Modern catalytic technologies for converting biomass to fuels

CATALYSIS CENTER FOR ENERGY INNOVATION

An Energy Frontier Research Center

supported by the

U.S. Department of Energy,

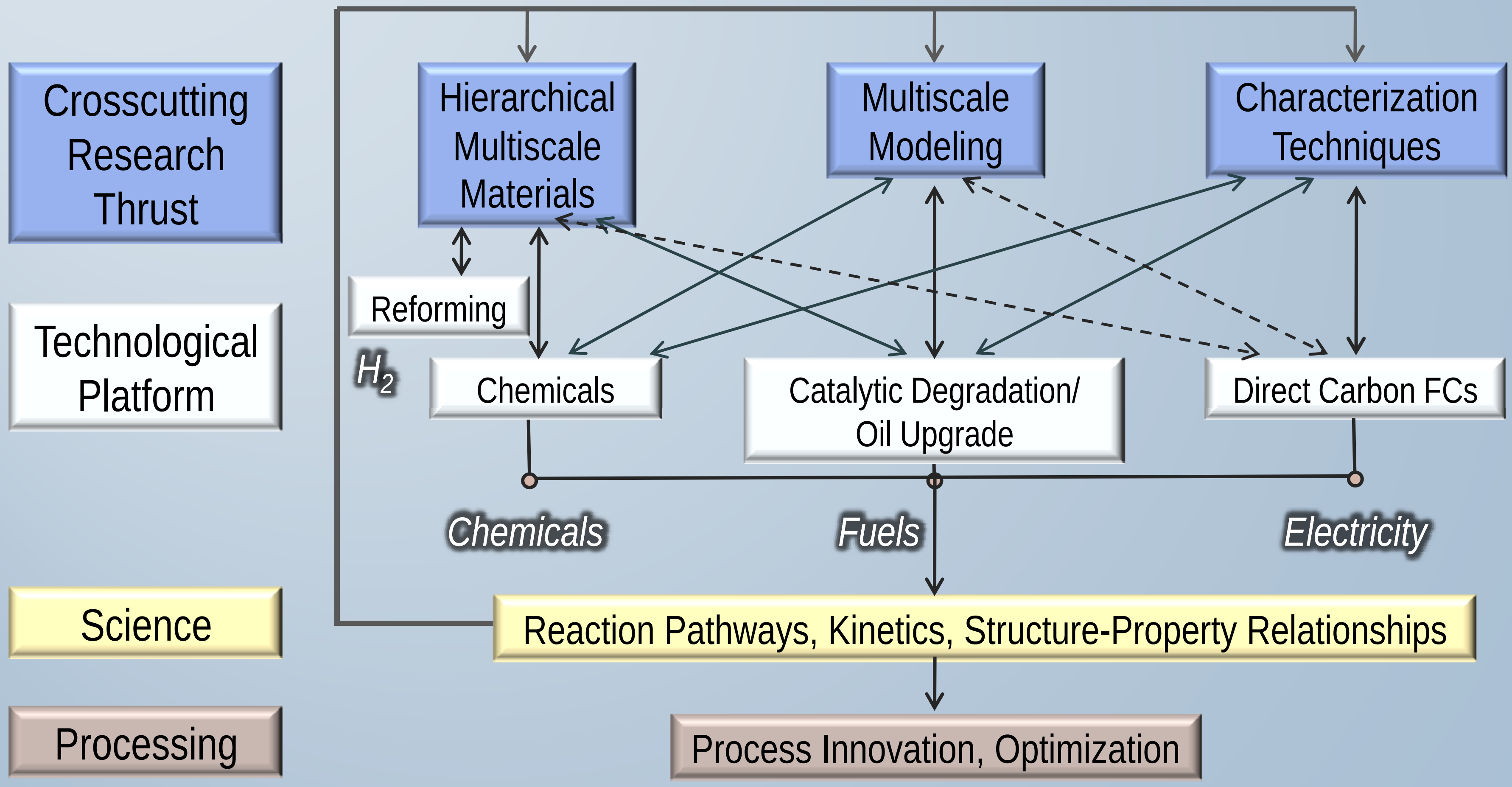
Office of Basic Energy Sciences

Presented by Dion Vlachos, Director

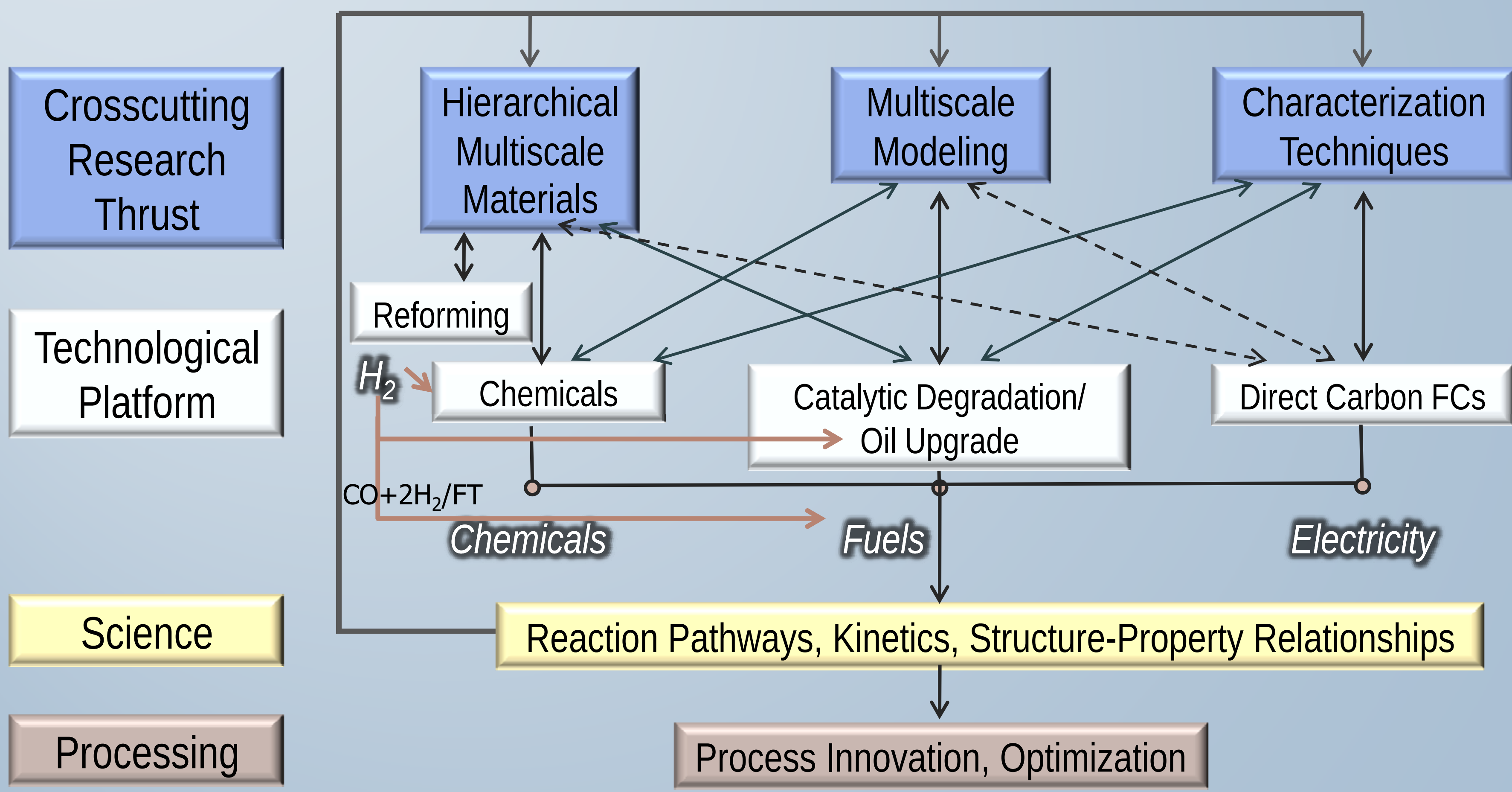
Objectives and Approach

- **Objectives**
  - Develop the enabling science leading to improved or radically new (heterogeneous) catalytic technologies for viable and economic operation of biorefineries from various (lignocellulosic) biomass feed stocks
  - Develop technology and enable technology transfer
  - Educate the workforce needed to further develop and implement these new technologies, which in turn will lead to further sustainable economic growth and reduced energy dependence of the U.S.
- **Approach**
  - Develop paradigms for major technologies of biorefineries by picking prototype platforms

Research Thrusts

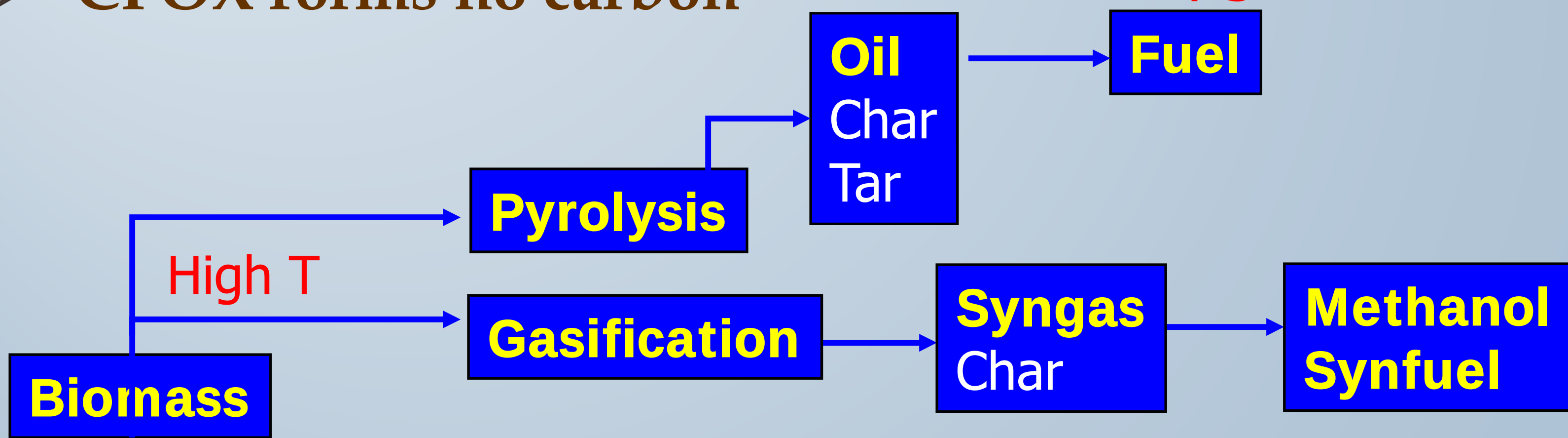


Research Thrusts



Thermochemical transformation of lignocellulosic biomass

- Traditional paths entail high temperatures and suffer from carbon
- **CPOX forms no carbon**



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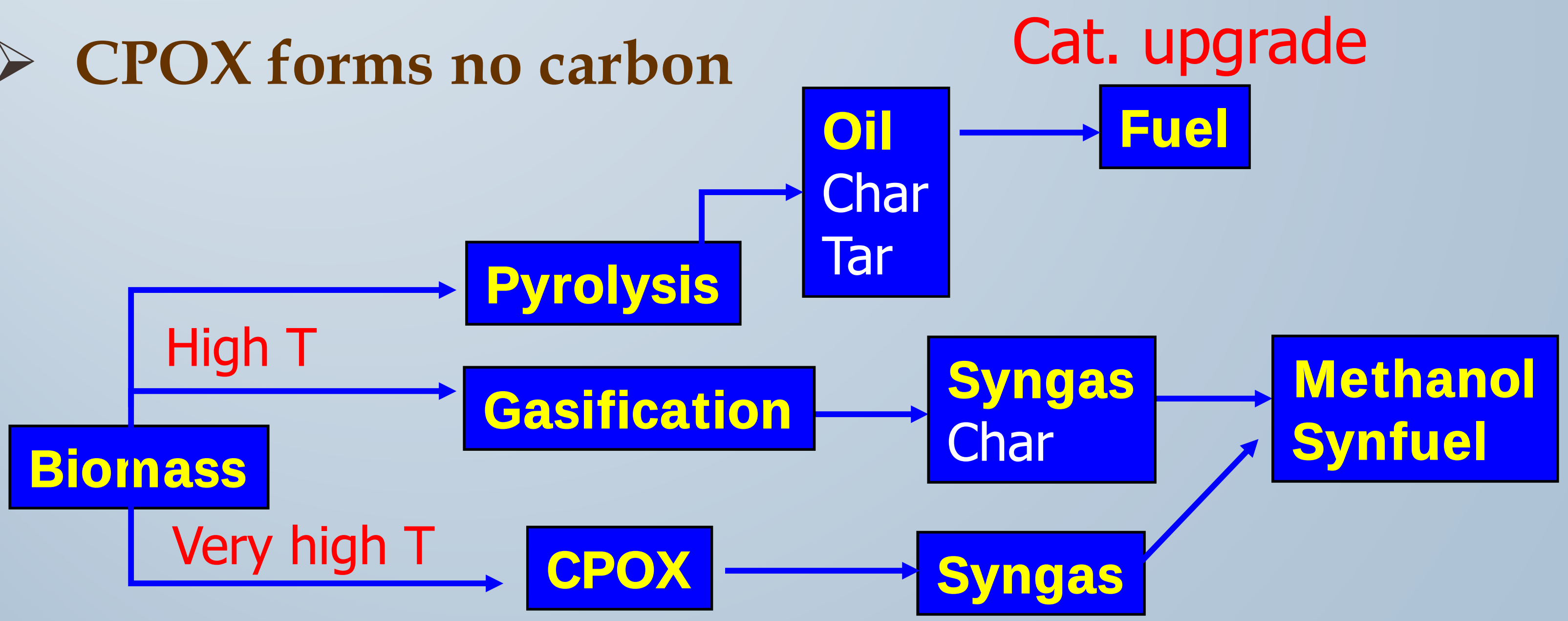
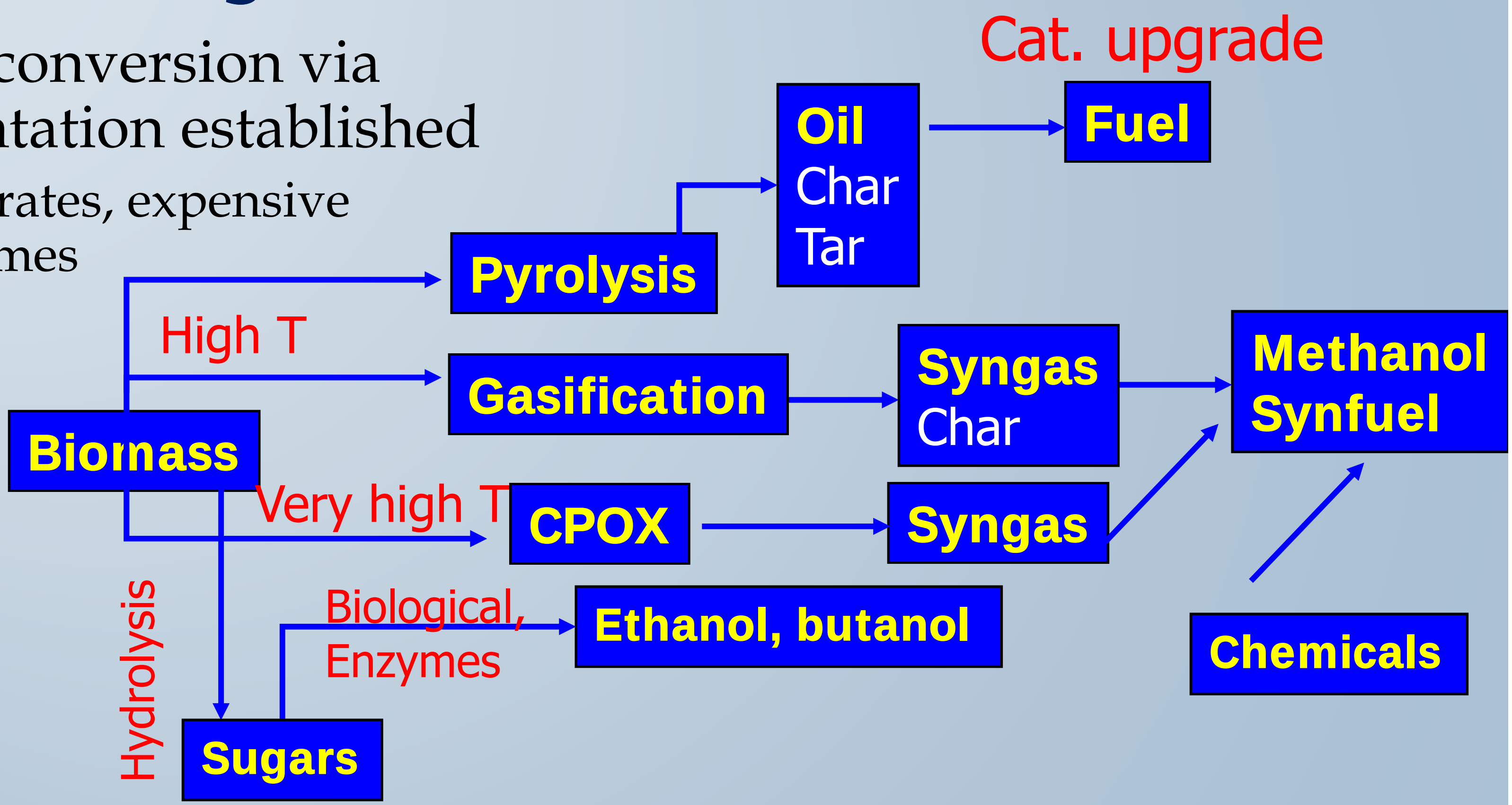


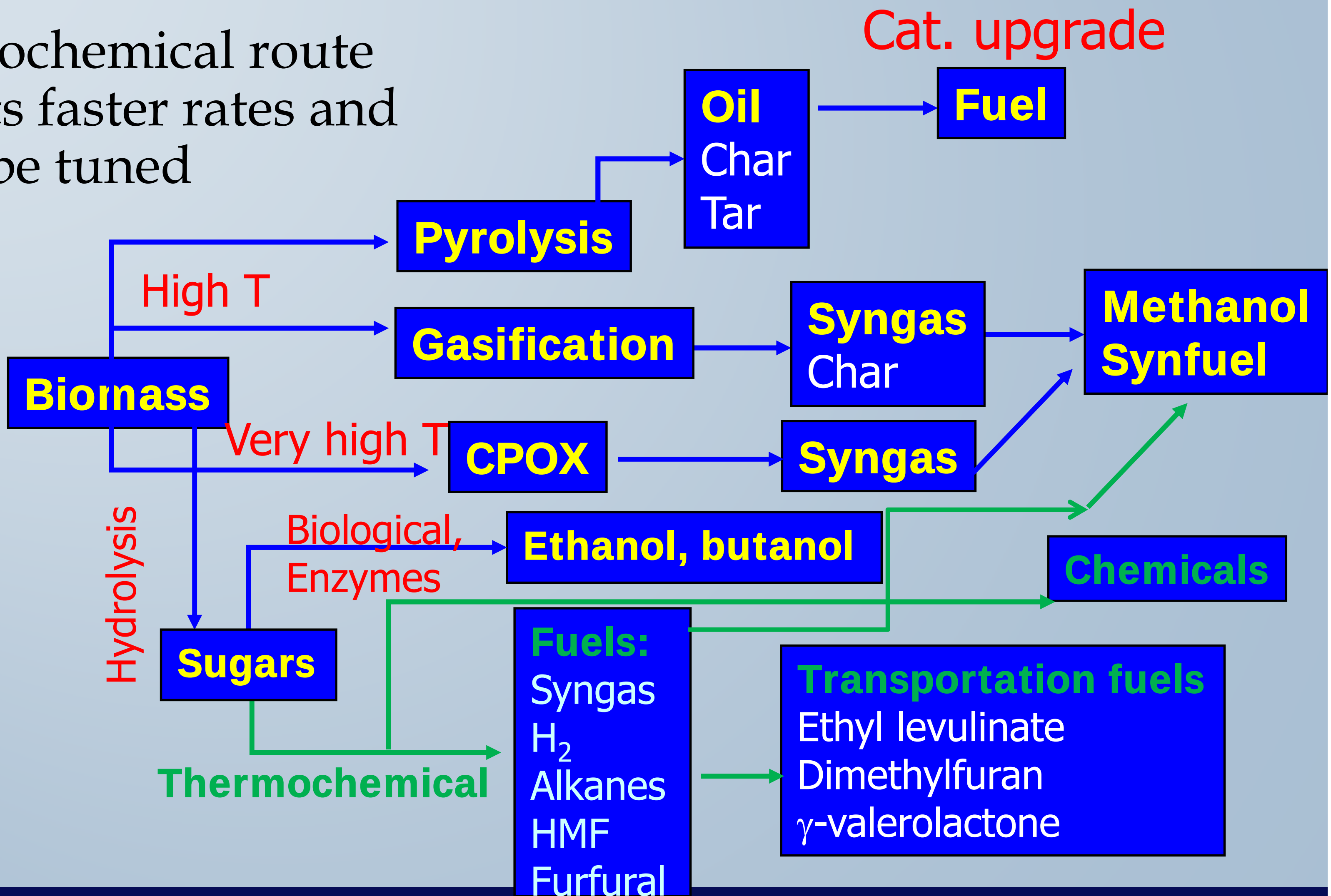
Thermochemical transformation of lignocellulosic biomass

- Sugar conversion via fermentation established
  - Low rates, expensive enzymes



Thermochemical transformation of lignocellulosic biomass

- Thermochemical route exhibits faster rates and could be tuned

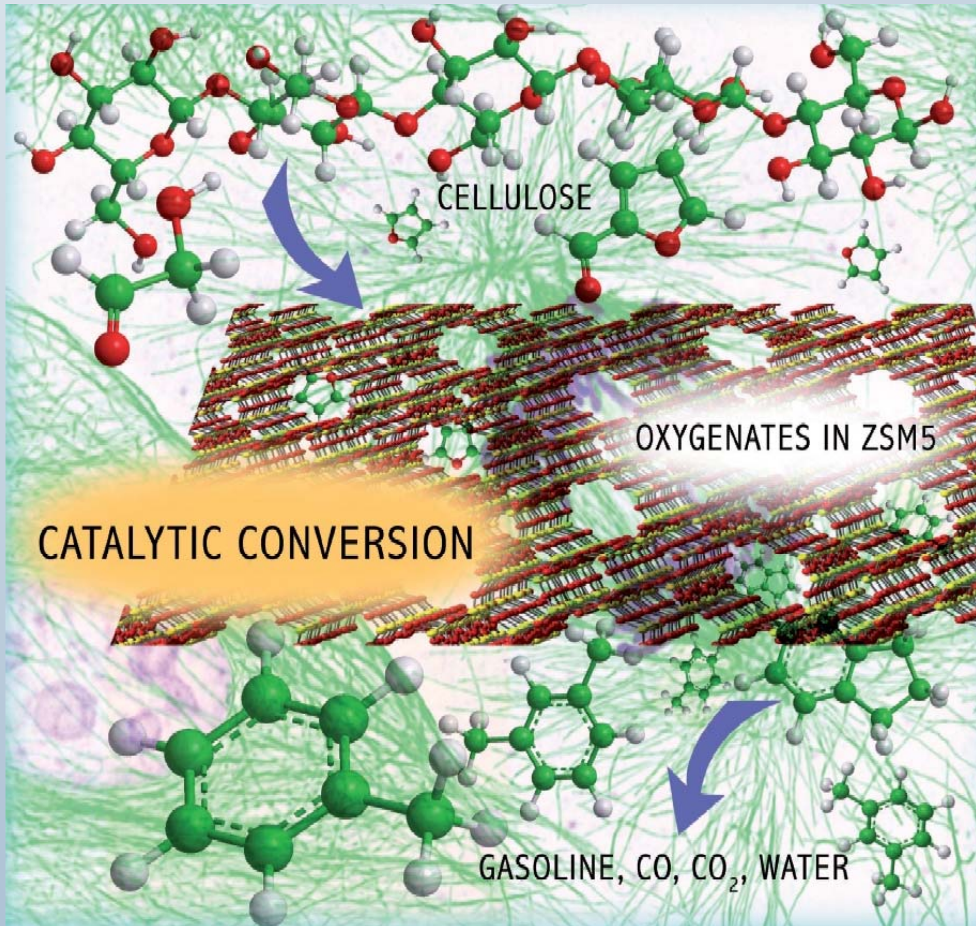


Catalytic Fast Pyrolysis/Bio-Oil Upgrade

Overarching Goal: Develop the science-based to enable the conversion of cellulose to fuels

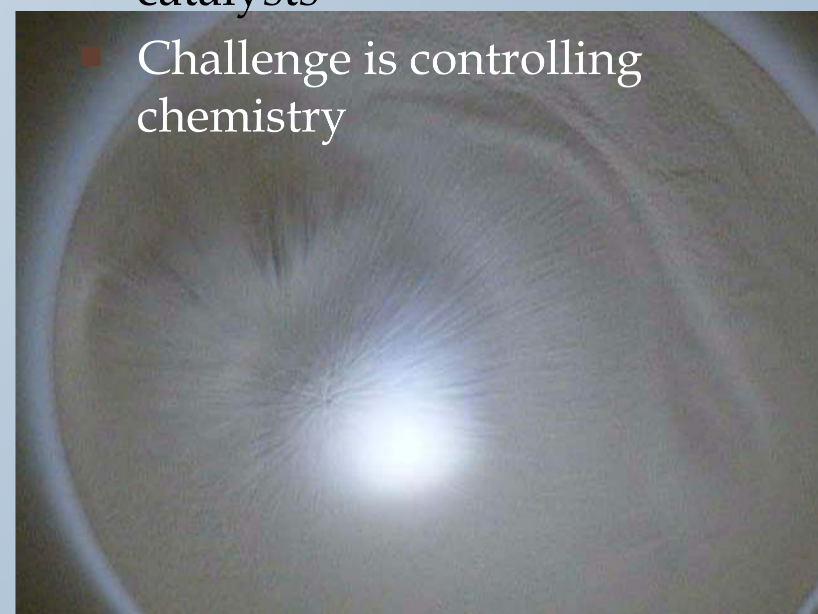
- Develop an understanding of the catalytic fast pyrolysis
- Develop and characterize suitable catalysts
- Develop models for diffusion and reaction inside and outside microporous materials
- Perform kinetic studies

Catalytic Fast Pyrolysis



Carlson et al., Green Gasoline by Catalytic Fast Pyrolysis of Solid Biomass-derived Compounds, ChemSusChem, **1**, 397-400 (2008)

- Solid biomass converted into aromatics in a single reactor at short residence times:
  - Liquid fuel that fits into existing infrastructure
  - Low cost, recyclable zeolite catalysts
  - Challenge is controlling chemistry



Catalytic Fast Pyrolysis: Overall yields

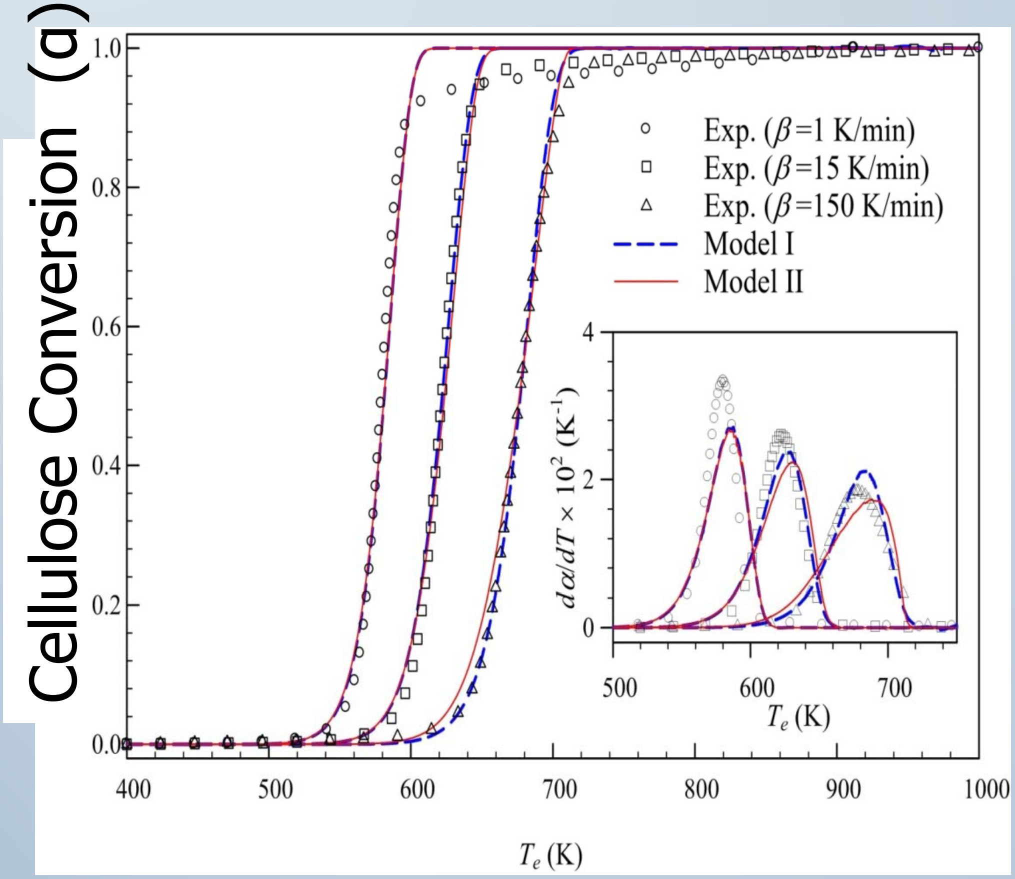
Reaction Conditions: Temperature 600°C; ZSM-5; Catalyst/Feed Ratio 19

Maximum Yield:

$C_6O_6H_{12} \rightarrow 12/22\ C_7H_8$ (63 % Yield) + 48/22 CO (36 % Yield) + 84/22 H_2O

Carlson, Vispute, and Huber, Green Gasoline by Catalytic Fast Pyrolysis, ChemSusChem

Cellulose Pyrolysis in TGA at fast heating



Cellulose pyrolysis at three different heating rates in TGA

- Cellulose can be 100% pyrolyzed
- Cellulose pyrolysis to anhydrosugars is endothermic
- Kinetics and heat transfer effects both need to be taken into account

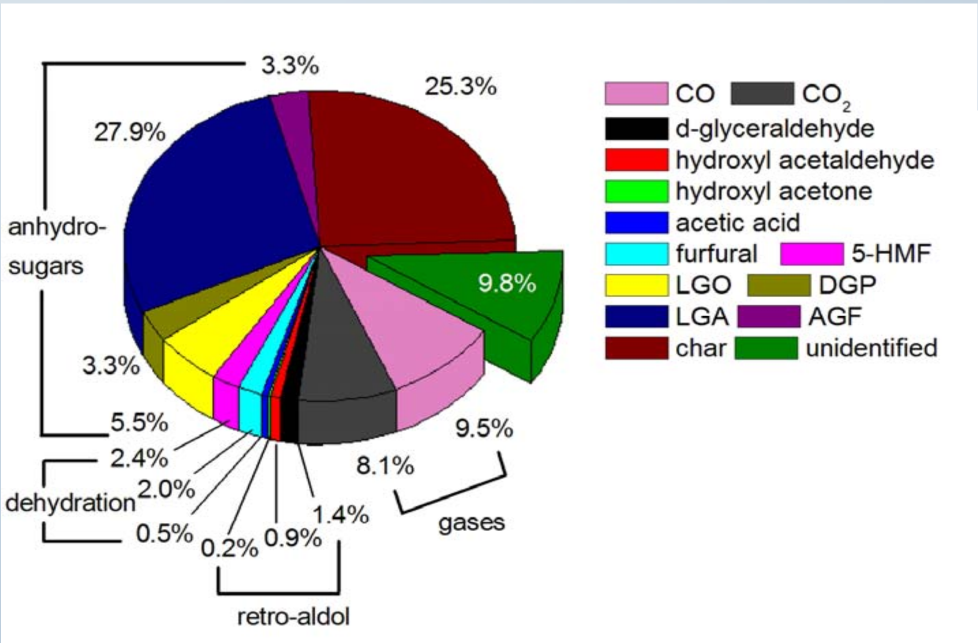
$$\frac{d\alpha}{dt} = k(1-\alpha), k(T_s) = k_0 \exp\left(-\frac{E_A}{RT_s}\right)$$

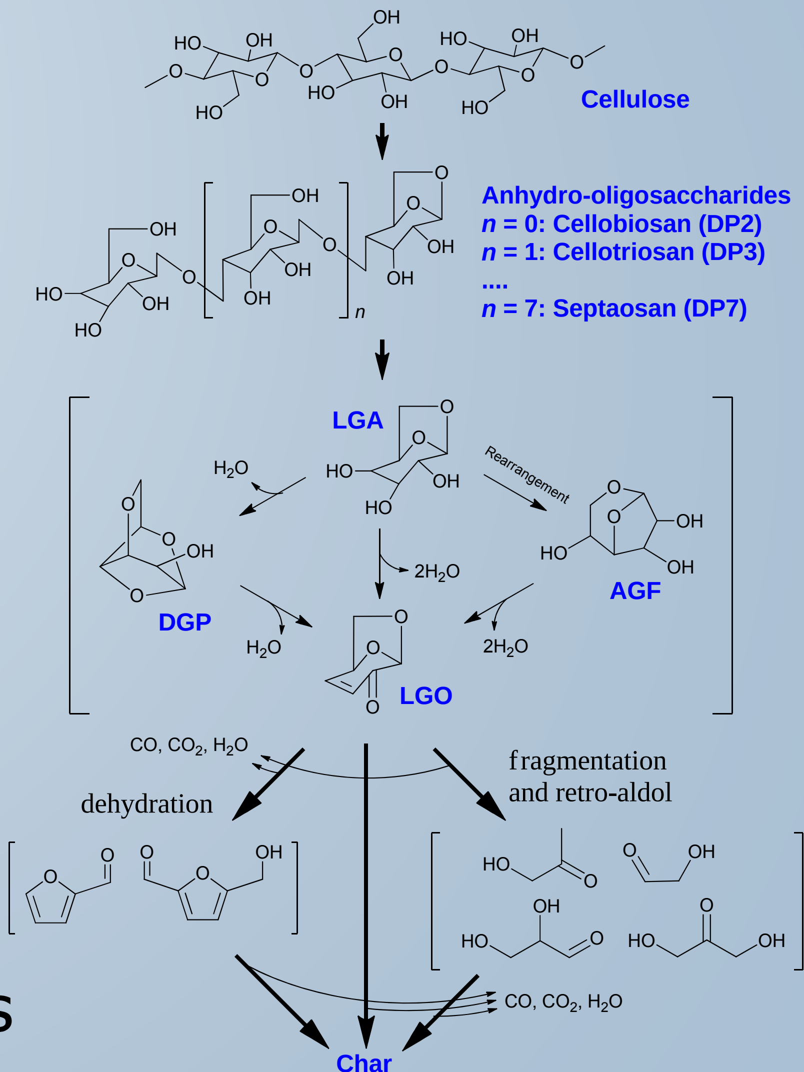
Energy Balance

$$hA_r(T_e - T_s) = m_0(1-\alpha)c_p \frac{dT_s}{dt} + m_0 \frac{d\alpha}{dt}\Delta H$$

Lin et al., Kinetics and Mechanism of Cellulose Pyrolysis, J. Phys. Chem. C (2009) 113, 20097-20107

Cellulose Pyrolysis Chemistry

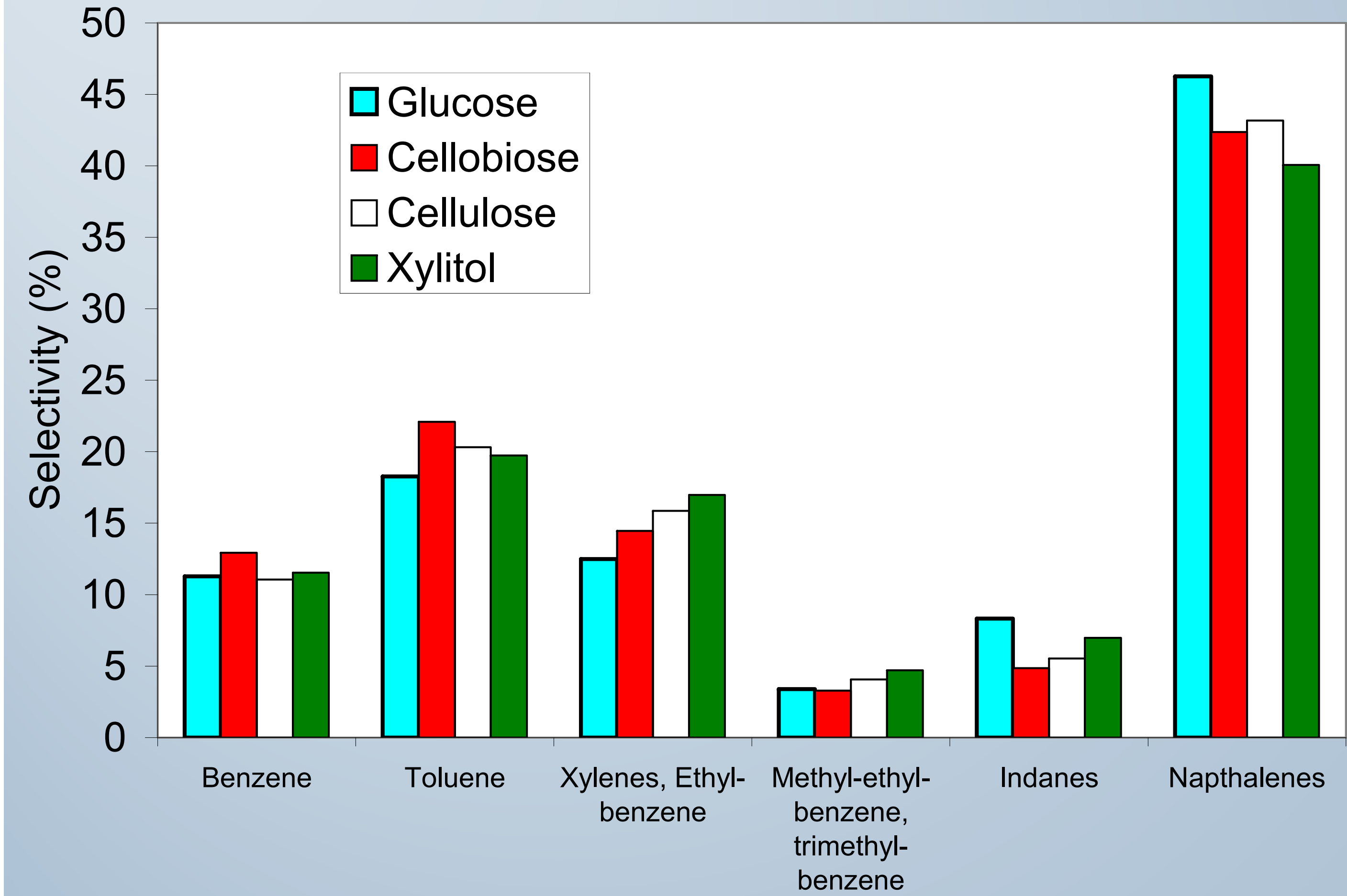




- Cellulose pyrolysis to anhydro-sugars
- Complicated gas chemistry
- Coke can form from gas reactions

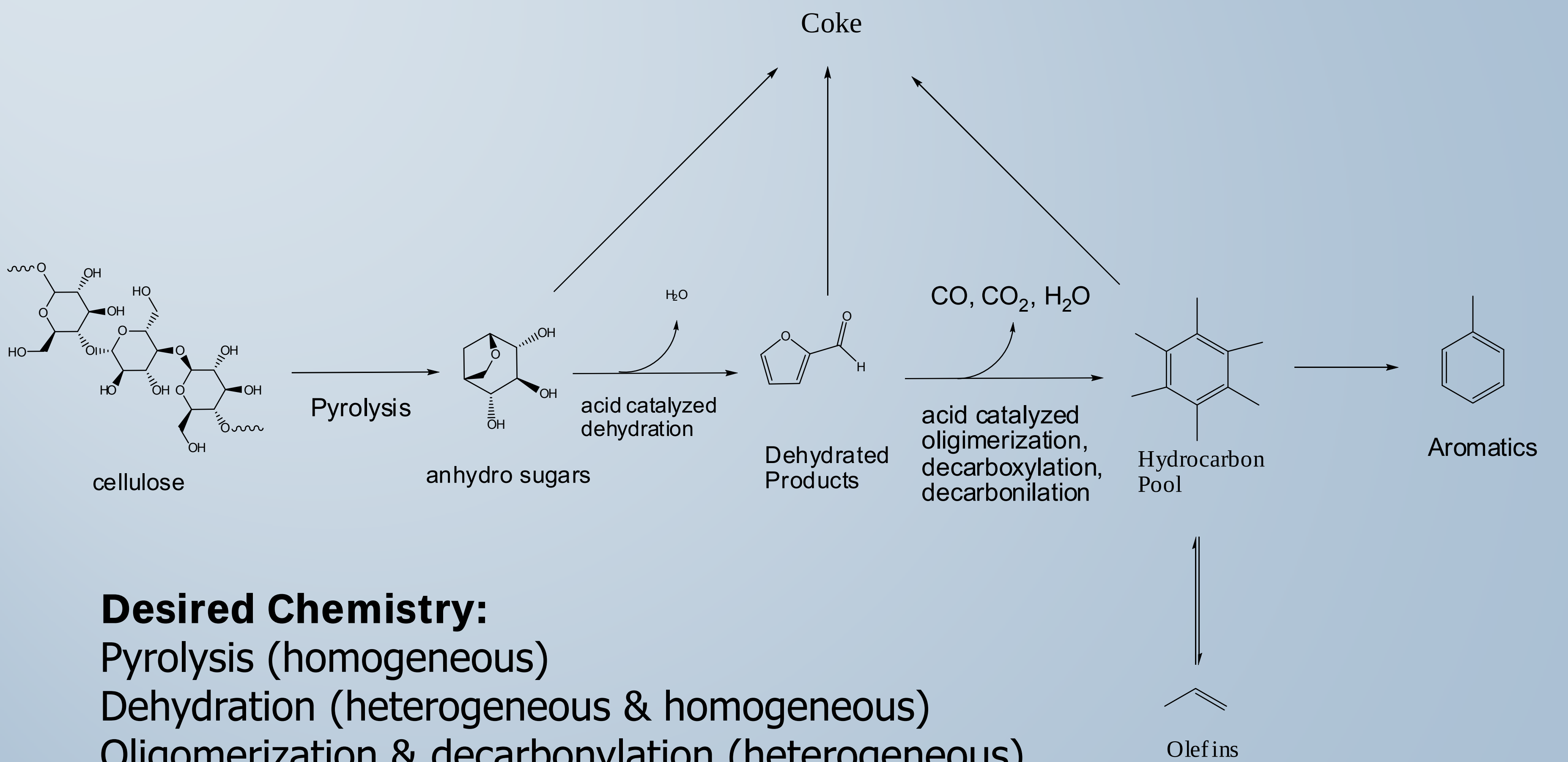
Lin et al., Kinetics and Mechanism of Cellulose Pyrolysis, J. Phys. Chem. C (2009) 113, 20097-20107

Gasoline Range Aromatics



- Octane number of aromatics is 110
- Aromatics can be blended at 25% level in gasoline
- Aromatics can be hydrogenated to other fuels
- BTX is more valuable than gasoline

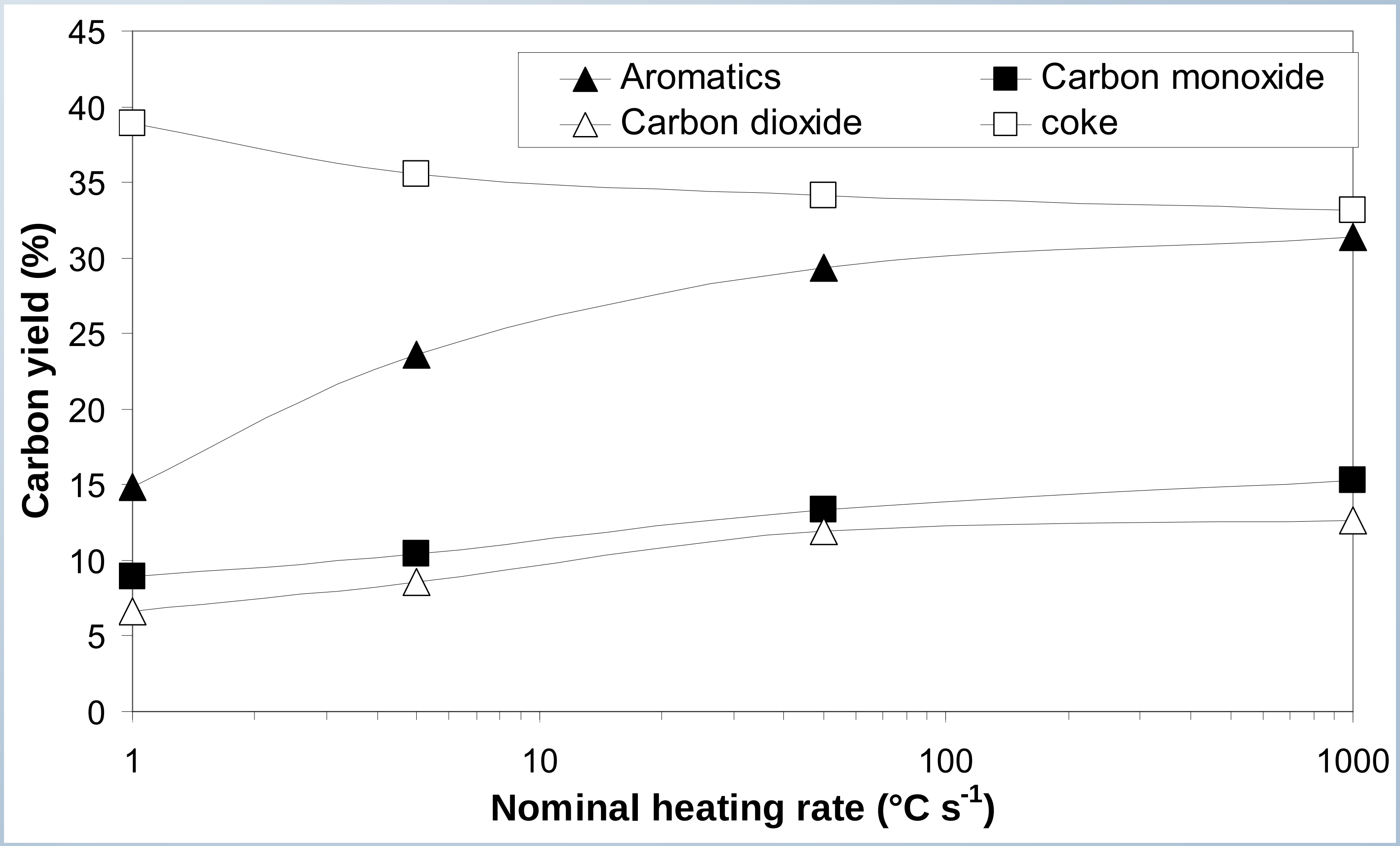
Reaction Mechanism



Desired Chemistry:
Pyrolysis (homogeneous)
Dehydration (heterogeneous & homogeneous)
Oligomerization & decarbonylation (heterogeneous)

Undesired Chemistry:
Homogeneous and Heterogeneous coke formation

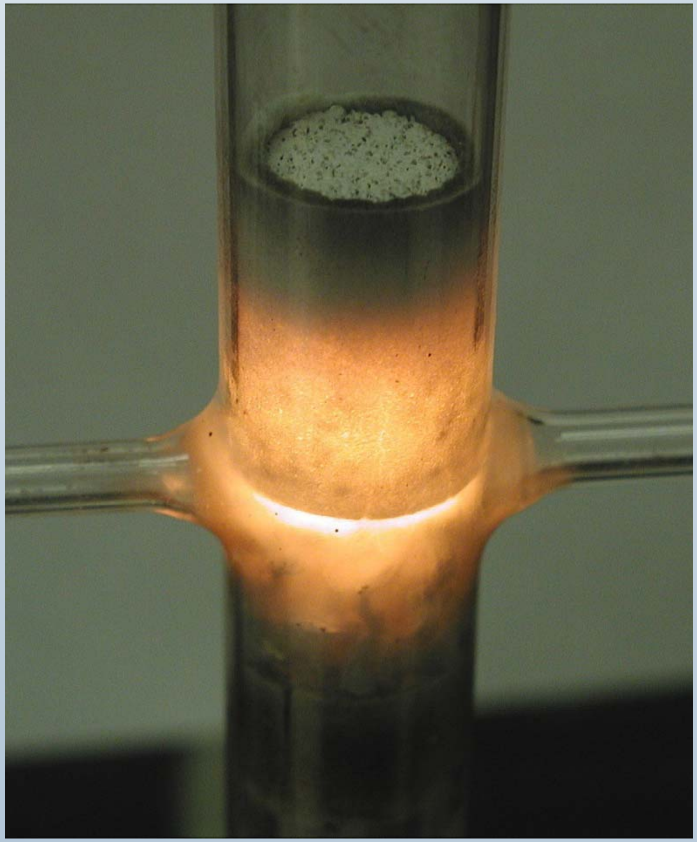
Effect of Heating Rate on Catalytic Fast



Reaction Conditions: Temperature 600ºC; ZSM-5;
Feed: Glucose; Catalyst to Feed Ratio 19

$C_6O_6H_{12} \rightarrow$ 12/22 C_7H_8 (63 % Yield) + 48/22 CO (36 % Yield) + 84/22 H_2O

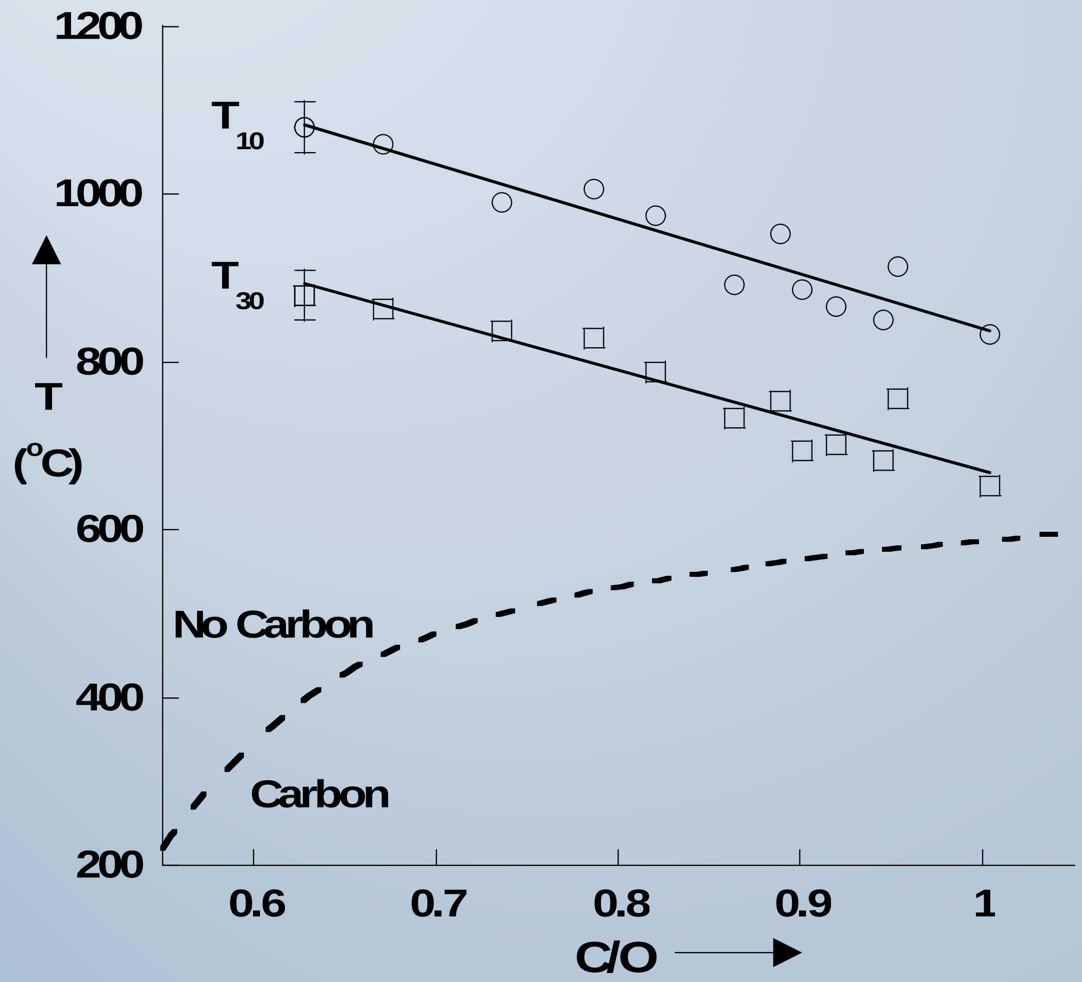
Catalytic Partial Oxidation (CPOX)

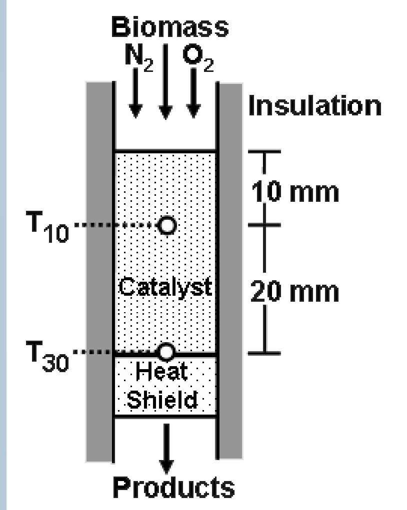


- Fuel and O_2 enter at the top
- Valuable chemicals produced: syngas (H_2 & CO), olefins, oxygenates, etc.
- Runs auto-thermally
- Short contact times (Milliseconds)

CPOX of Cellulose

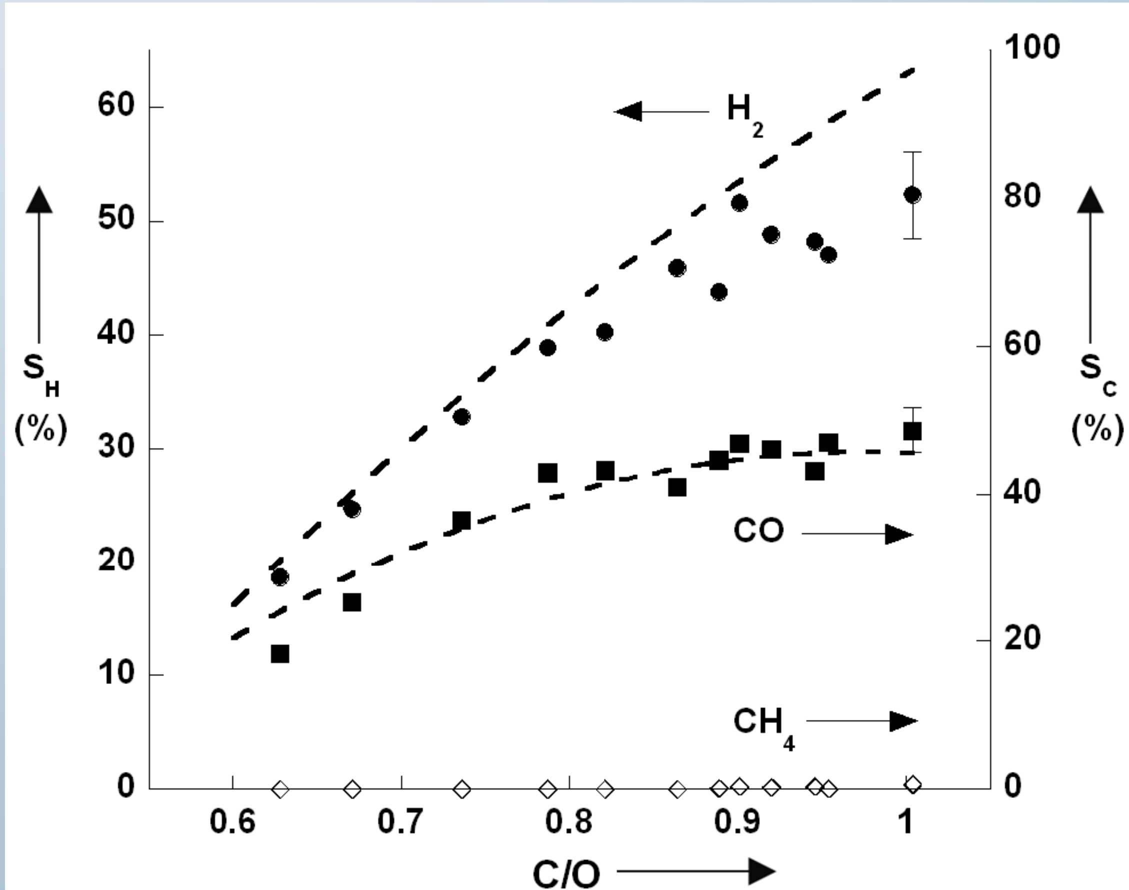
Catalytic Reforming of Cellulose





Always operate predicting no carbon

Catalytic Reforming of Cellulose



Produce equilibrium synthesis gas

Higher C/O = more H_2 + CO

Less than 1% methane

At C/O < 1.0, no oxygenates

Comparison of CPOX to Gasification

Faster – 10 to 100X

- Possibly smaller (portable); Faster, more flexible start-up

Cleaner – Catalyst breaks down volatile organics

- Possibly eliminates downstream clean-up stages

Provides WGS capabilities

- Can add steam to adjust H_2/CO ratio for desired output
- Possibly eliminates separate shift stage

Remaining Issues

- Ash handling
- Mechanism / Modeling
- Bio-oill upgrade