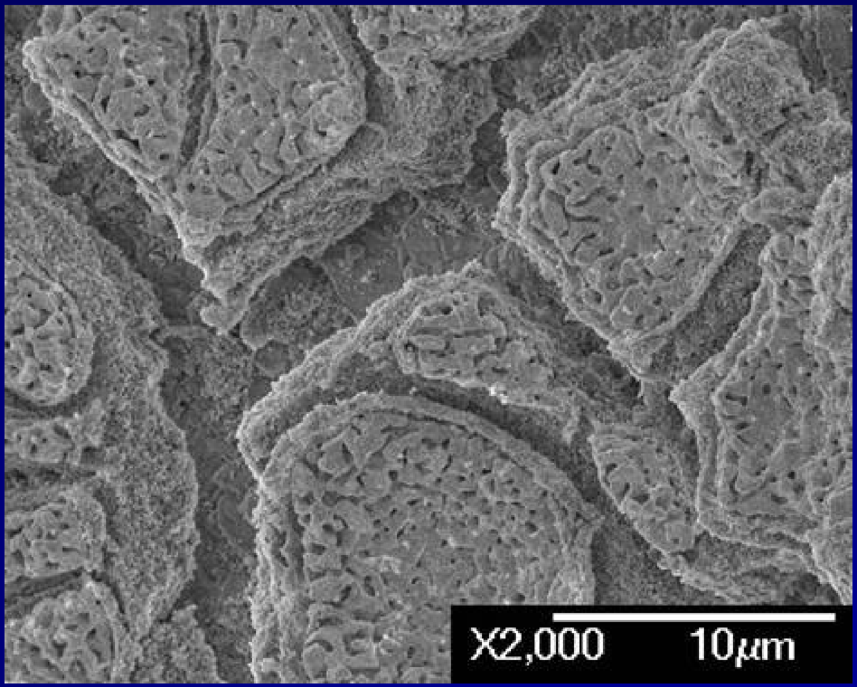
- mostly complete in first mm

Selectivities dominate

- wash coat and small channels makes hydrogen
- no wash coat and large channels makes olefins

10% Rhodium Before and After Use





Spatial and Transient Analysis

80 ppi

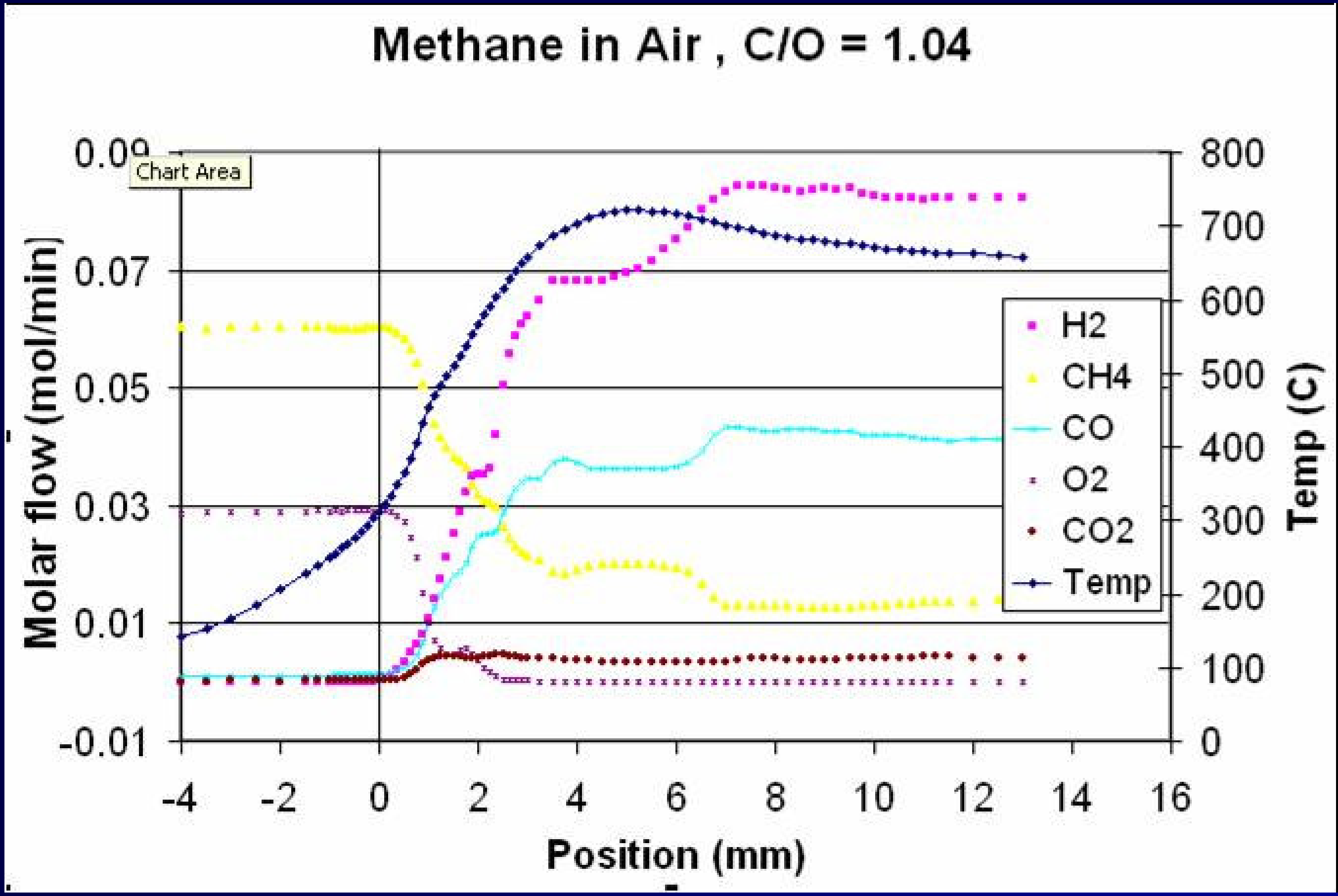
45 ppi

microcapillary

- Side hole sampling
- No void behind the capillary
- Minimal disruptions to the flow field
- Capillary can move in and out
- Spatial temporal profiles

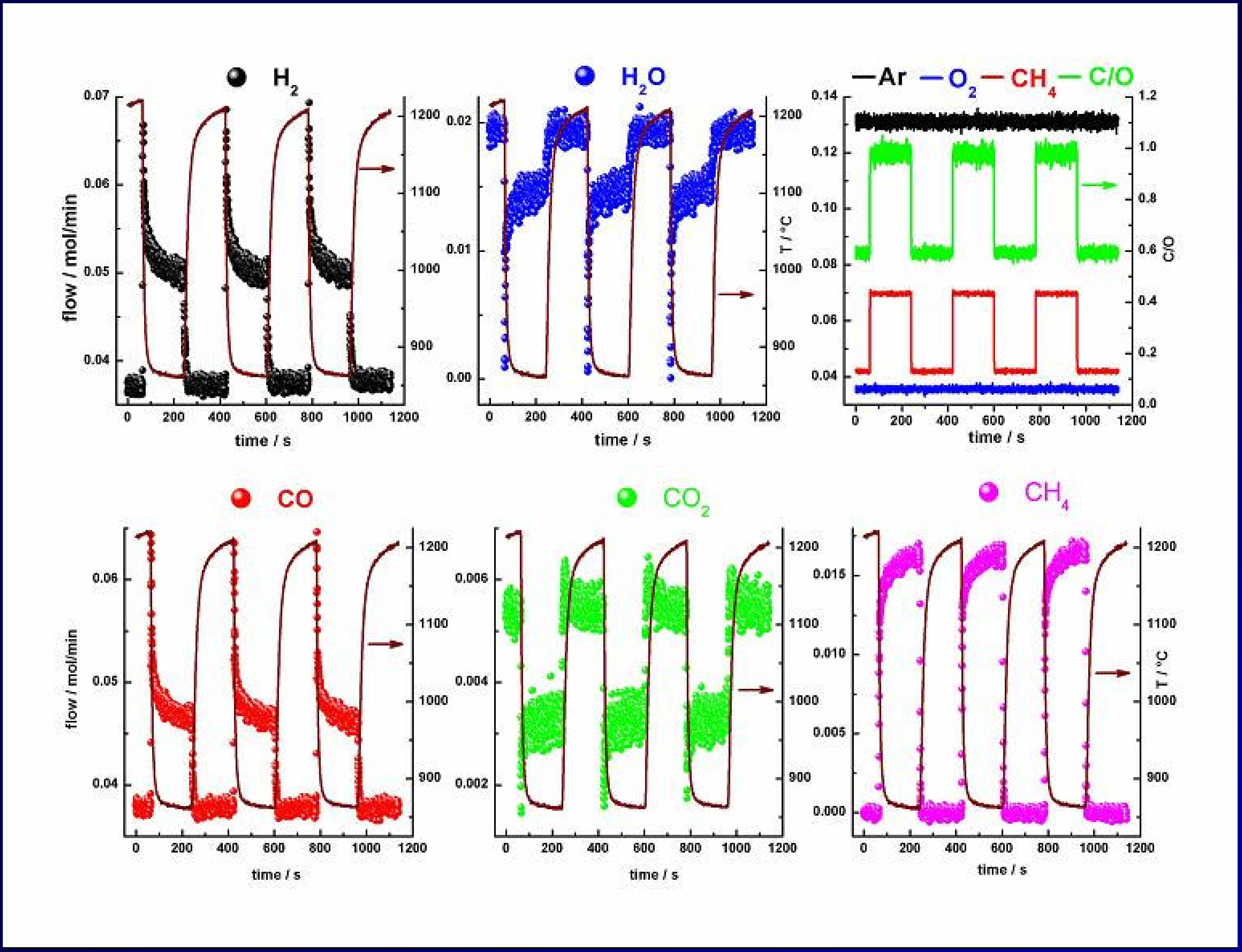
.05 sec, 0.3 mm resolution

Spatial Analysis:
Experimental Results

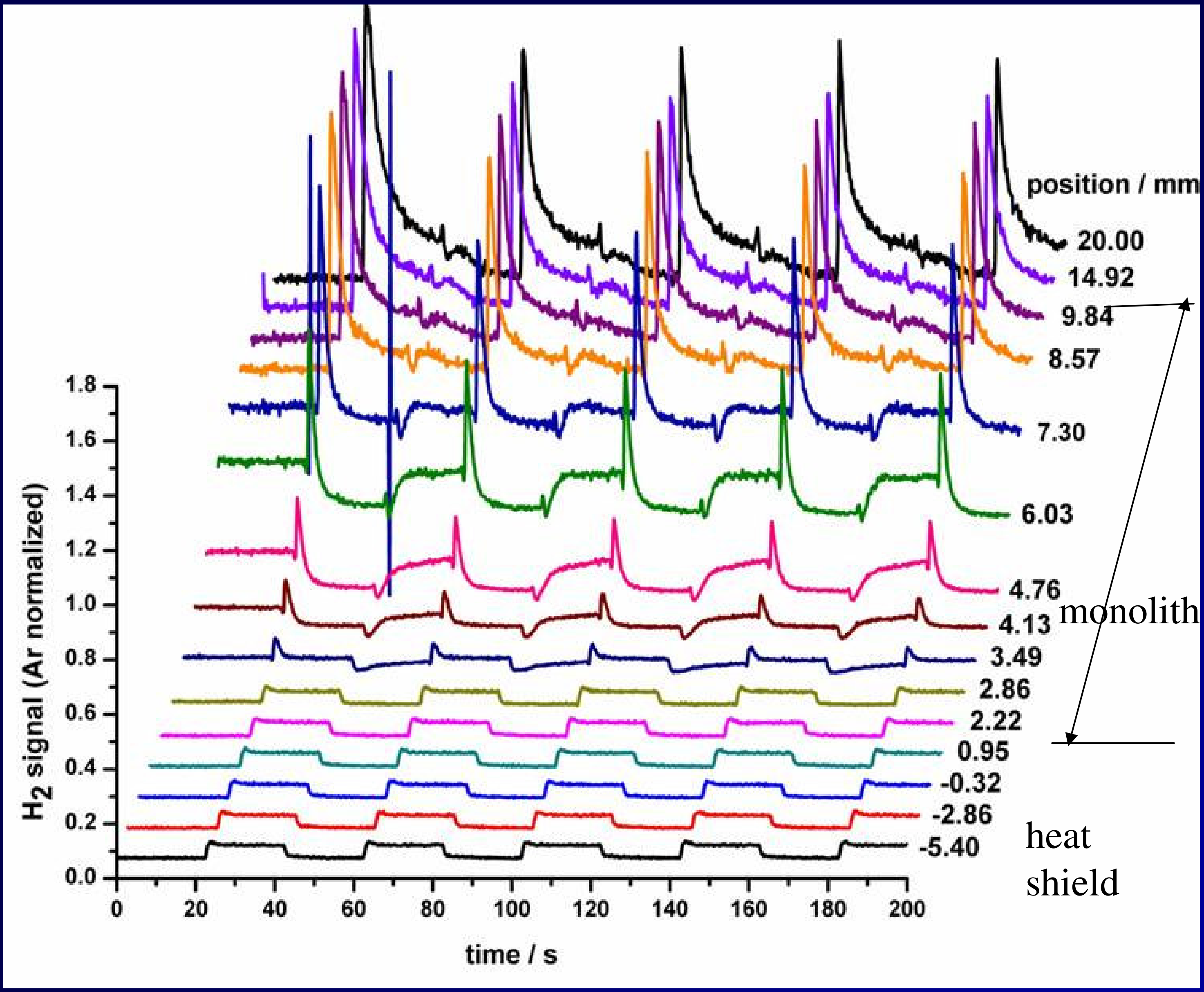


- Catalyst:
  - Rhodium
  - Washcoat
  - 80 ppi
- Methanation observed in simulations
- Repeatable

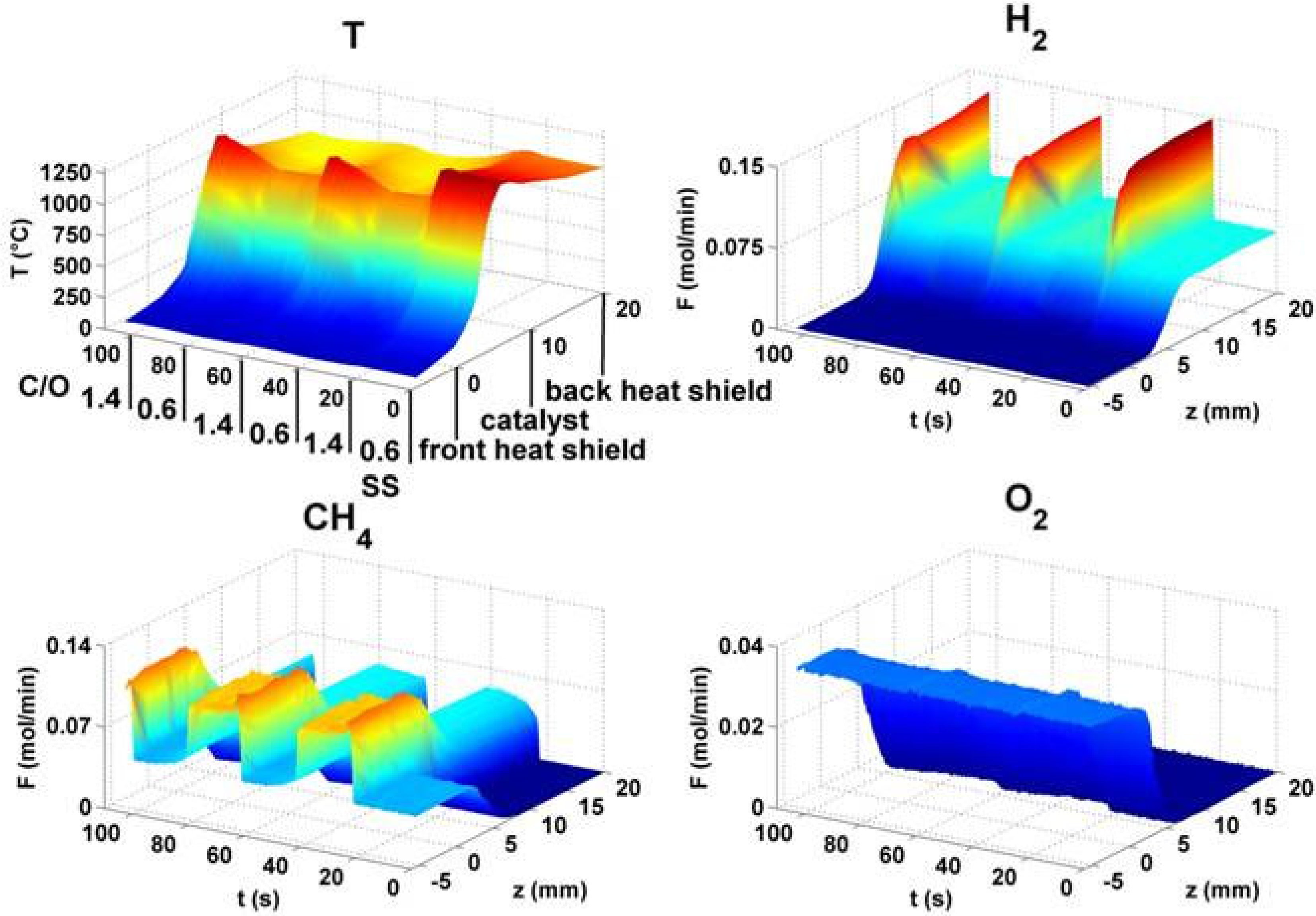
Transient Switch C/O



Spatial-temporal profiles



Spatial-temporal profiles



Hydrogen and Chemicals from Biomass

biodiesel

alcohols

glycols

glycerol

sugar

carbohydrates

trees

Renewable Chemicals From Biodiesel

Soy oil + $CH_3OH \rightarrow$ biodiesel + glycerol

methyl linoleate 52%

isomers with 1, 2, and 3 double bonds

2% in Minnesota diesel pool in 2005

Renewable Chemicals

biodiesel → H_2		80%
→	olefins	90%
→	ethylene, propylene	50%

2-Propanol

- $CH_3CHOHCH_3$
- Autoignition : 399°C
- Boiling Point : 82°C
- Flammability Limits : 2.0-12.0% in air

1-Propanol

- $CH_3CH_2CH_2OH$
- Autoignition : 371°C
- Boiling Point : 97°C
- Flammability Limits: 2.1-13.5% in air

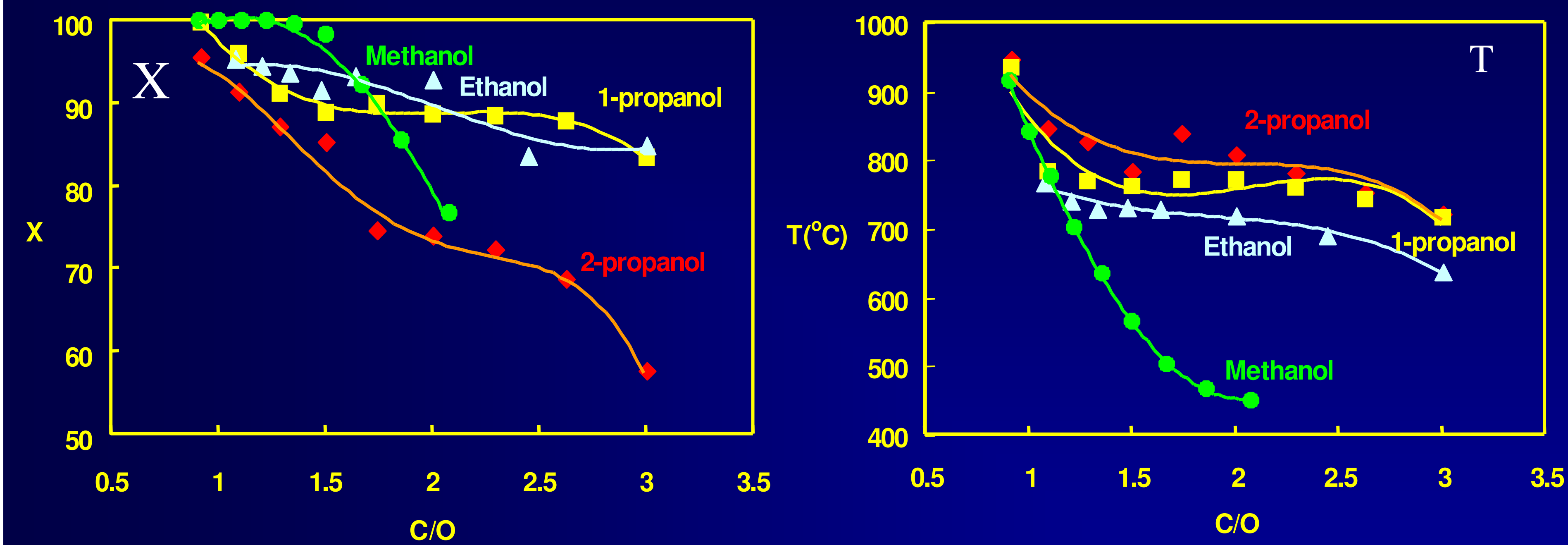
Ethanol

- CH_3CH_2OH
- Autoignition : 363°C
- Boiling Point : 78°C
- Flammability Limits: 3.3-24.5% in air

Methanol

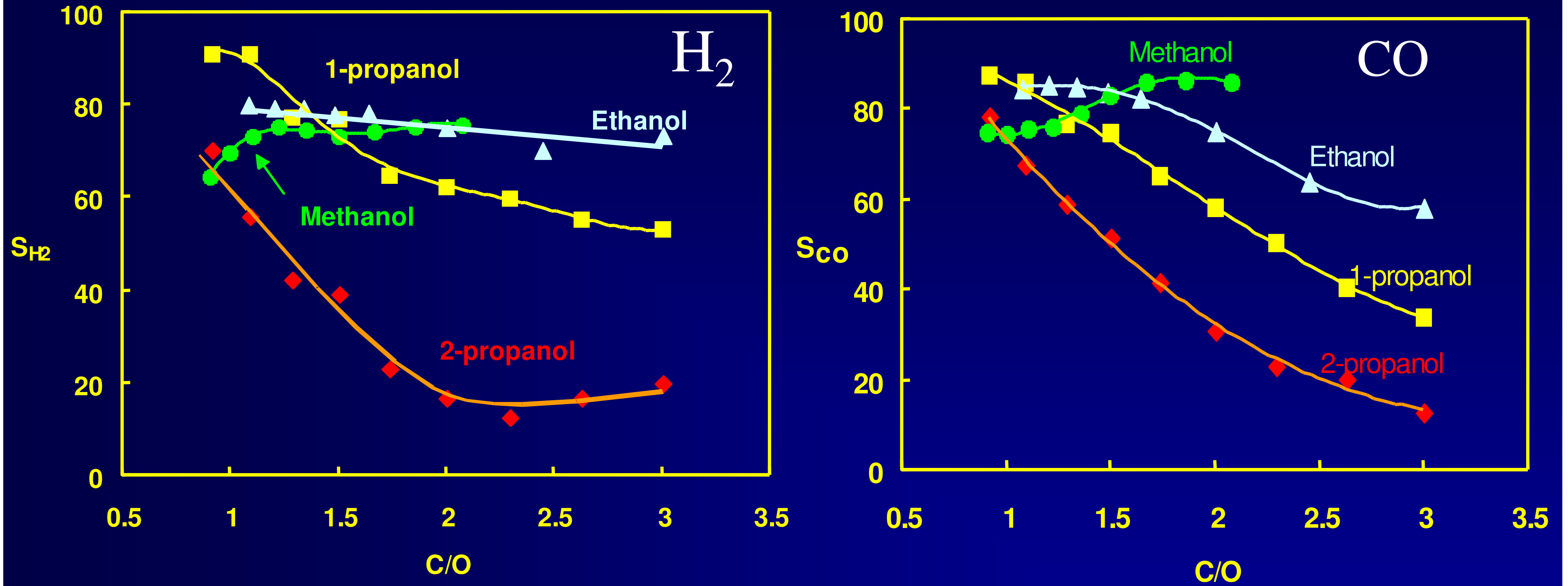
- CH_3OH
- Autoignition : 464°C
- Boiling Point : 65°C
- Flammability Limits: 6.0-36.0% in air

Fuel Conversion and Temperature



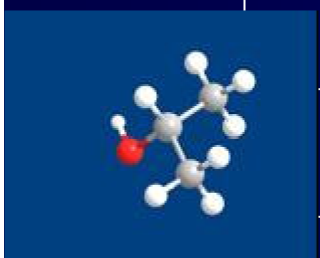
- 2-propanol is least reactive
- Temperature increases with increase in chain length

Syngas



- Syngas production increases with increase in chain length
- Straight chain alcohols produce more syngas than 2-propanol

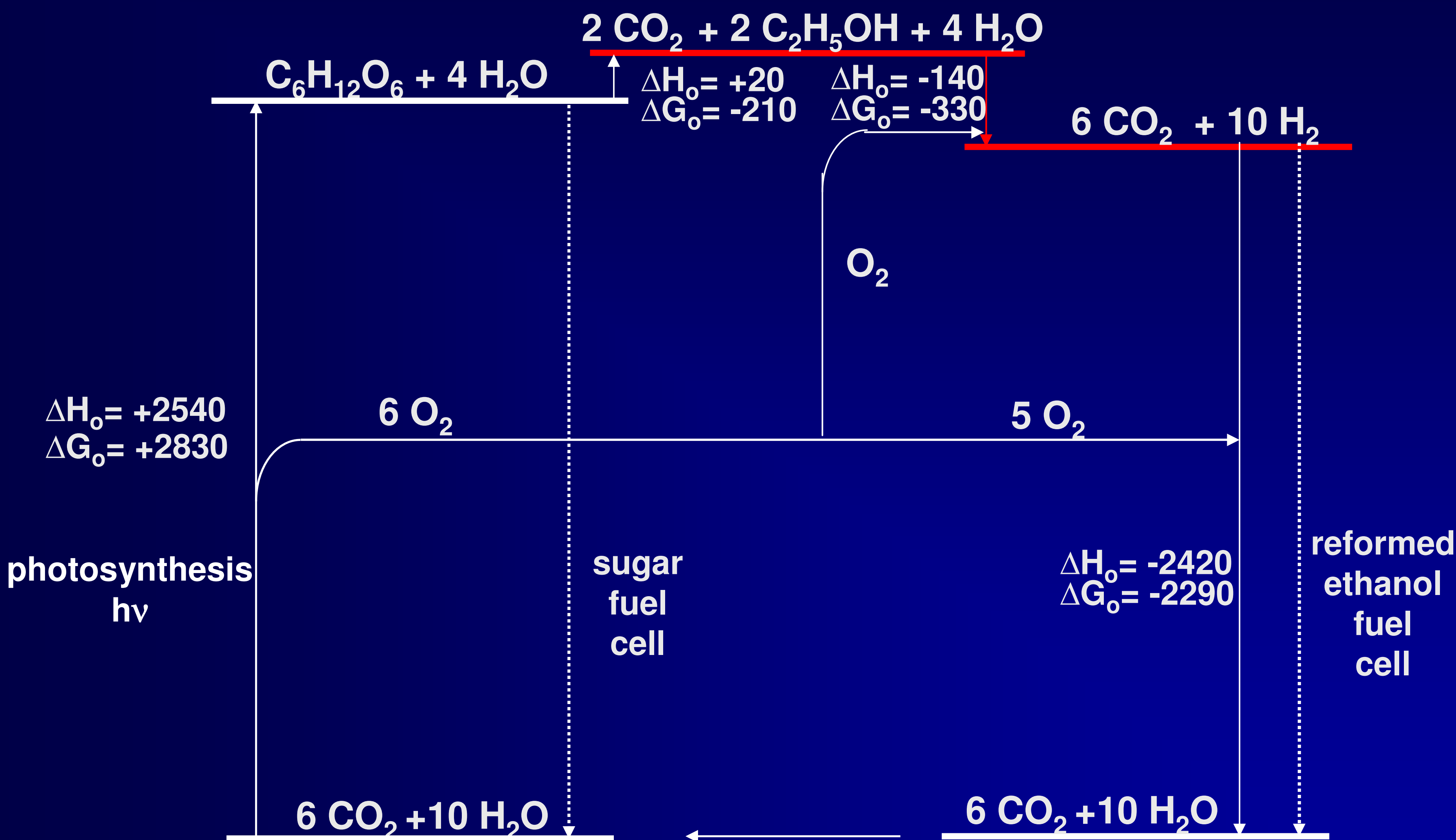
1-Propanol and 2-Propanol Products



		Products	2-Propanol	1-Propanol
Partial Oxidation →	H_2 and CO	√	70%	90%
Combustion →	H_2O and CO_2	√	35%	25%
Dehydration →	C_3H_6	√	25%	5%
Dehydrogenation →	CH_3COCH_3	√	60%	25%***
Other Products →	C_2H_4	√	5%	25%

*** Propanal selectivity

Energy Diagram for Ethanol

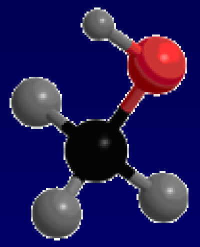


Carbohydrates

Methanol

Boiling Point = 65 °C

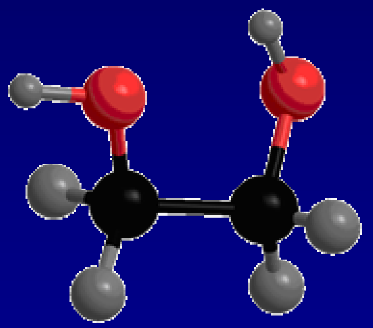
$H\text{-}(CH_2O)\text{-}H$



Ethylene Glycol

Boiling Point = 195 °C

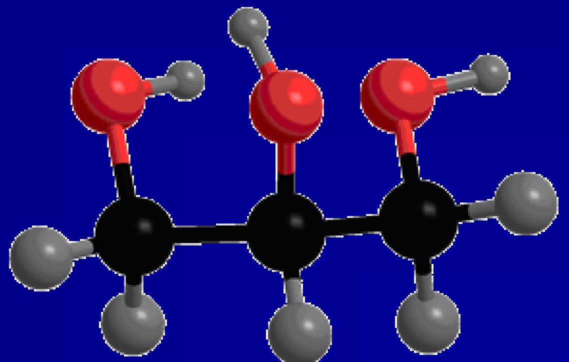
$H\text{-}(CH_2O)_2\text{-}H$



Glycerol

Boiling Point = 290 °C

$H\text{-}(CH_2O)_3\text{-}H$



Mechanism

Surface

$ROH \rightarrow RO(s) \rightarrow H_2 + CO$

surface alkoxy makes syngas

only C_1 species

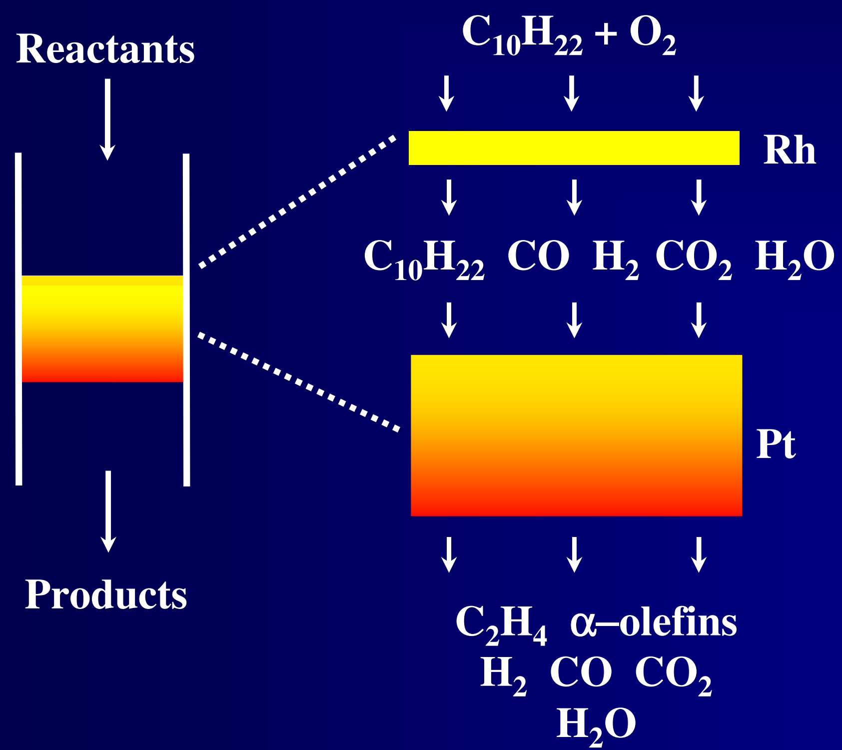
Homogeneous

$$H_3C - \overset{H}{\underset{OH}{C}} - CH_3 \rightarrow H_3C - \overset{\cdot}{\underset{OH}{C}} - CH_3 \rightarrow H_3C - \underset{O}{\underset{\|}{C}} - CH_3$$

chemistry very selective

no secondary products

Mechanism



Oxidation zone

surface chemistry

hotter

no carbon

makes mostly C_1 products

Reforming zone

no oxygen

homogeneous chemistry

contains carbon

makes olefins

Why Does it Work?

- High flow velocities
- High T
- High T gradients

- Fastest reactions dominate
- Inhibit homogeneous reactions
- Successive reactions inhibited
- Inhibits carbon buildup

Challenges

mixtures
sulfur
modeling

Summary

Higher alkanes can be converted to H_2 and olefins

- >80% H_2
- >140% H_2 with steam added
- 80% olefins
- 50% ethylene and propylene

Alcohols and carbohydrates can be converted to H_2

- steam reforming and partial oxidation
- 4 H_2 per C_2H_5OH

Biodiesel can be converted to olefins and olefinic esters

- 80% H_2
- 40% ethylene and propylene
- ester linkage preserved
- >20% olefinic esters