



Changing the Way the World Produces Energy

Reduced Complexity in Representation of Fischer-Tropsch Chemistry

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Enter

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Microchannel Fischer-Tropsch (FT)



1. Microchannel technology has advantages over conventional tubular reactors
2. Microchannel technology enables more effective scale-up processes
3. Simplified modeling approach works for the complex Fischer-Tropsch (FT) chemistry
4. Velocys pilot plant demonstration of microchannel Fischer-Tropsch (FT)



Introduction



Fischer-Tropsch (FT) Synthesis for liquid fuels

Smaller scale plants for

- Hard to reach feed stocks
 - Remote sources of natural gas isolated from pipelines
 - Off-shore replacement of flaring, re-injecting
- Smaller feed stocks
 - Biomass-to-liquids (BTL)
 - Waste-to-liquid (WTL)

Challenge of smaller scale:

- Achieve high capacity
- Scaled-down size
- Robust process models to predict performance for widely varying synthesis ("syn") gas streams

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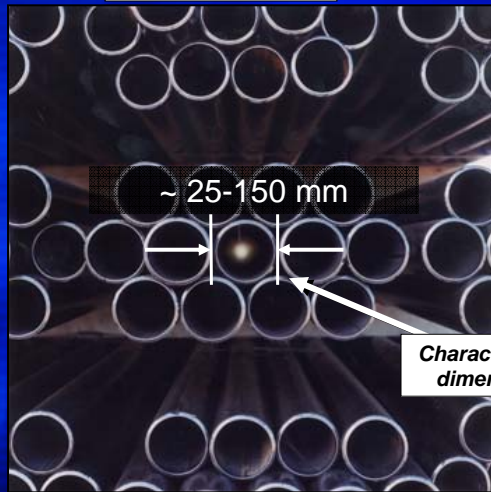


Microchannel Technology

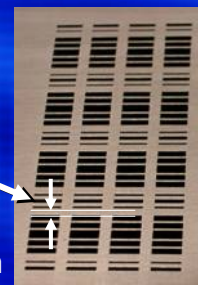
Microchannel Technology



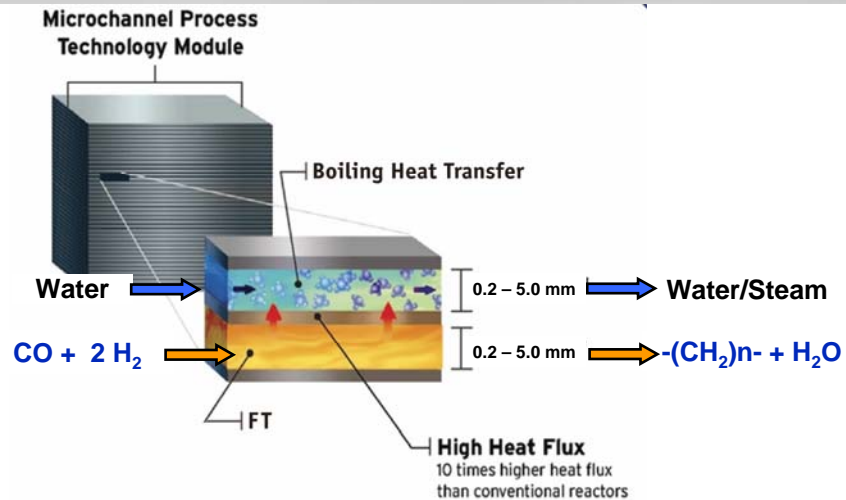
Conventional



Microchannel



Microchannel Fischer-Tropsch Reactor

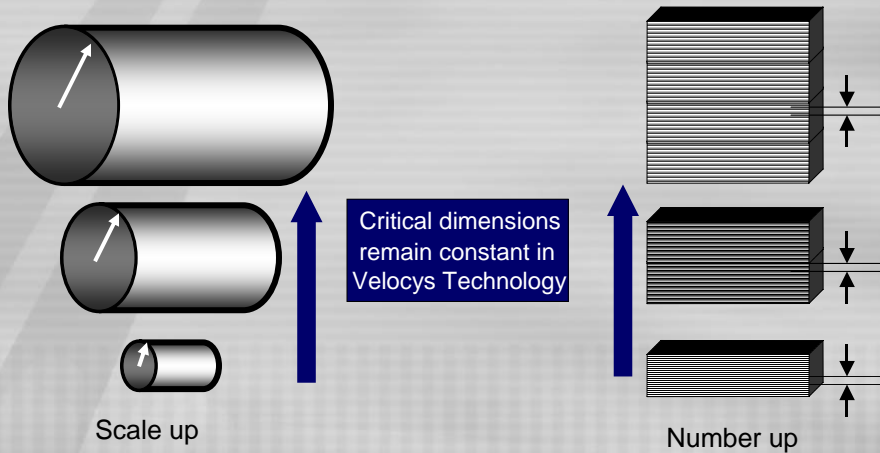


Close integration of the exothermic Fischer-Tropsch synthesis and steam generation

Reducing development risk by “Numbering-up” vs Scaling-up



Velocys devices minimize time and cost to commercialization



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Velocys Scale-up Methodology



Laboratory Scale

- Internal channel dimensions same as commercial scale
- Number of channels increase; size of channels does not from this point

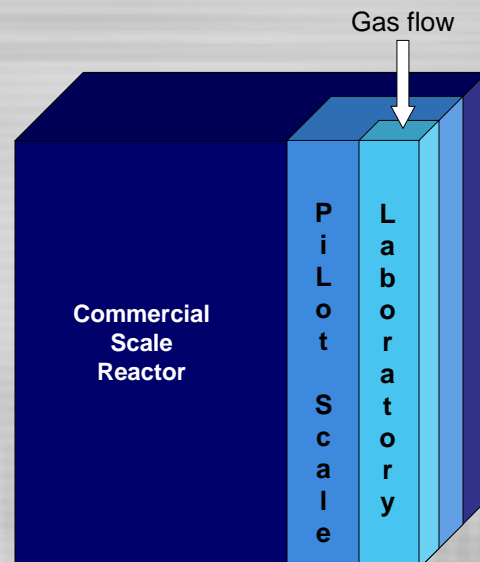
Pilot Scale

- Multiple channels

Commercial Scale

- >1000 channels

Commercial scale reactor is the basic building block of a world-scale plant



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Kinetic Rate Model for FT

Kinetic rate model



FT is a complicated reaction

- Classic polymer kinetics for paraffins
 - Initiation
 - Chain propagation
 - Termination
- Light hydrocarbons ($C_1 - C_4$) can have a different rate mechanism
- Water Gas Shift from water product

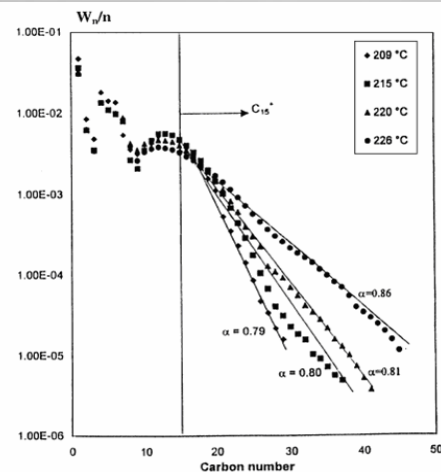
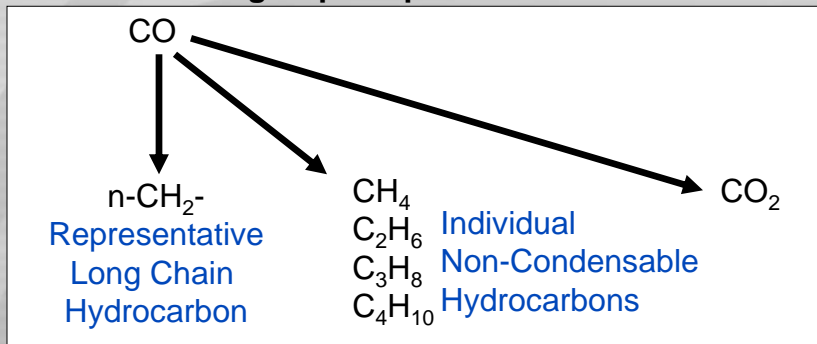


Fig. 4. Anderson-Schulz-Flory for the eggshell catalyst distribution at different temperatures. $P = 1.52$ MPa, GHSV = 348/h, $H_2/CO = 2$ (inlet).

Kinetics Approach



Focus on three groups of products



The focus of this model

- Conversion of CO
- Selectivity to undesired non-condensable gases
- Heat production for channel and coolant design

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Reactions and rate forms



Rxn #		
1	$3\text{H}_2 + \text{CO} \rightarrow \text{H}_2\text{O} + \text{CH}_4$	$R_{\text{CH}_4} = k_1 \exp(E_1 / RT) C_{\text{H}_2}^1$
2	$5\text{H}_2 + 2\text{CO} \rightarrow 2\text{H}_2\text{O} + \text{C}_2\text{H}_6$	$R_{\text{C}_2\text{H}_6} = k_2 \exp(E_2 / RT) C_{\text{H}_2}^1$
3	$7\text{H}_2 + 3\text{CO} \rightarrow 3\text{H}_2\text{O} + \text{C}_3\text{H}_8$	$R_{\text{C}_3\text{H}_8} = k_3 \exp(E_3 / RT) C_{\text{H}_2}^1$
4	$9\text{H}_2 + 4\text{CO} \rightarrow 4\text{H}_2\text{O} + \text{C}_4\text{H}_{10}$	$R_{\text{C}_4\text{H}_{10}} = k_6 \exp(E_6 / RT) C_{\text{H}_2}^1$
5	$\text{H}_2\text{O} + \text{CO} \rightarrow \text{H}_2 + \text{CO}_2$	$R_{\text{CO}_2} = k_4 e^{-E_4/RT} C_{\text{H}_2\text{O}} C_{\text{CO}}$
6	$29\text{H}_2 + 14\text{CO} \rightarrow 14\text{H}_2\text{O} + \text{C}_{14}\text{H}_{30}$	$R_{\text{FT}} = \frac{k_6 e^{-E_6/RT} C_{\text{H}_2} C_{\text{CO}}}{[1 + k_6 e^{-E_6/RT} C_{\text{CO}}]} *$

* Yates and Satterfield, Energy & Fuel, v.5, 1991

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Building the Kinetic Model

Catalyst development

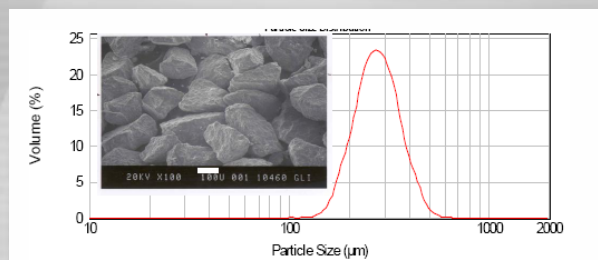


Cobalt on alumina

- High activity, low methane selectivity
- 500 gm batch

Laboratory scale microchannel testing

- 0.2 gm catalyst
- Feed gas: 2:1 H₂:CO with 4% Argon at 25 atm
- Contact time: 300 milliseconds
- Temperature varied from 210°C to 230°C



Catalyst Kinetic Fit of Results



T [°C]	CO Conversion		Methane Selectivity	
	Experiment	Model	Experiment	Model
210	54-65%	51.3%	10.0%	9.7%
220	68.0%	67.2%	13.0%	13.8%
230	76-77%	78.6%	20.0%	19.3%

Conversion, selectivity within 2%

- Exception: 210°C where deactivation is seen

Activation energies

- FTS: 100 kJ/gm-mole
 - In line with Eliason and Bartholemew [*Appl. Cat. A.*, **186**, 1993]
- Noncondensable hydrocarbons: 160 kJ/gm-mole
- Water Gas Shift to CO₂: 100 kJ/gm-mole

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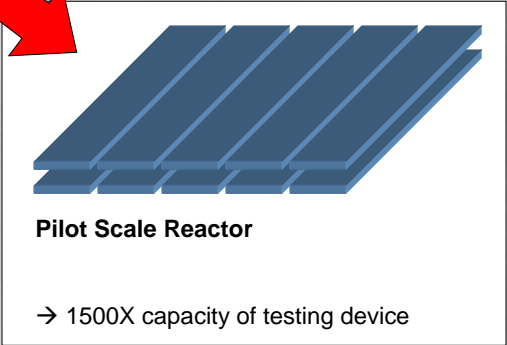


Predicting Performance

Pilot Scale Reactor



Kinetics

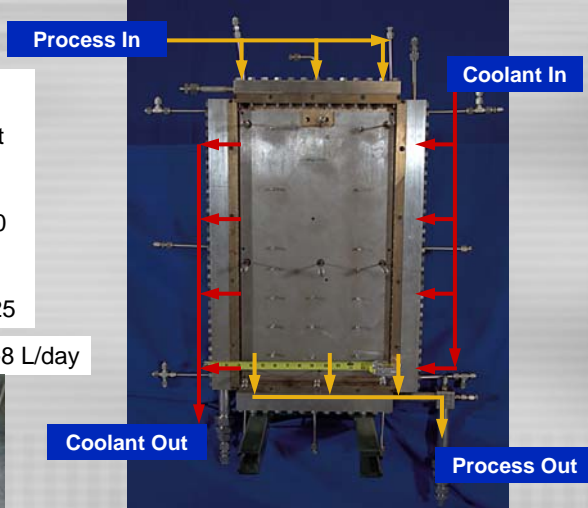


Pilot Scale Reactor

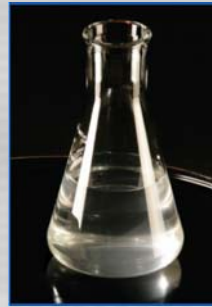


Cross Flow Design
Partial Boiling Water Coolant
Process length ~ 0.6 m
Process microchannels = 40
Coolant Length ~ 0.3 m
Coolant microchannels = 425

Liquid HC product Capacity = 4-8 L/day



Pilot Scale Demonstration



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Pilot Scale Reactor: Experimental Results vs. Model



320psig, 2:1 inlet molar $H_2:CO$

Diluent levels on 10 to 14% range

Contact times

- 390 to 520 millisecond contact times

Temperatures

- 207°C to 216°C

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Pilot Scale Reactor: Experimental Results vs. Model



Contact Time [ms]	T [°C]	CO Conversion		Methane Selectivity		Non-Condensable Selectivity		Maximum Bed T [°C]
		Experiment	Model	Experiment	Model	Experiment	Model	
390	207	43.7%	41.5%	12.3%	11.8%	12.8%	13.2%	217
390	216	59.4%	59.8%	17.1%	17.0%	17.9%	19.0%	233
520	215	68.5%	66.9%	16.1%	17.6%	16.8%	19.7%	228

Model Prediction:

- Good match for both conversion, selectivity to CH₄
 - Within 2%
- Temperature rises in hot spot: 10-17°C
 - Kinetic parameters for hydrocarbon non-condensables are robust

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Why not use tubular reactors?

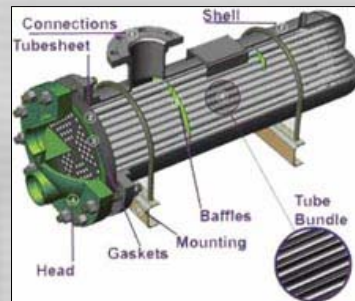


Conventional tubular reactors

- 2.5 cm tubes
- 10 second contact time

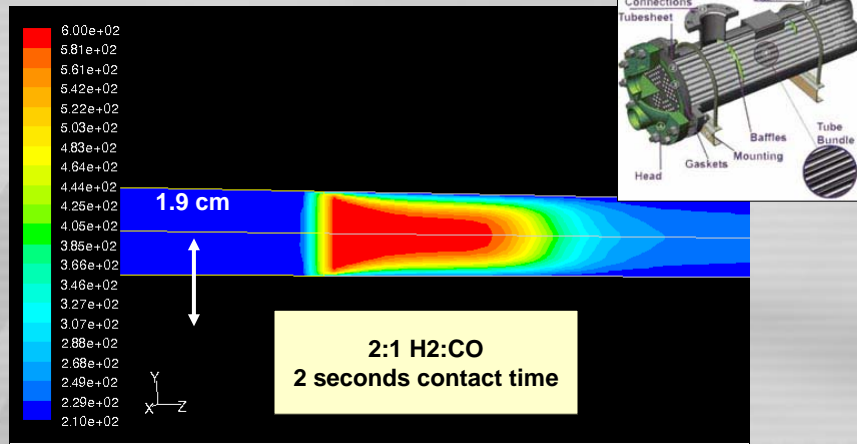
Why not run our catalyst powder with

- A smaller diameter (1.9 cm)?
- Shorter contact time (2 seconds)?



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Challenge with tube & shell reactors



Hot spot with reduced contact times
unless at microchannel dimensions

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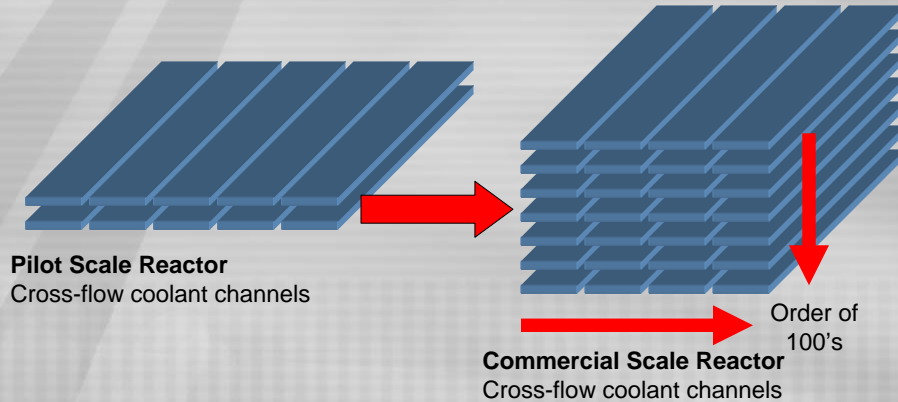
Next Steps

Scale up to commercial reactor



Commercial reactor uses pilot scale channel design in greater numbers

- Larger matrix of reactor channels

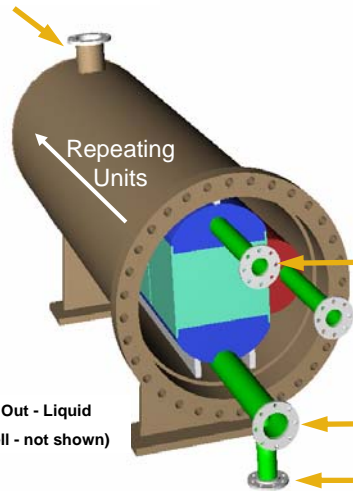


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Commercial FT Reactor Assembly



Coolant Out - Vapor



Specifications

- Shell Diameter = ~1.25 m
- Shell Length = ~4 m
- Coolant flow length = ~0.6m
- Process flow length = ~0.6m

Process In

Coolant In

Process Out

Steam trace

Coolant Out - Liquid
(under shell - not shown)

Summary



Microchannels make a catalyst better by controlling exotherm

Simplified kinetics

- Derived from laboratory scale data
- Predicts results in pilot scale reactor

Commercial reactor numbers up pilot scale reactor with more channels

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