Microfibrous Entrapped Catalyst (MFEC) Structure for Alternative Fuel Production

Hongyun Yang [1], Symon Sheng [2], Norman E. Sammons Jr.[1], Troy J. Barron [1] and Bruce J. Tatarchuk [2],

(1)IntraMicron Inc., Auburn, AL,
(2)Center for Microfibrous Materials, Auburn University

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Outline

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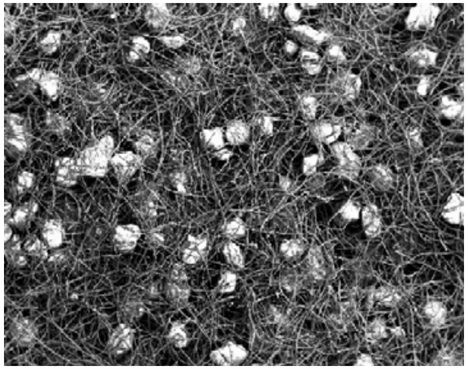
IntraMicron Inc.



Microfibrous Materials

IntraMicron Inc. is a Licensee of Auburn University's Microfibrous Technology (2001). It is located at Auburn, Alabama. It is one of a few manufacturers of micron-size metal fibers in the world. Its major R&D areas are:

(1)Desulfurization, (2) FTS, (3) Air filtration, (4) CO oxidation (5) Fiber related products

Introduction

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- Fossil Fuels and Alternative Fuels
  - Petroleum based liquid fuels
    - Fuel infrastructure based on liquid fuel
    - Limited reservoir (84 million bpd for 44 years)
  - Alternative sources
    - Natural Gas (NG), Coal
    - Solar, Wind, Tide, Geothermal, Biomass, Nuclear
- Alternative Liquid Fuels
  - Synfuels (high quality, gasoline, jet fuel, diesel)
  - Methanol and ethanol
  - Biodiesel

Alternative Fuel Production by XTL

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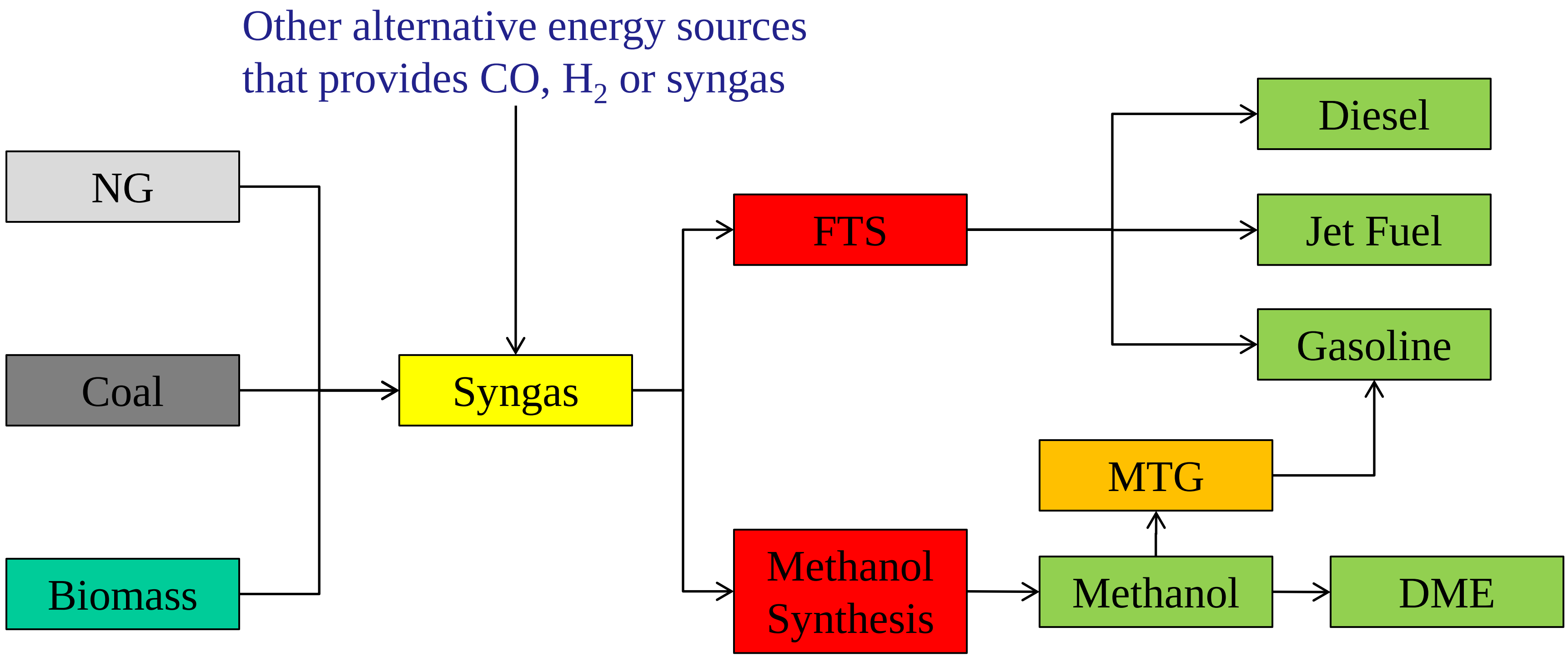

Small scale GTL and BTL units are of significant research interests

(1)Stranded small scale NG reservoirs

(2)Small scale BTL units

(3)Good modularity and mobility

"Conventional GTL technologies are not economically viable at small scales of less than 10 000 barrels of oil per day (bpd). However, only about 6% of the world's gas fields are large enough to sustain a GTL plant of that size." CTO of Oxford Catalyst Group

Exothermic Reactions

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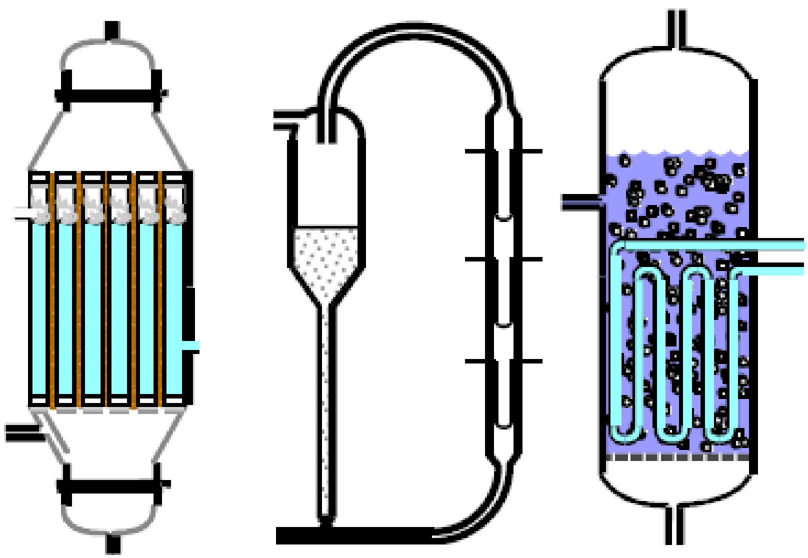
- Fischer-Tropsch Synthesis
  - $CO+H_2=-CH_2- +H_2O$ ΔH= -165kJ/mol $T_{adiabatic}$=1750 C
  - Co (LTFTS) and Fe (HTFTS)
  - Polymerization nature
  - Selectivity vs. temperature
  - Catalyst deactivation and thermal runaway
- Methanol Formation
  - $CO+2H_2=CH_3OH$ ΔH= -124kJ/mol $T_{adiabatic}$=1370 C
  - $Cu\text{-}ZnO/Al_2O_3$
  - Reverse reaction of methanol reforming
  - Catalyst deactivation and methanol reforming at high temperatures

The need of fast heat removal vs. low effective thermal conductivity of packed beds (0.0x-0.2 W/k-m)

Industry Reactors

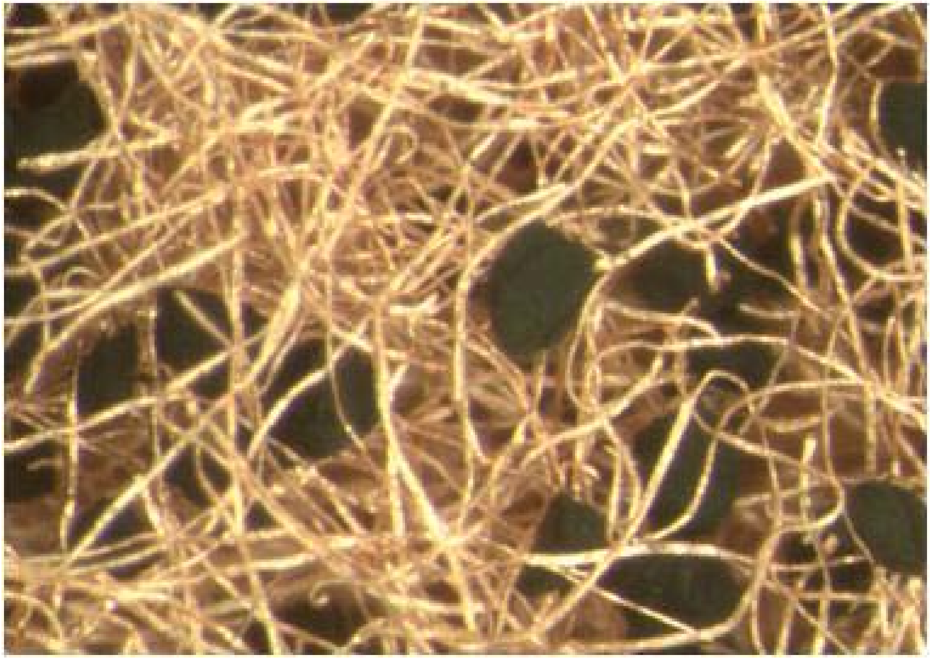
- Packed Beds
  - High gas velocity and low single pass conversion
  - Multiple thin tubes
- Fluidized Beds
- Slurry Phase Reactors



Conventional reactors are large.

Novel Reactors: Microchannel, Honeycomb reactors, **MFEC Reactor**

Microfibrous Entrapped Catalyst (MFEC)



Co FTS catalyst (before reduction) in 12μm
Copper fiber media

Porous media for pre-manufactured catalyst loading

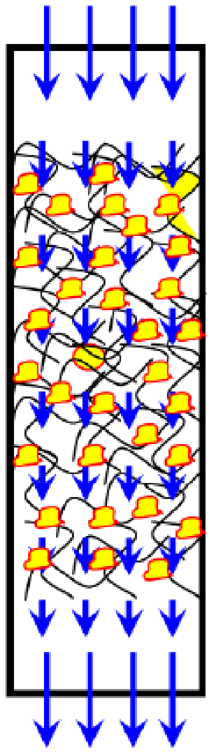
<u>Definition:</u> Microfibrous Materials made of highly conductive metal (e.g. copper) fibers provide for the mechanical and electrical entrapment of catalyst or sorbent particles within sinter-locked networks of a micron-sized fiber matrix with fast heat transfer characteristics.

Characteristics of MFEC

	Volume %		Weight %		Size (µm)	
	MFEC	PB	MFEC	PB	MFEC	PB
Fibers	2-8	-	37-100	-	1.5-32	-
Catalyst Particles	0-30	60-70	0-63	100	20-300	1-5mm
Void	62-98	30-40	0	0	-	-

Microfibrous Matrix

(1) Uniform velocity profile
(2) No channeling
(3) High thermal conductivity
(4) Better wall contacting
(5) Fast heat transfer
(6) Near isothermal temperature profile



Small Catalyst/Adsorbent Particulates

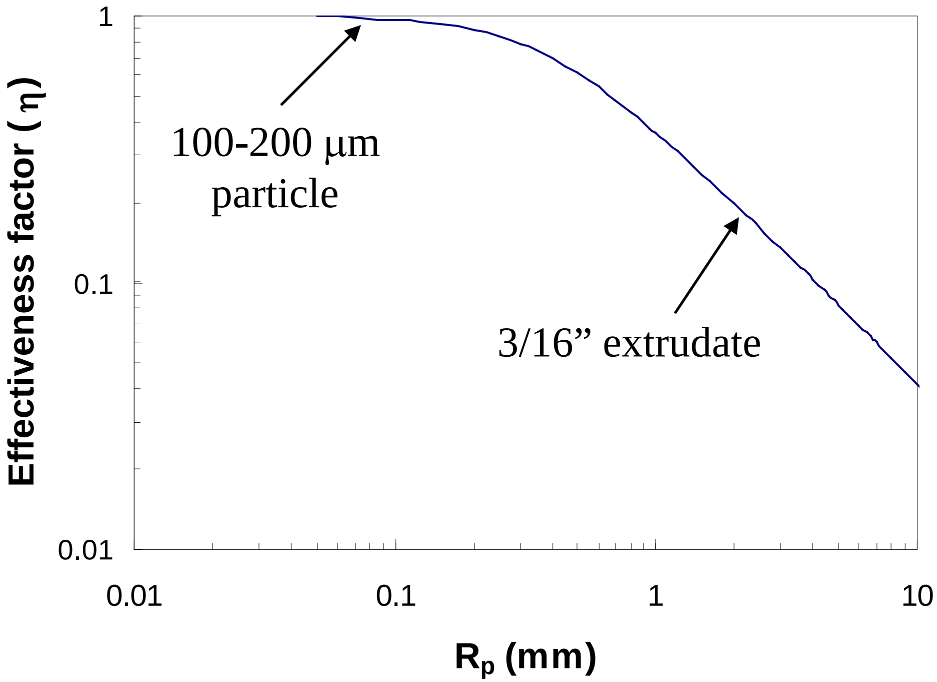
(1) High external surface area
(2) Reduced intraparticle diffusion resistance
(3) Fast mass transfer
(4) Improved selectivity to large molecules

Microfibrous Entrapment

(1) Frozen Fluidized Bed
(2) Uniform particle distribution
(3) Random reactor orientation
(4) No further particle –product separation

FTS Kinetics and Transport Analysis Packed Beds vs MFEC

- Control mechanism
  - Pore diffusion limitation



Pseudo-first order reaction rate K=0.06 s^{-1}.

H_2 Diffusivity in the pores D=1.2×10^{-9} m^2/s [1]

$$\eta_{Packed} = 0.2 \qquad \varepsilon_{Packed} = 0.40$$

$$\eta_{MFEC} = 1.0 \qquad \varepsilon_{MFEC} = 0.85$$

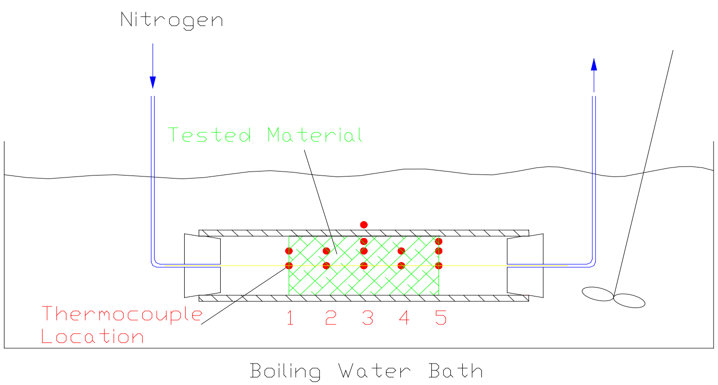
$$\frac{r_{MFEC}}{r_{Packed}} = \frac{\eta_{MFEC}}{\eta_{Packed}} \cdot \frac{1-\varepsilon_{MFEC}}{1-\varepsilon_{Packed}} = 1.25$$

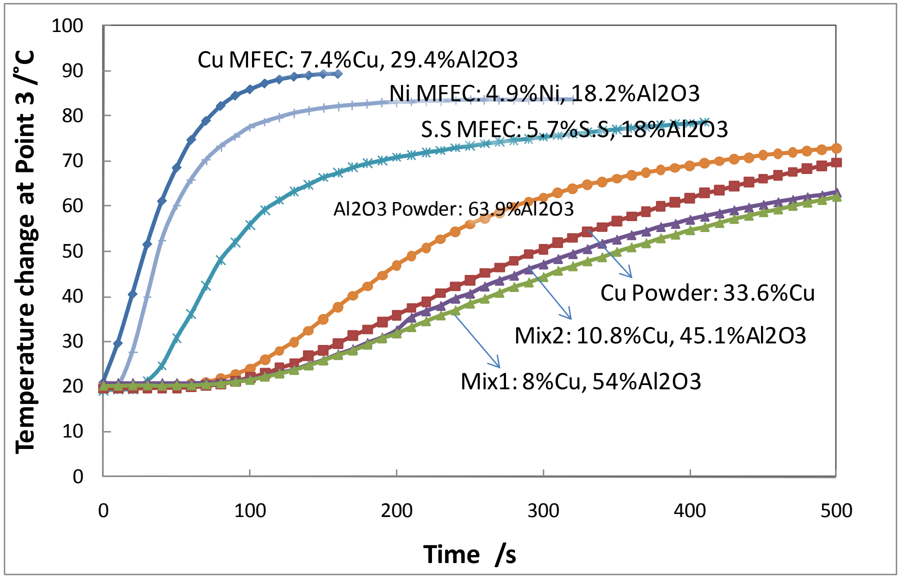
$$\frac{r_{MFEC}}{r_{Packed}} = \frac{1\times(1-0.85)}{0.2\times(1-0.4)} = 1.25$$

MFEC and Packed Beds have similar volumetric reaction rate,but packed beds cannot be made of small partciles.

[1]. Post et al., Diffusion Limitation in Fischer-Tropsch Catalyst, AIChE J., 1989, 35, 1107-1114

Performance of Microfibrous Entrapped Catalysts





Media	K (W/m-K)
Cu Fiber	400
Catalyst Supports	7.2
Syngas	0.426 [1]
Al_2O_3 Packed bed	**0.2**
Copper MFEC [3]	**9.7**
Ni MFEC	**3.8**
Stainless Steel	**1**

Results:
5-48 times increase in thermal conductivity
10 times increase in wall heat transfer coefficient

Velocity and Temperature Profile

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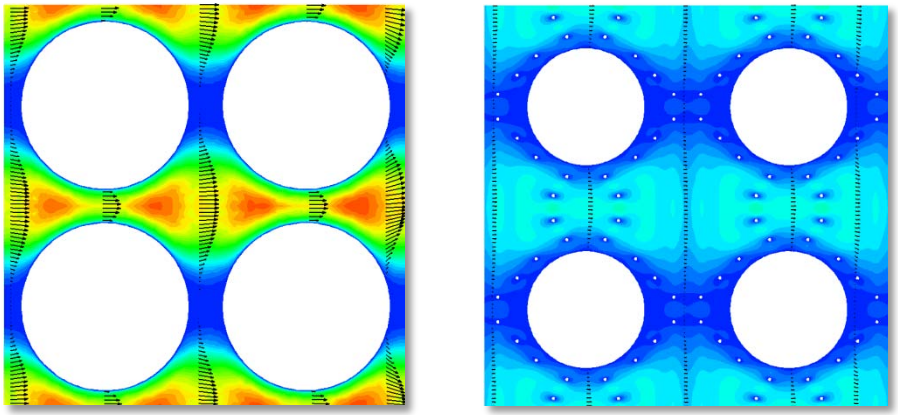
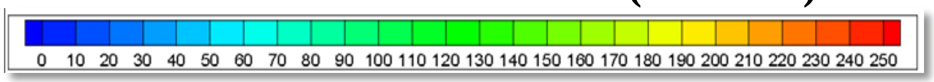
Velocity Profile

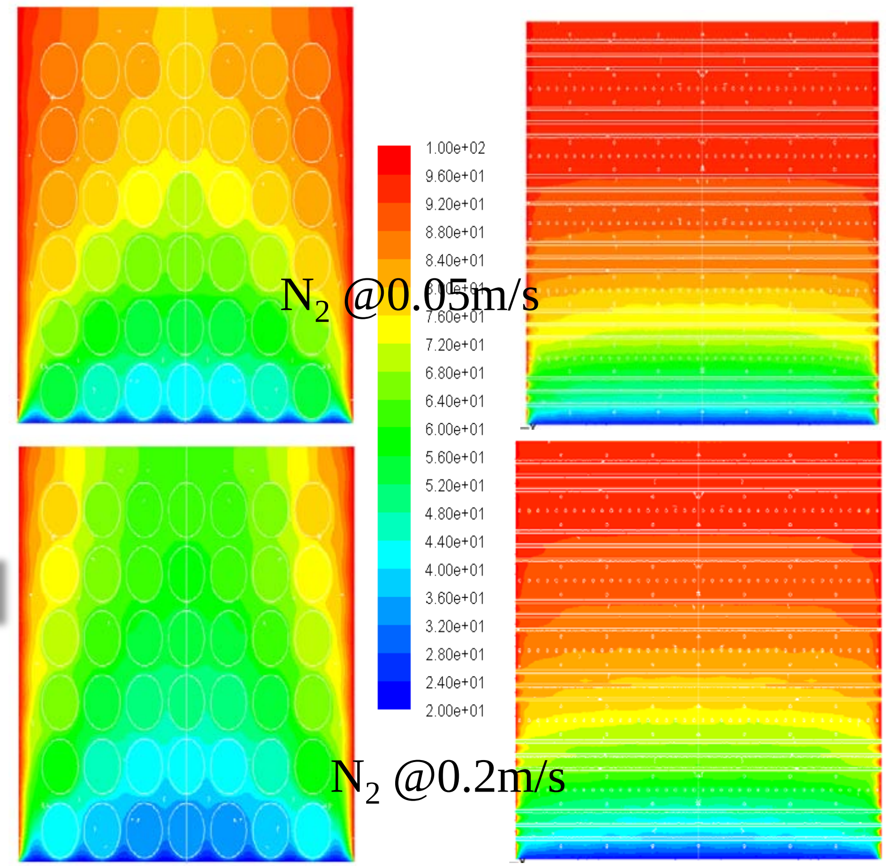


Packed Bed (60 vol.%)

Microfibrous Bed (20 vol.%)



Temperature Profile



Packed Bed (60 vol.%)

Microfibrous Bed (20 vol.%)

Compared to Packed Bed, Microfibrous bed provides much uniform temperature and velocity profile inside the bed. Thus, reaction can be considered to take place in a near-isothermal, plug flow condition.

Cu MFEC Performance in FTS

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- Centerline temperature rise from reactor wall
- ¾ inch O.D. downflow reactor, 15% Co/Al_2O_3 Pressure 20bar;
- Utilize a 1/8 inch 6-point thermocouple to indicate the temperature profile at centerline during the FTS reaction;
- PB was diluted with fresh alumina to same catalyst density;
- Same catalyst bed volume, 15.7cc(2.5g), locates from point 3 to 6,

Centerline temperature rise from reactor wall (T-Twall) @ steady state reaction

		Packed Bed		Copper MFEC	
flow rate /h^{-1}		830.4		830.4	
Wall T /˚C		225		235	
Conversion		0.543		0.538	
Point Location		T /˚C	T-Twall /˚C	T /˚C	T-Twall /˚C
Gas heat Up	1	216.4	-8.6	226.5	-8.5
	2	219.6	-5.4	228.5	-6.5
	3	222.6	-2.4	232.2	-2.8
reaction Section	4	228.7	3.7	234.9	-0.1
	5	231.9	6.9	237.1	2.1
	6	229.5	4.5	235.8	0.8
Average 4~6		230.03	5.03	235.93	0.93

$$T_c \approx T_{wall}$$

Alpha_220C=0.86

ASF FTS Product Distribution

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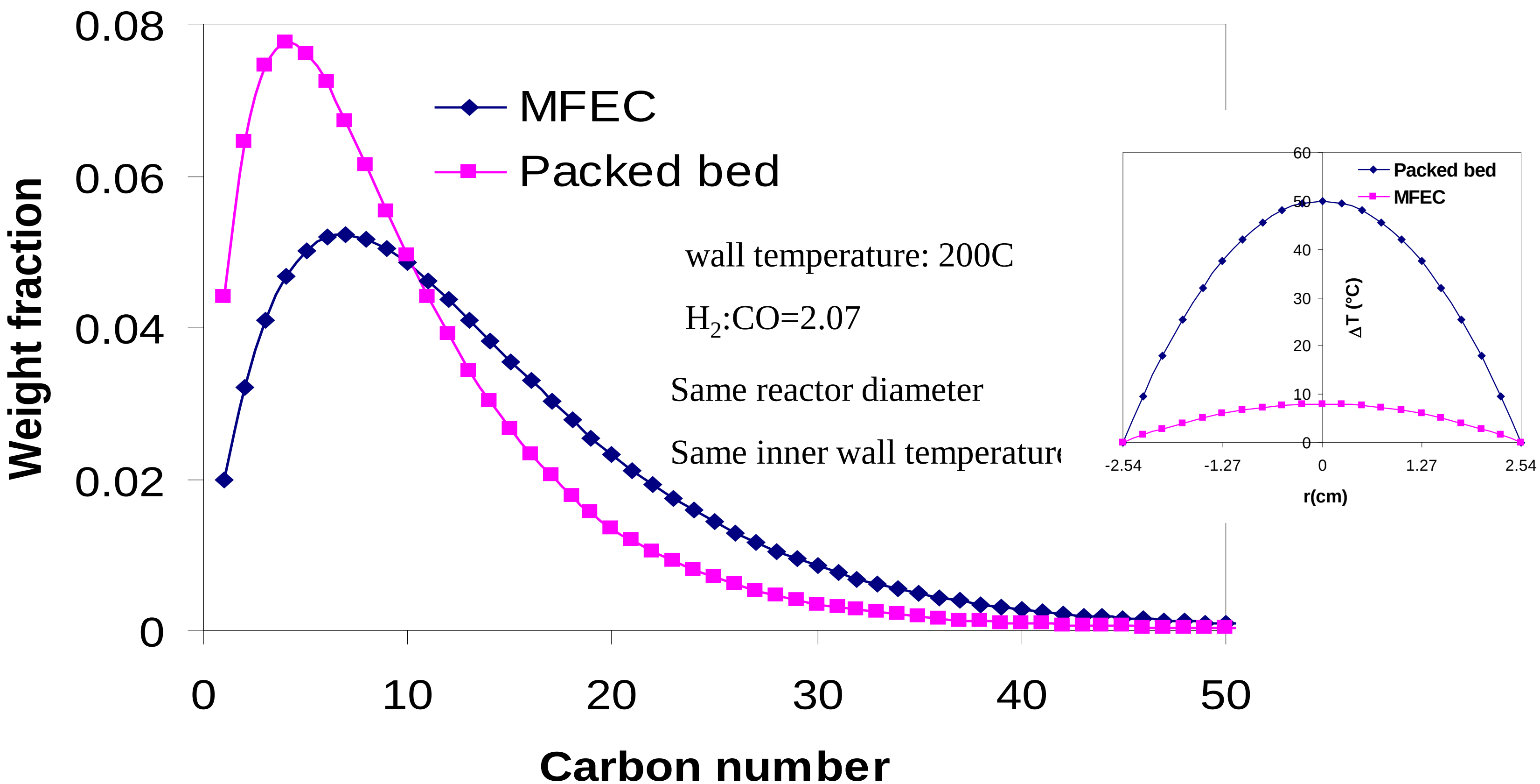


Assumptions:

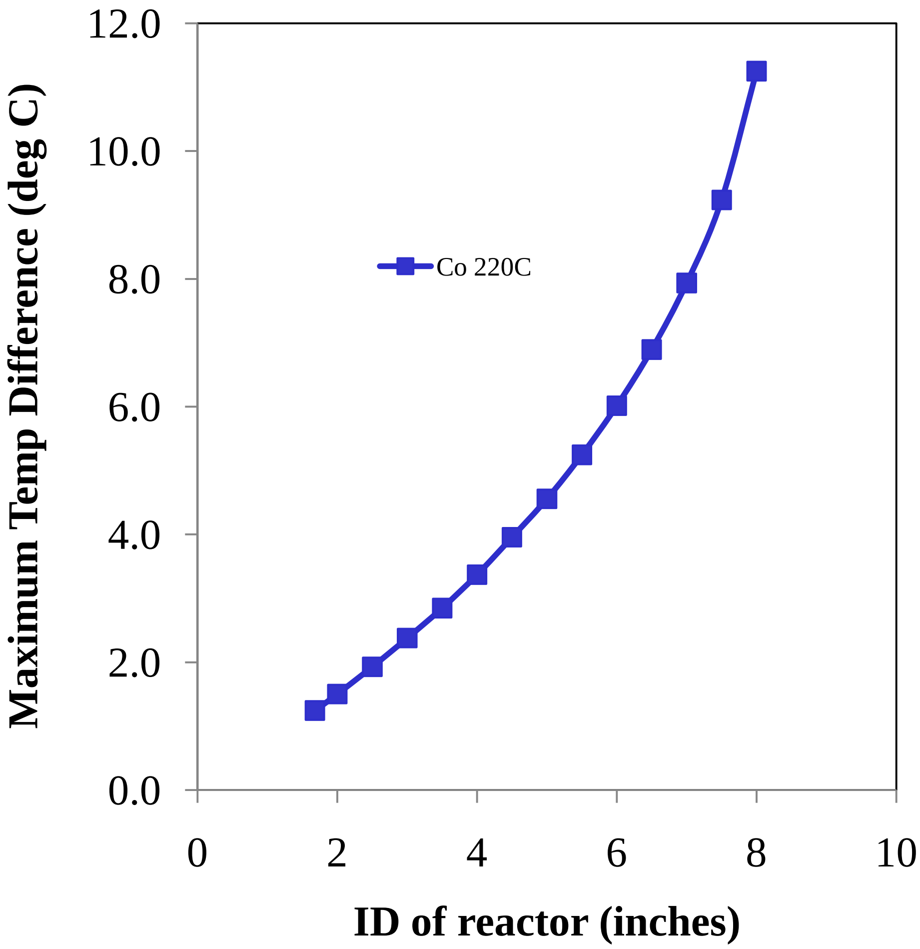
(1) Plug flow, (2) Temperature gradient in packed bed is 50 C and that in MFEC is 8 C w/ 5vol% fiber

Calculation based on Ru catalyst, $\alpha = 1 - 0.00343 \cdot (T - 165)$ (T in C) [1]

ASF model : $M_i = (1-\alpha) \cdot \alpha^{(i-1)}$ (M_i molar fraction of C_i)

[1] Fit to Ru data in Fig. 13 pg. 275, Catal. Rev. Sci. Eng., 41(3&4), 255-318 (1999).

Large Reactor Size



For Packed Bed Tubular Reactor:
reactor size limitation: ID<10mm without gas recycle[5] , ID<80mm with gas recycle[19].
Typical reactor tube id is no greater than 2 inches.

For MFEC Tubular Reactor :
No recycle
Max. ID for LT Co: 8 inches (20 cm)
Criteria: selectivity to JP5 drops to 95% of the highest possible selectivity at optimized reaction conditions.

Part count of MFEC FT reactor is 1/16 of a typical FT reactor of 2" ID.

ARGE Reactor (500 bpd) has 2050 tubes.

Storch et al 1951. The fischer-tropsch and related synthesis, John wiley & sons, New York
Van Vuuren 1982. CSIR CENG 432

Balance of Plant (BOP) Case Study

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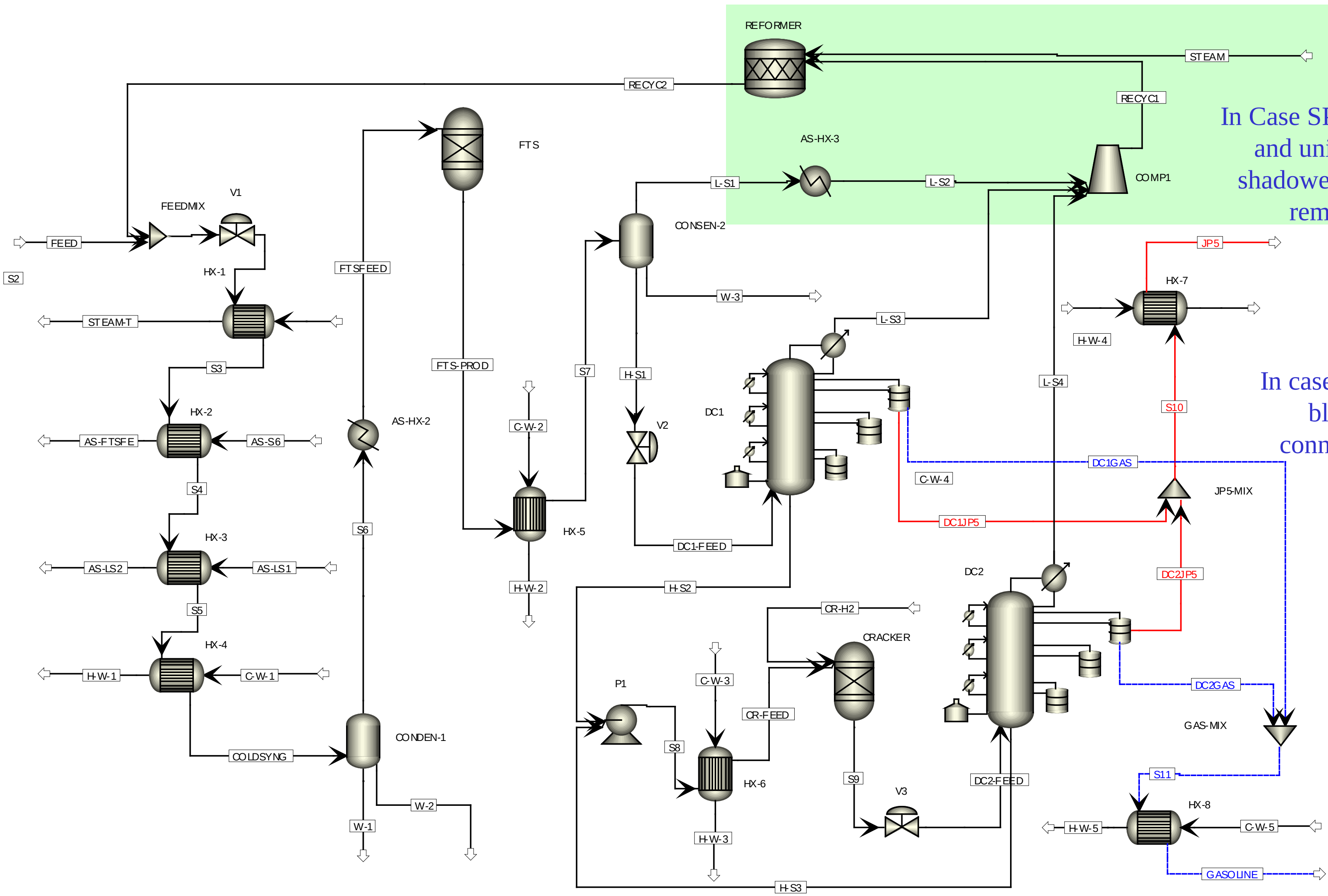
- Cases for producing JP5 only (J)
  - Packed Bed (J-PB)
  - MFEC (J-MFEC)
- Cases for producing JP5 and light naphtha (C_5-C_8)
  - Packed Bed (J+L-PB)
  - MFEC (J+L-MFEC)
- Single pass cases (SP): no light hydrocarbon recycle
  - Packed Bed (SP-PB)
  - MFEC (SP-MFEC)

ASPEN Flow Sheet for FTS



In Case SP's, all lines and units in the shadowed area are removed

In case JP's, all dashed blue lines and connected units are removed

Reduce Balance of Plant

Case #	BOP	J-PB	J-MFEC	J+L-PB	J+L-MFEC	SP-PB	SP-MFEC
FTS [1]	Wt. (t)	177	126	105	82	60	54
	Vol. (m^3)	135	103	80	66	43	43
Cracker	Wt. (t)	1.9	2.4	1.7	2.1	1.3	1.4
	Vol. (m^3)	2.3	3.5	1.8	2.8	0.85	1.1
Heat Exchanger	Wt. (t)	6.5	5.2	4.7	3.8	3	3
	Vol. (m^3)	7.1	5.2	4.7	3.5	2.7	2.7
Column	Wt. (t)	6.7	5.9	5.3	5.3	4.0	4.0
	Vol. (m^3)	13.9	11.4	8.6	8.6	4.3	4.4
Other	Steam reformer, compressors, valves, condensers, pumps and pipes are not included						
Total	Wt. (t)	192	139	116	93	68	62
	Vol. (m^3)	158	123	95	81	75	75
Product bbd	Jet fuel	500	500	300	333	140	185
	C5-C8			200	167	95	85

Other Applications

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- Other Exothermic Reactions/Processes
  - Methanol, maleic anhydride, phthalic anhydride, formaldehyde, acrylonitrile, acrylic acid, 1,2-dichloroethane, and vinyl chloride, air compression, concentrated acid dilution, vapor condensation
- Other Endothermic Reactions/Processes
  - steam methane reforming and liquid evaporation

Summary

IntraMicron

- MFEC can reduced the catalyst loading by using small sized particles.
- MFEC can provide near-isothermal temperature profile inside the reactor.
- MFEC bed can provide temperature control and improve the product selectivity.
- BOP of alternative fuel production platforms can be reduced and more logistic.

Acknowledgement

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Questions?