



# Microchannel Catalytic Process for Converting Biomass Derived Syngas to Transportation Fuels

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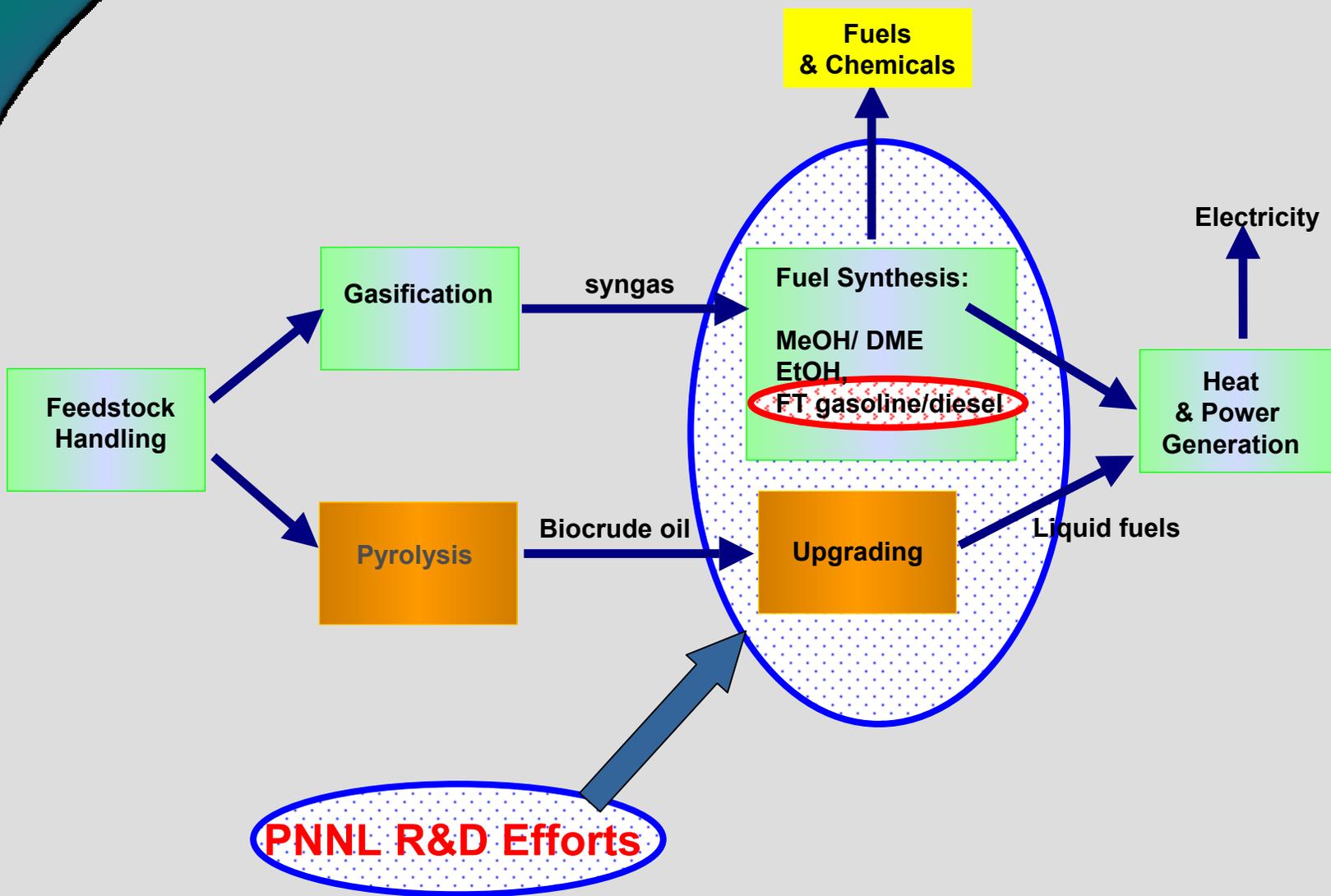
# Outline

- ▶ Biomass derived syngas to fuels
  - Background
  - Challenges
- ▶ Conventional GTL technology vs. Microchannel Reactor Technology
- ▶ Microchannel reactor-engineered catalysts performance demonstration
- ▶ Modeling for catalyst optimization
- ▶ Microchannel GTL reactor conceptual design

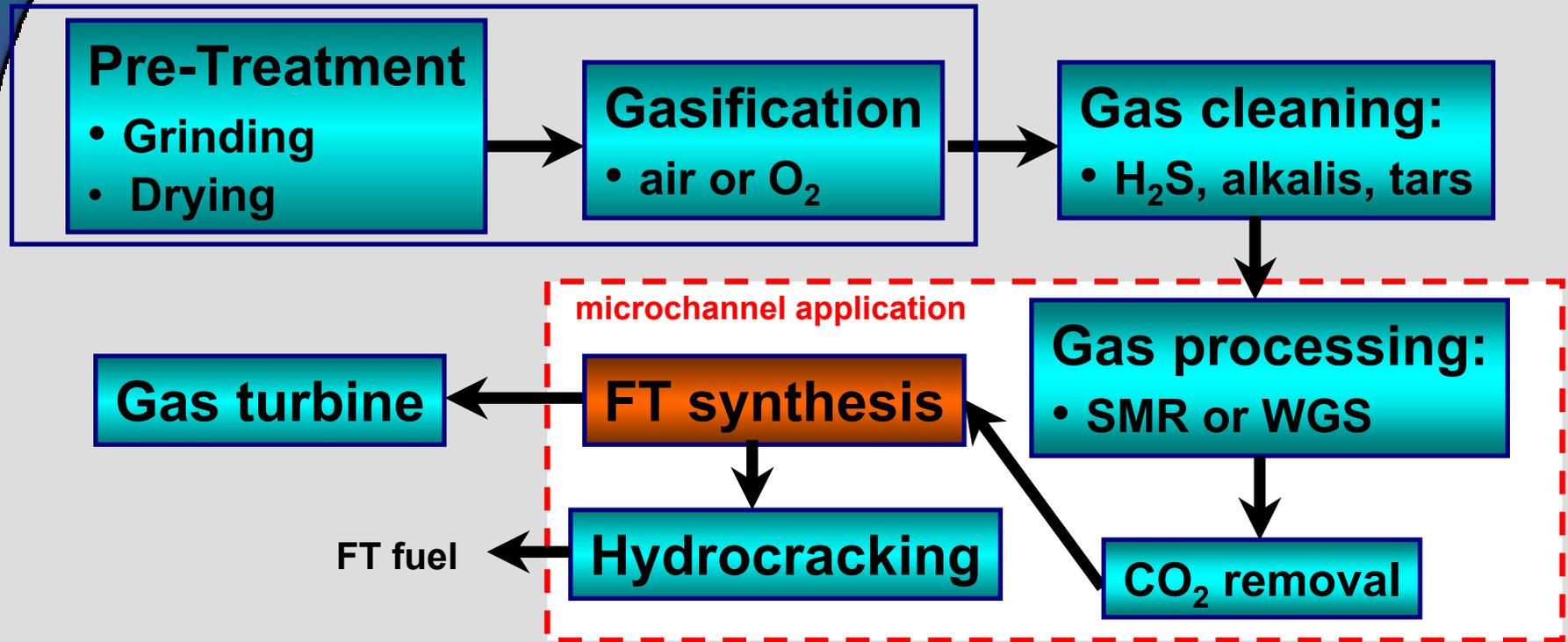
# Clean Fuels from Biomass

- ▶ Compared to the fossil fuels, Biomass—Renewable energy source when CO<sub>2</sub> emissions for its use is absorbed by newly grown biomass.
- ▶ Growing interest: Fuels from biomass --- Environmental concerns such as green house gas emission control.

# DOE Biomass SYNGAS Platform



# Fischer-Tropsch Fuels From Biomass



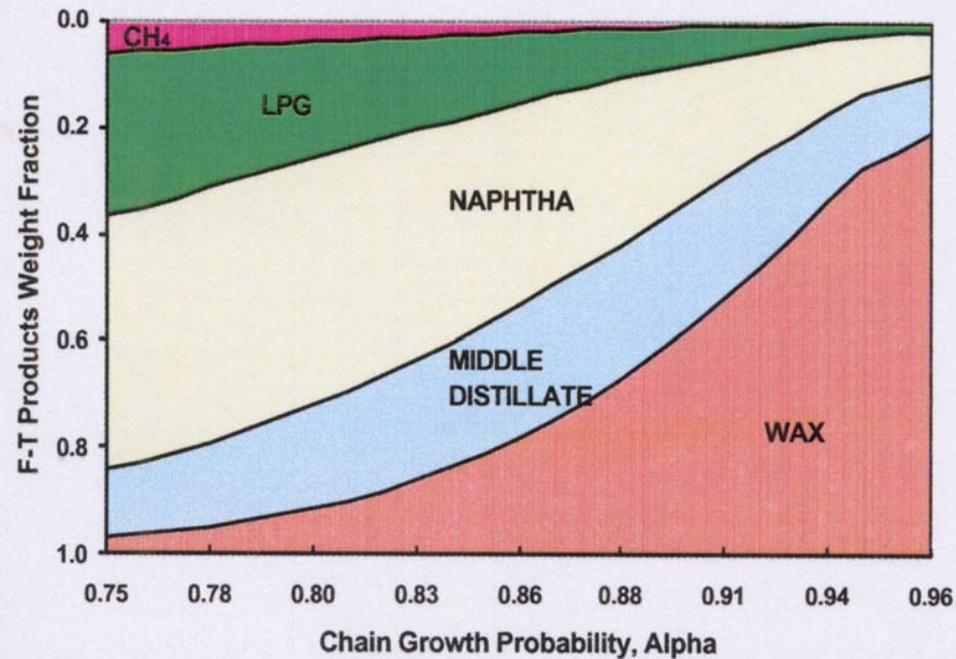
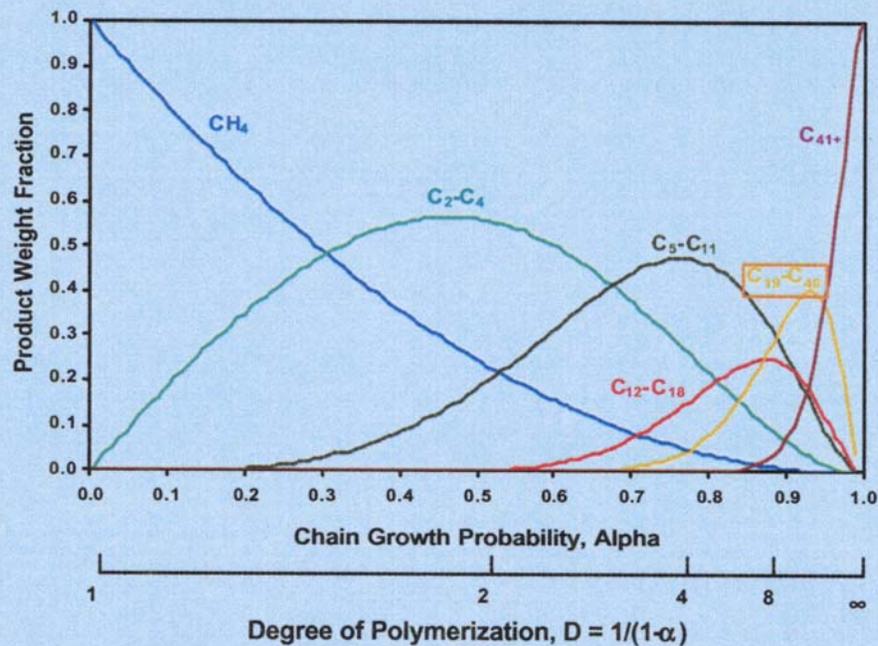
# Fischer-Tropsch Synthesis Reactions

- ▶ Paraffins:  $(2n+1) \text{H}_2 + n\text{CO} \rightarrow \text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O}$
- ▶ Olefins:  $2n \text{H}_2 + n\text{CO} \rightarrow \text{C}_n\text{H}_{2n} + n\text{H}_2\text{O}$
- ▶ Alcohols:  $2n \text{H}_2 + n\text{CO} \rightarrow \text{C}_n\text{H}_{2n+1}\text{OH} + (n-1) \text{H}_2\text{O}$
- ▶ Water gas shift:  $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$
- ▶ Boudouard Reaction:  $2 \text{CO} \rightarrow \text{C} + \text{CO}_2$
- ▶ Coke formation:  $\text{H}_2 + \text{CO} \rightarrow \text{C} + \text{H}_2\text{O}$

- **Multiphase (G-L-S)**
- **Strongly exothermic ( $\Delta H_r = -180 \text{ kJ/mol}$ )**
- **Mass transfer limited**

# Degree of Polymerization Affects F-T Product Distribution

**ASF distribution:**  $W_n = (1 - \alpha)^2 n \alpha^{n-1}$

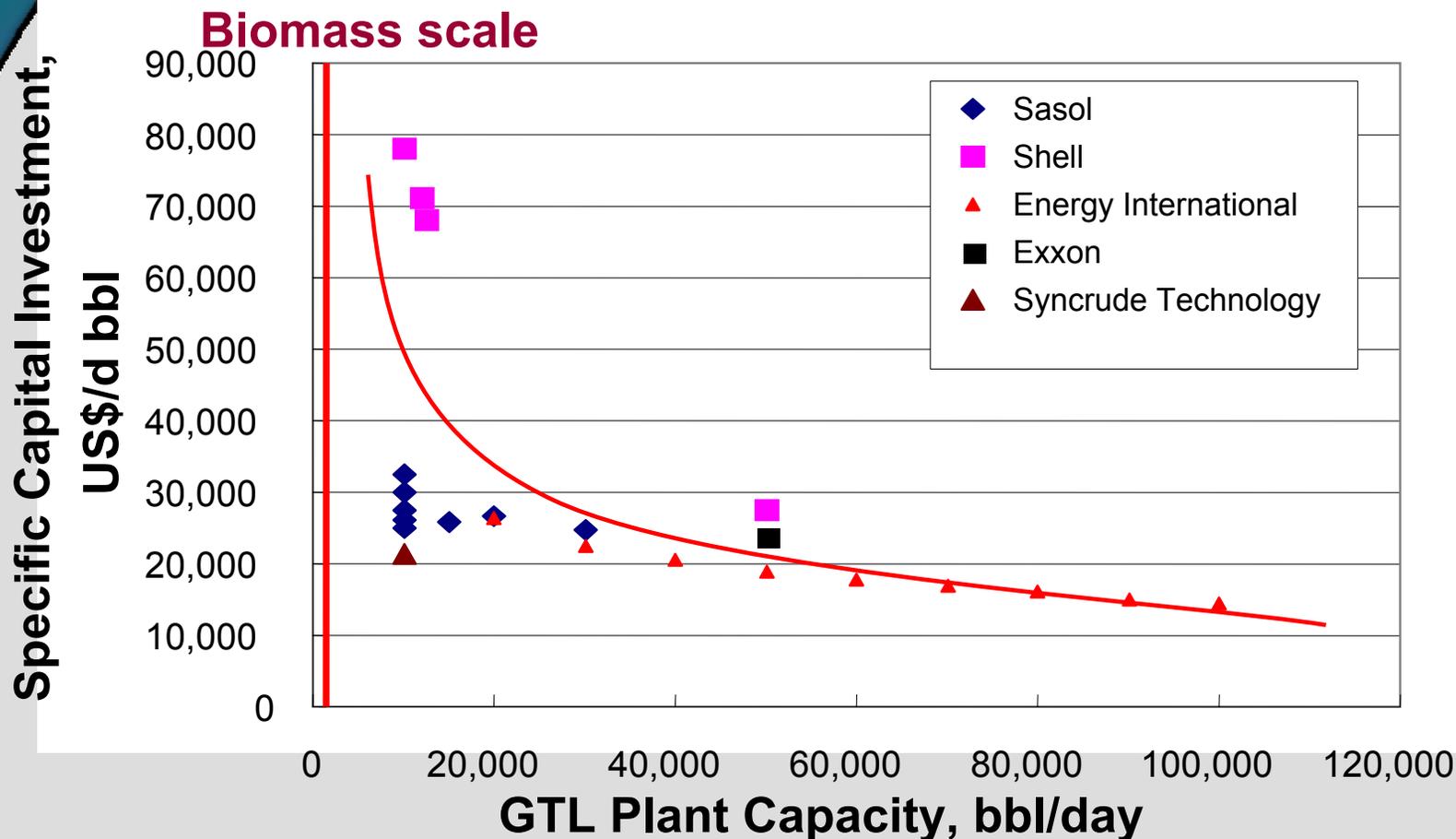


# Challenges of Biomass Syngas to Fuels

- ▶ Stranded feedstock
  - No existing pipelines to move syngas to large central facilities
- ▶ Conversion facilities are small in scale: <1000 tons biomass/day
  - Equivalent to <~1100BPD liquid FT fuels
  - Not economic to convert to fuels using conventional technologies
- ▶ Costly CO<sub>2</sub> clean up
- ▶ Low Pressure, ~14bar

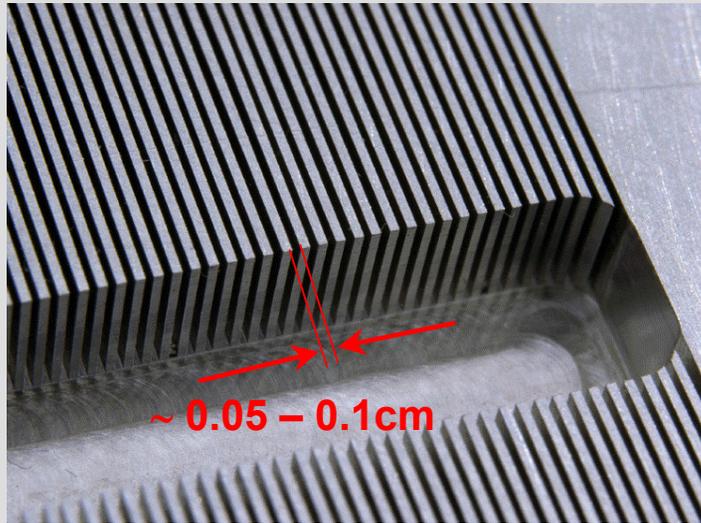
*Microchannel reaction technology provides the potential to cost effectively convert syngas to fuels*

# Conventional GTL Plant Capital Investment



➤ **Conventional GTL plant is not cost competitive at the capacity typical of biomass feedstocks**

# Characteristics of Microchannel Reactor

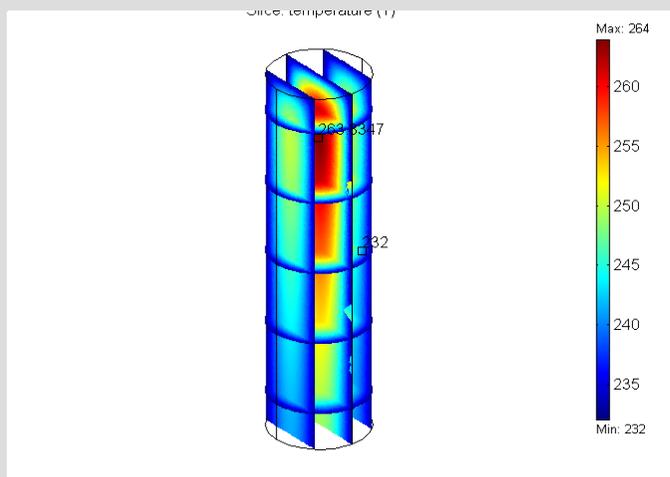


- ▶ Heat and mass transfer advantages -- Intensifies syngas-to-fuel process
  - Enhances productivity
  - Improves product selectivity
  - Minimizes catalyst deactivation
- ▶ Provides a potential cost-competitive solution at the scale relevant to biomass
- ▶ Allows potential integration of unit operations (simplification of gas conditioning with synthesis step)
- ▶ Achieves advanced performance through
  - Microchannel reactor
  - Engineered catalyst

# Temperature Gradients in FT Reactors

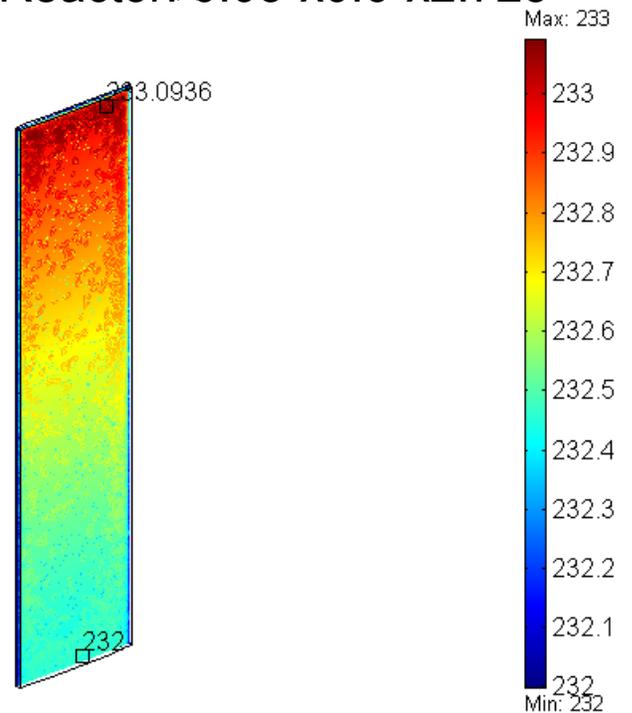
CT=0.3sec, P=20atm, catalyst vol = 0.8cc

Packed Bed Reactor: 0.25"ID x 1" L

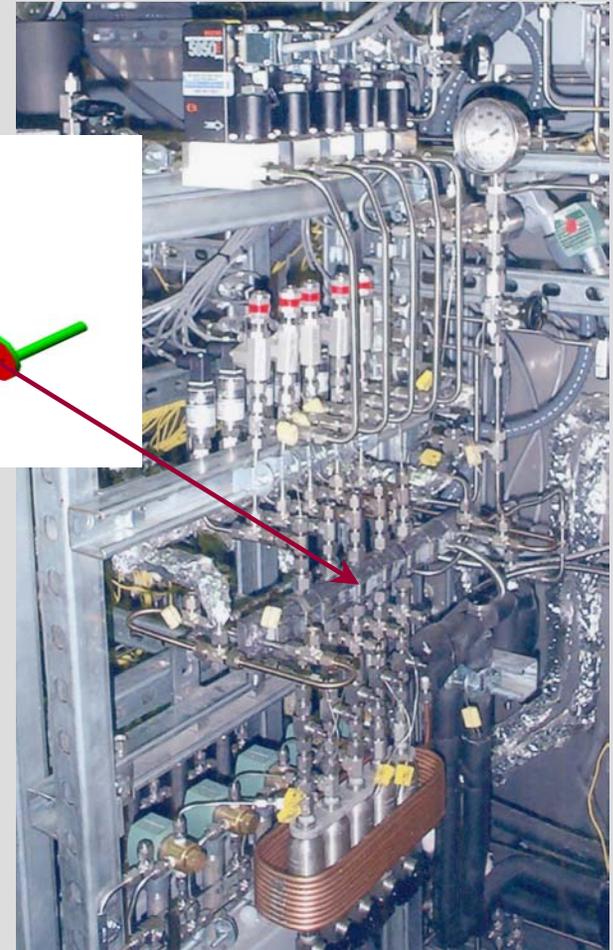
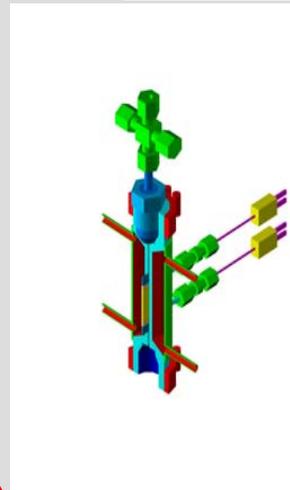
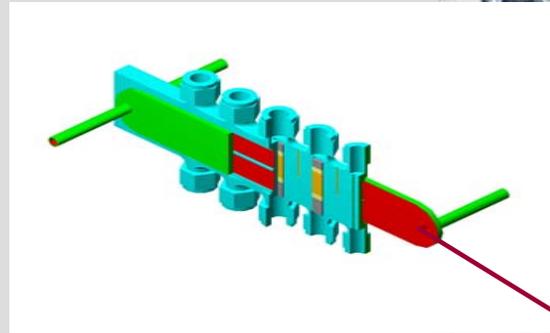


Hot spot: 262 C

Microchannel Reactor: 0.03"x0.6"x2.725"



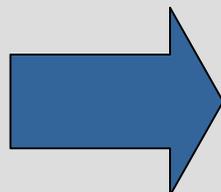
# Microchannel reactor development @ PNNL



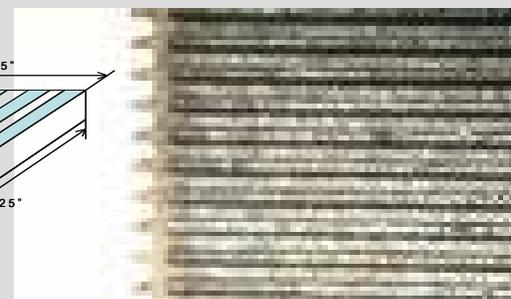
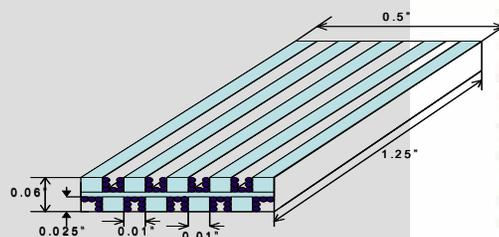
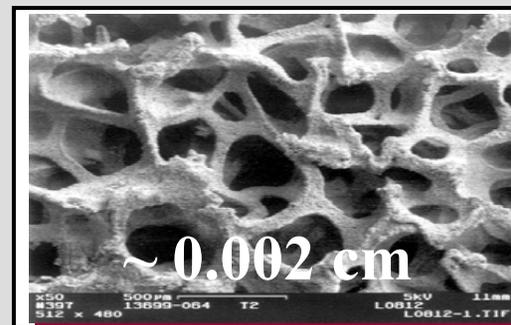
# Engineered Catalysts

Catalyst tailored for microchannel reactor

## Conventional



## Microchannel



Support	Porous Ceramic	Porous Metal and Metallic Structured Monolith
Heat Transport Efficiency	Low	High
Mass Transport Efficiency	Low	High
Activity	Limited	High

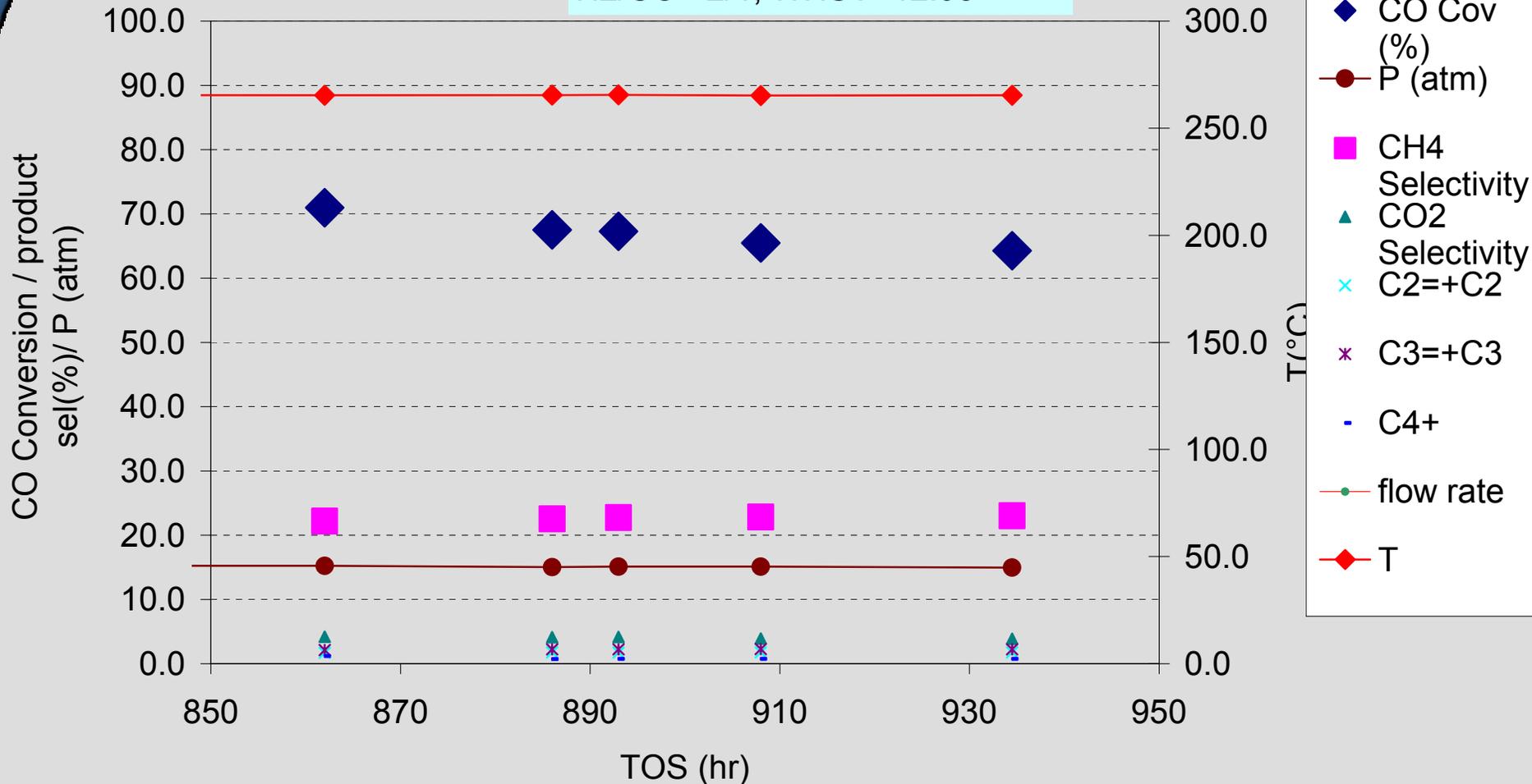
# Accomplishments to Date

- ▶ **High throughput: 60 x greater than conventional (GHSV=60,000hr<sup>-1</sup> at 15 atm, H<sub>2</sub>/CO = 1-2.5)**
- ▶ **Demonstrated tailored product distribution in gasoline and diesel slates ---potentially eliminate hydrocracker**
- ▶ **Preliminary results indicate the potential of no costly CO<sub>2</sub> separation**
- ▶ **Promising economics – low capital cost**

# P=15atm, 60,000 GHSV

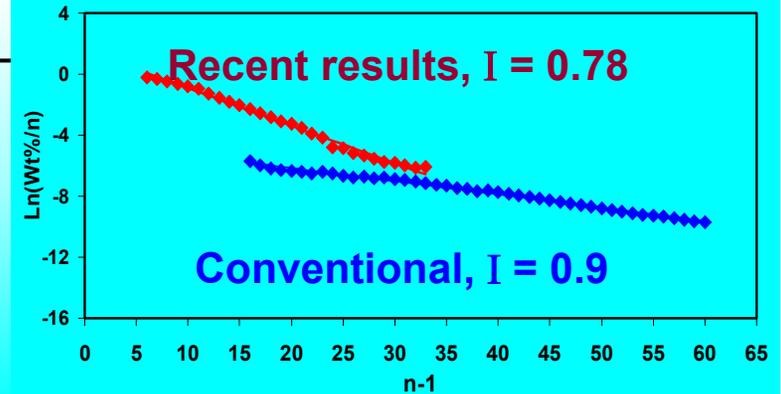
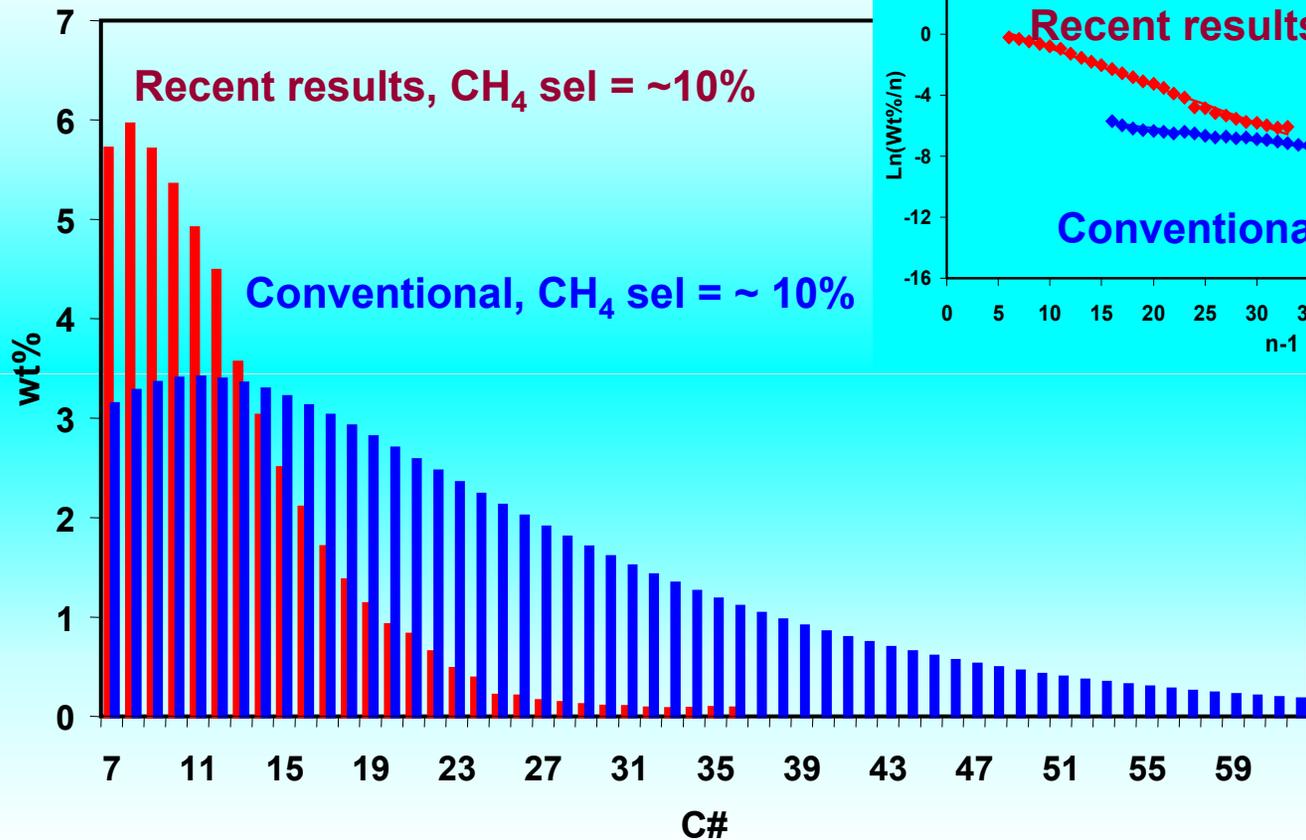
BF009

H<sub>2</sub>/CO= 2/1, WHSV=12.98



# Tailoring of Product Distributions

$H_2/CO=2$ ,  $250^\circ C$ , similar WHSV ( $3.73 \text{ gCO/gcat/hr}$ )

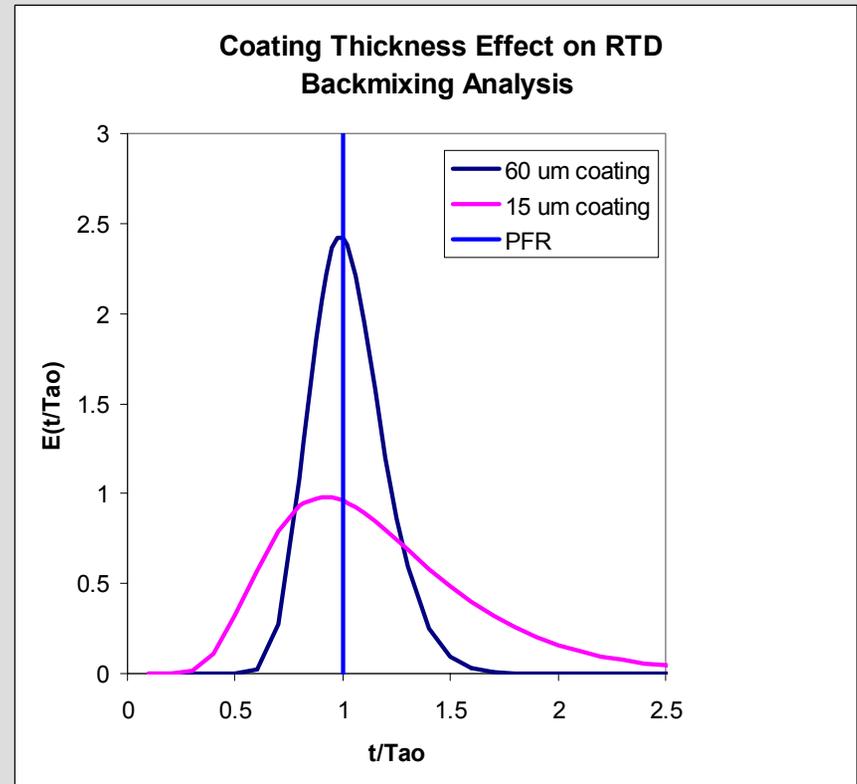


- Narrower product distribution
- Lower  $CH_4$  selectivity and alpha

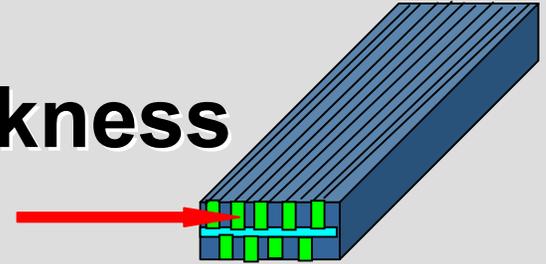
# Catalyst Modeling: --Optimizing coating thickness

Axial Dispersion:

$$\frac{\partial c}{\partial \theta} = \frac{1}{Pe} \frac{\partial^2 c}{\partial z^2} - \frac{\partial c}{\partial z}$$

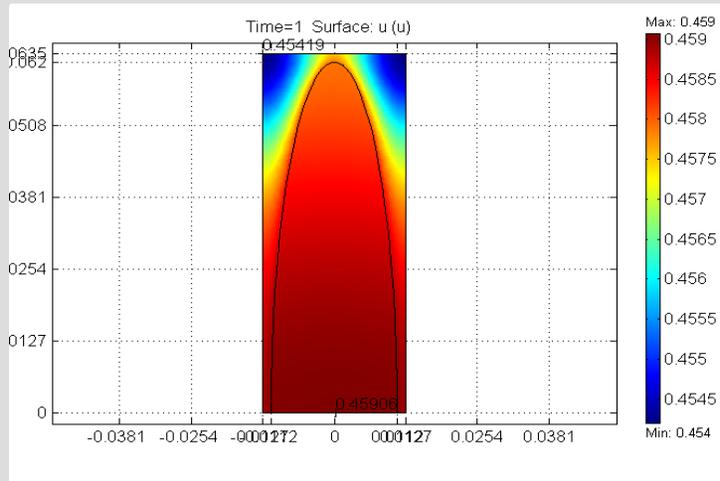


# Catalyst Modeling: --Optimizing coating thickness



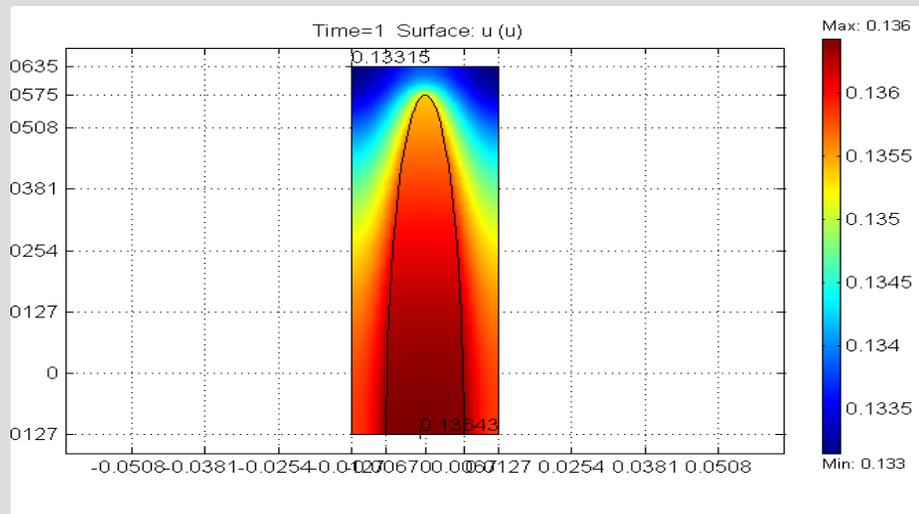
▶ Gas phase

$$u(x, y) \frac{\partial c}{\partial z} = D \left( \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} \right)$$



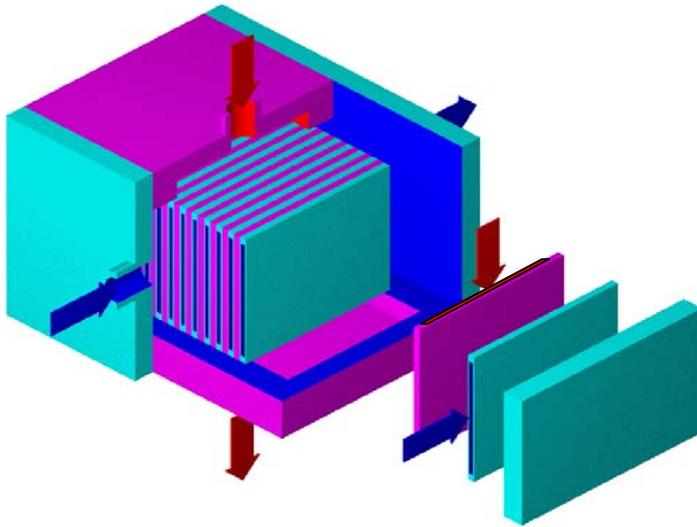
▶ Wash coating catalyst phase

$$ke^{-\frac{E}{RT}} c = Deff \left( \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} \right)$$



# Conceptual Design of Fischer Tropsch Synthesis Reactor for Biomass to Fuel Production

**Throughput: 1000 bbl/day**



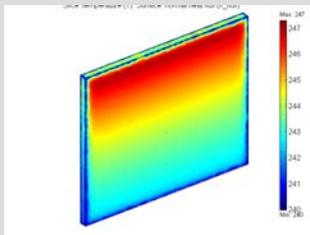
## Module Design:

- Cell dimension: 12"x18"x10"
- Channel dimension: 12"x0.1"x10"
- Number of channels: 5057
- Number of cells: 168 (each cell contains 30 channels)
- Total footprint: 210 cft

## Hydrodynamics and RTD

- Pressure Drop: 16 psi
- Re: 1,072
- Pe: 27,000

Max temperature gradient: 7 °C



# Summary

- ▶ Developed a unique structured catalyst system suitable for the deployment in microchannel reactor applications. Provides high throughput GTL technology in converting biomass derived syngas to liquid transportation fuels.
- ▶ Experimentally demonstrated tailored product distribution for synfuel production with engineered catalysts integrated with microchannel reactors.
- ▶ Modeling approach was used for reactor/catalyst design and optimization.
- ▶ Compared to the conventional petroleum/natural gas based GTL technology, biomass-derived feedstock has the nature of small scale, and the use of microchannel reactor technology is potentially cost-competitive.

# Acknowledgements

- ▶ This work is sponsored by the US DOE EE Renewable Energy, Office of the Biomass Program.
- ▶ Pacific Northwest National Laboratory is operated by Battelle for the US Department of Energy.