Status and Developments in Fischer-Tropsch Synthesis

Issues of Importance to Biomass Conversion and Jetfuel Production

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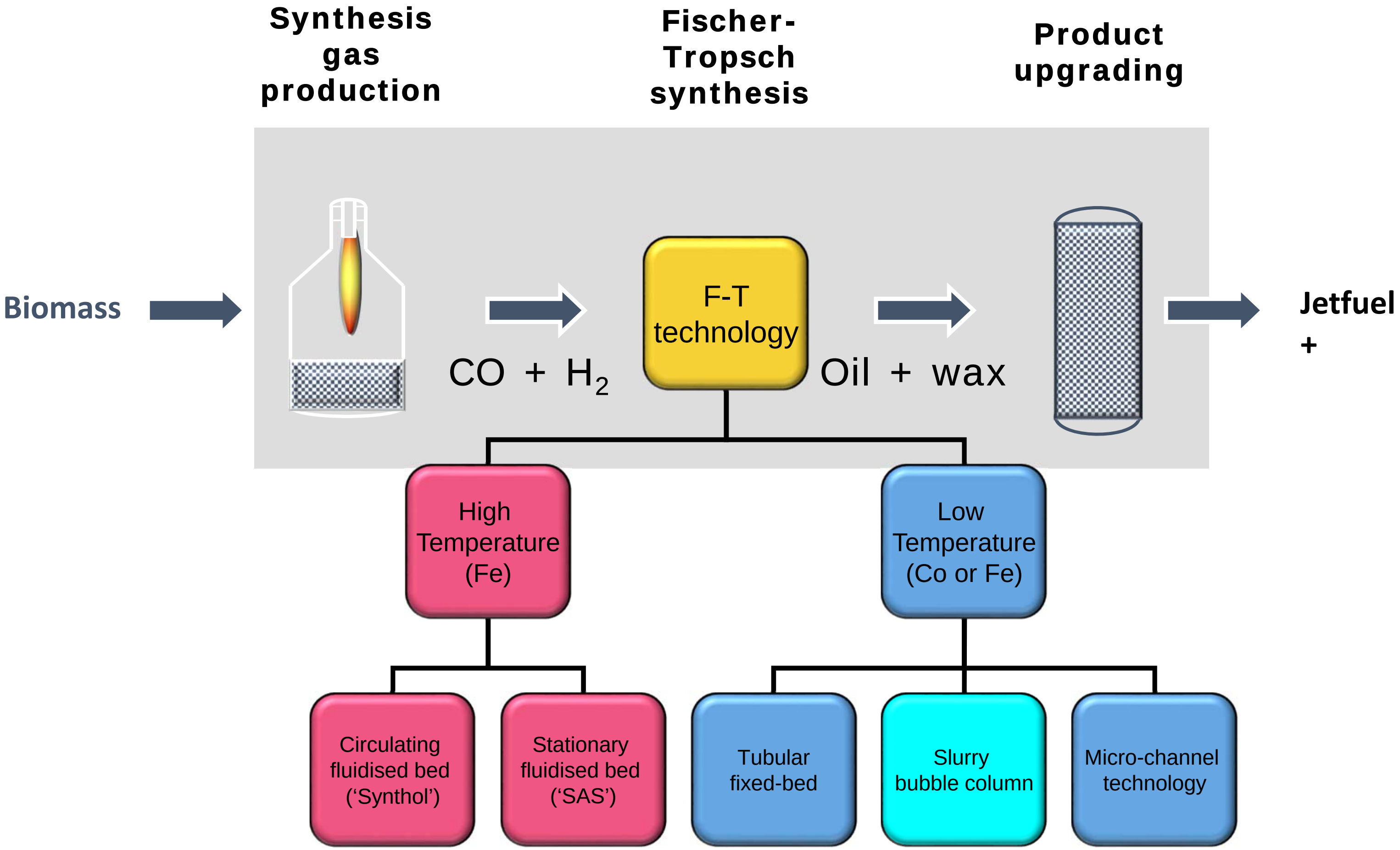
The Fischer-Tropsch Process



Synthesis gas production

Fischer-Tropsch synthesis

Product upgrading

Biomass

$CO + H_2$

F-T technology

Oil + wax

Jetfuel

+

High Temperature (Fe)

Low Temperature (Co or Fe)

Circulating fluidised bed ('Synthol')

Stationary fluidised bed ('SAS')

Tubular fixed-bed

Slurry bubble column

Micro-channel technology

Figure: Based on Dag Schanke, Statoil, 2009

Key Challenges in Biomass-to-Fuels

- Challenging feedstock
    - High water content
    - High oxygen content
        - Very low energy efficiency
        - Low carbon efficiency
    - Moderate H_2/CO ratio
        - Need to import hydrogen or release CO_2
    - Distributed feedstock
        - Optimal process integration is difficult
    - High level of impurities
        - Severe impurity removal and control

There are significant implications on the Fischer-Tropsch synthesis and on overall process design

Key FT related technology elements

- Catalyst
  - Iron or cobalt
- Reactor technology
  - Fixed-bed
  - Slurry
  - Microchannel
- Process design FT
  - The H_2/CO ratio
  - Conversion and recycle
- Product separation and upgrading
  - Jetfuel
- Overall process design
  - FT integration with biomass treatment and gasification
  - Water management

Potential providers of Cobalt Fischer-Tropsch Technology

Technology provider	Support/ modifier	Promoter	Reactor type	Reactor scale (bbl/d)	Reference
Sasol	γ-Alumina/ Si (TEOS)	Platinum	Slurry	16,000	1
Shell	Titania	Mn; V	Fixed-bed	6,000	2
GTL.F1	Ni-aluminate/ α-Alumina	Rhenium	Slurry	1,000	3
ENI/IFP/ Axens	γ-alumina/ SiO_2;spinel	?	Slurry	20	4
Nippon Oil	Silica/ Zirconia	Ruthenium	Slurry	500	5
Syntroleum	γ-Alumina/ Si (TEOS); La	Ruthenium	Slurry	80	6
BP	ZnO	?	Fixed-bed		7
Exxon Mobil	Titania/ γ-Alumina	Rhenium	Slurry	200	8
Conoco-Phillips	γ-Alumina/ Boron	Ru/Pt/Re	Slurry	400	9
Compact GTL	Alumina?	Re?	Microchannel	500	10
Oxford cat. /Velocys	Titania-silica	Re	Microchannel	1000	11

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2. R.J. Dogterom, C.M.A.M. Mesters and M.J. Reynhout, Process for preparing a hydrocarbon synthesis catalyst, PCT patent WO2007068731 A1, Shell, 2007.
3. E. Rytter, T.H. Skagseth, H. Wigum and N. Sincadu, Enhanced strength of alumina based Co Fischer-Tropsch catalyst, PCT patent WO 2005072866, Statoil, 2005.
4. G. Bellussi, L.C. Carluccio, R. Zenarro and G. del Piero, Process for the preparation of FT catalysts with a high mechanical, thermal and chemical stability, WO2007009680 A1, ENI/IFP, 2007.
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7. J.J.H.M. Font Freide, J.P.Collins, B. Nay and C. Sharp, Stud. Surf. Sci. Catal., 163 (2007) 37.
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9. N. Srinivasan, R.L. Espinoza, K.L. Coy and K. Jothimurugesan, Fischer-Tropsch catalysts using multiple precursors, patent US6822008 B2, ConocoPhillips, 2004.
10. http://www.compactgtl.com
11. http://www.velocys.com

Iron or cobalt ?

- The hydrogen issue
  - Iron will produce needed hydrogen in-situ by the water-gas-shift reaction

$$CO + H_2O \rightarrow CO_2 + H_2$$

  - Cobalt needs a separate WGS reactor
  - *The best choice is not obvious. Need process simulations.*

- Cobalt has significantly lower deactivation rate

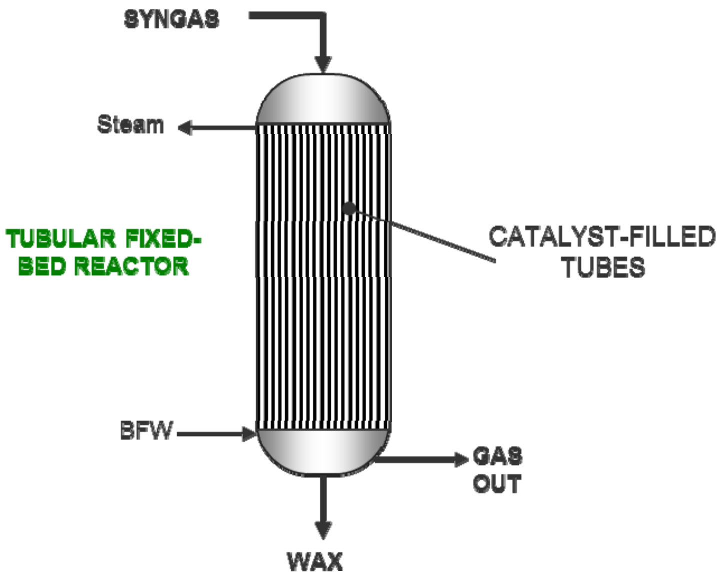
- Cobalt provides more desired product/less byproducts (oxygenates)

- Iron is cheap

Cobalt is the choice for biomass to jetfuel

Reactor technologies

Tubular fixed-bed



Principles of design and operation

- Catalyst-particles in long, small diameter tubes
- Syngas inlet at top
- 2-phase mixture (wax + gas) exits bottom
- Boiler feed water in reactor shell
- Heat removal by steam generation

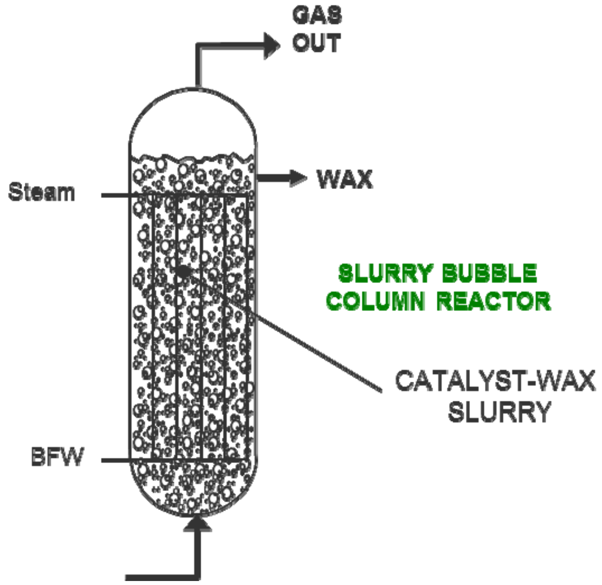
Strong points

- Long established scale-up methodology
- Strong economy of scale to maximum size
- Plug flow behavior
- “Simple” operations
- Very high strength catalyst not required
- Generally excellent catalyst/wax separation
- Bed inlet acts as poison removal zone
- Simple, in-situ catalyst regeneration process

Adapted and modified from Velocys

Reactor technologies

Slurry bubble column



Principles of design and operation

- Catalyst-wax slurry in reactor shell
- Low catalyst volume fraction (< 20%)
- Syngas bubbled through slurry
- Wax removal by internal filtration
- Boiler feed water in reactor tubes
- Heat removal by steam generation

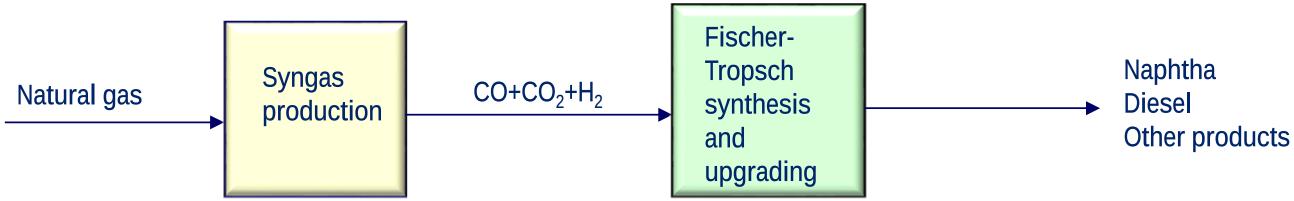
Strong points

- Isothermal behavior – thermally stable
- Generally robust to upsets
- Very strong economy of scale
- Accommodates high activity catalysts
- Low DP (liquid head and gas distributor)
- Small particles not mass transfer limited
- Catalyst replacement on line
- High on-stream factor
- Tail gas recycle only to achieve high conversion

Adapted and modified from Velocys

Demonstration of the GTL technology

Old slide



Natural gas

Syngas production

CO+CO_2+H_2

Fischer-Tropsch synthesis and upgrading

Naphtha
Diesel
Other products

Semi-commercial plant, Mossel bay, South-Africa:

Production capacity : Up to **1000 bpd** of oil and wax

Start-up : 2Q 2004

Investment cost : about 75 mill. USD

Contractor : Technip SpA Italy

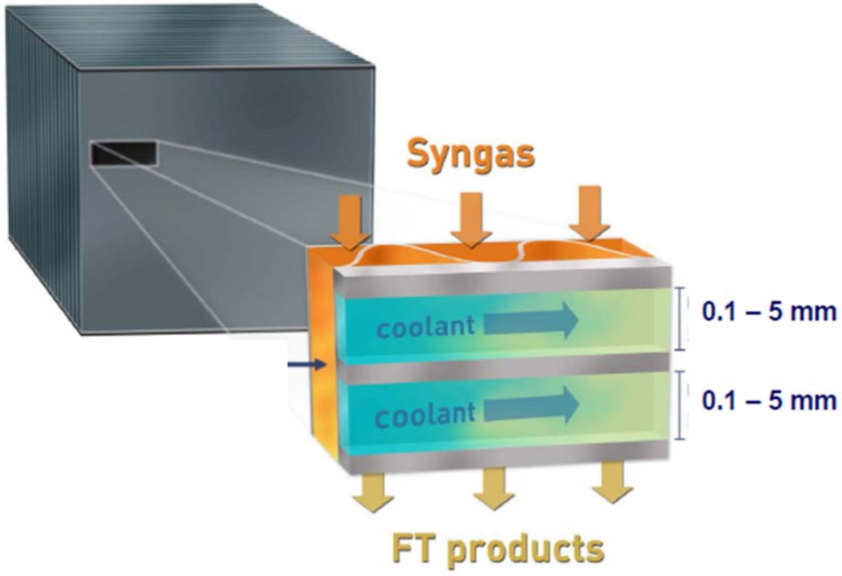
Project execution : Petro SA

Technology licensor : **GTL.F1** (Statoil, PetroSA, Lurgi)

The technology was declared commercial in October 2006

Reactor technologies

Microchannel



Principles of design and operation

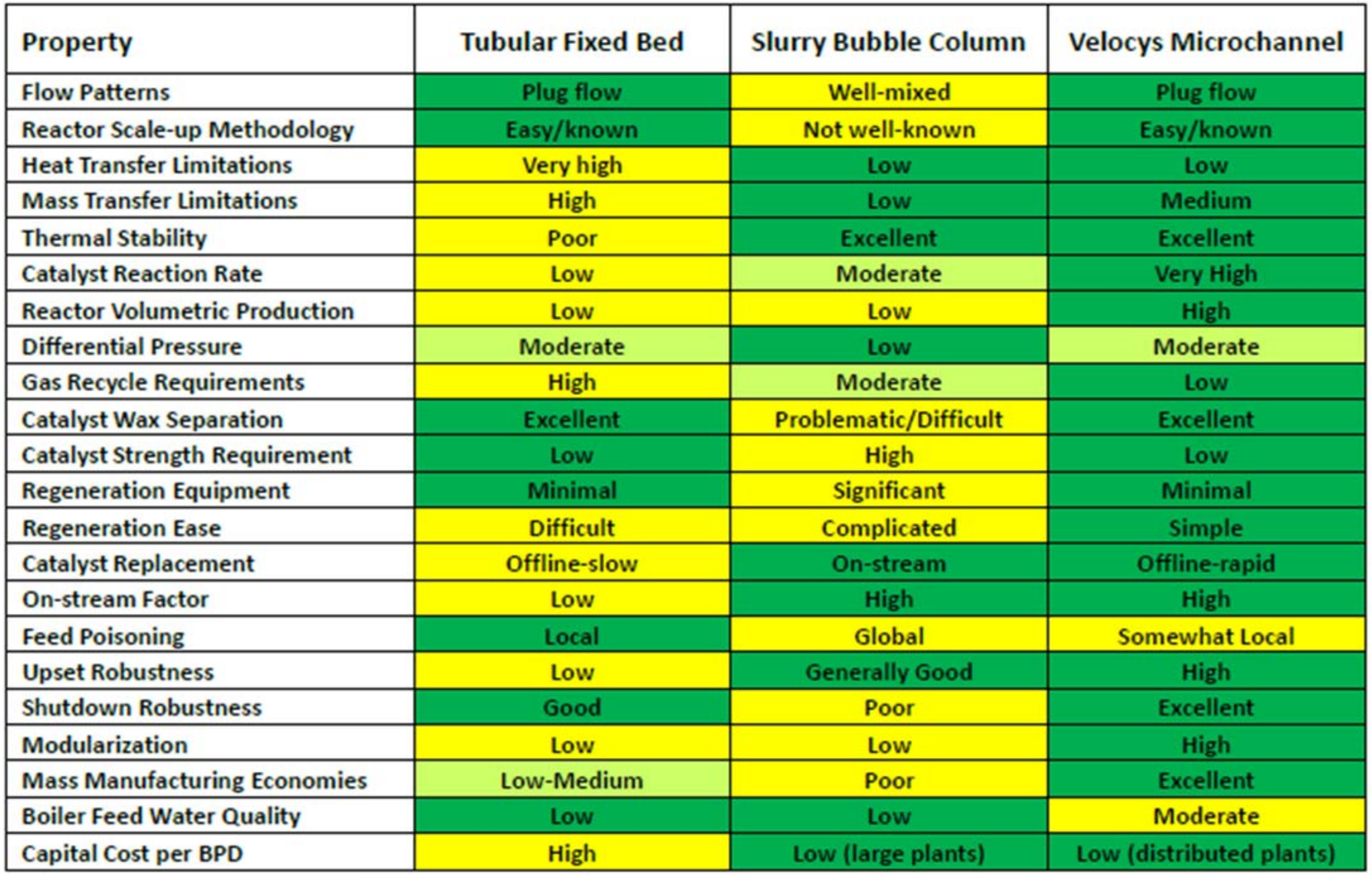
- Particulate catalyst in small channels
- High catalyst volume fraction (~50%)
- Syngas downflow, products exit bottom
- Cross-flow coolant water/steam generation
- Heat removal by steam generation

Strong points

- Isothermal behavior – thermally stable
- Extremely robust to upsets
- Strong economy of mass manufacturing
- Accommodates high activity catalysts
- Installed spares relatively cheap
- High on-stream factor
- Tail gas recycle only to achieve high conversion
- Extremely high volumetric productivity
- Ease of modularization

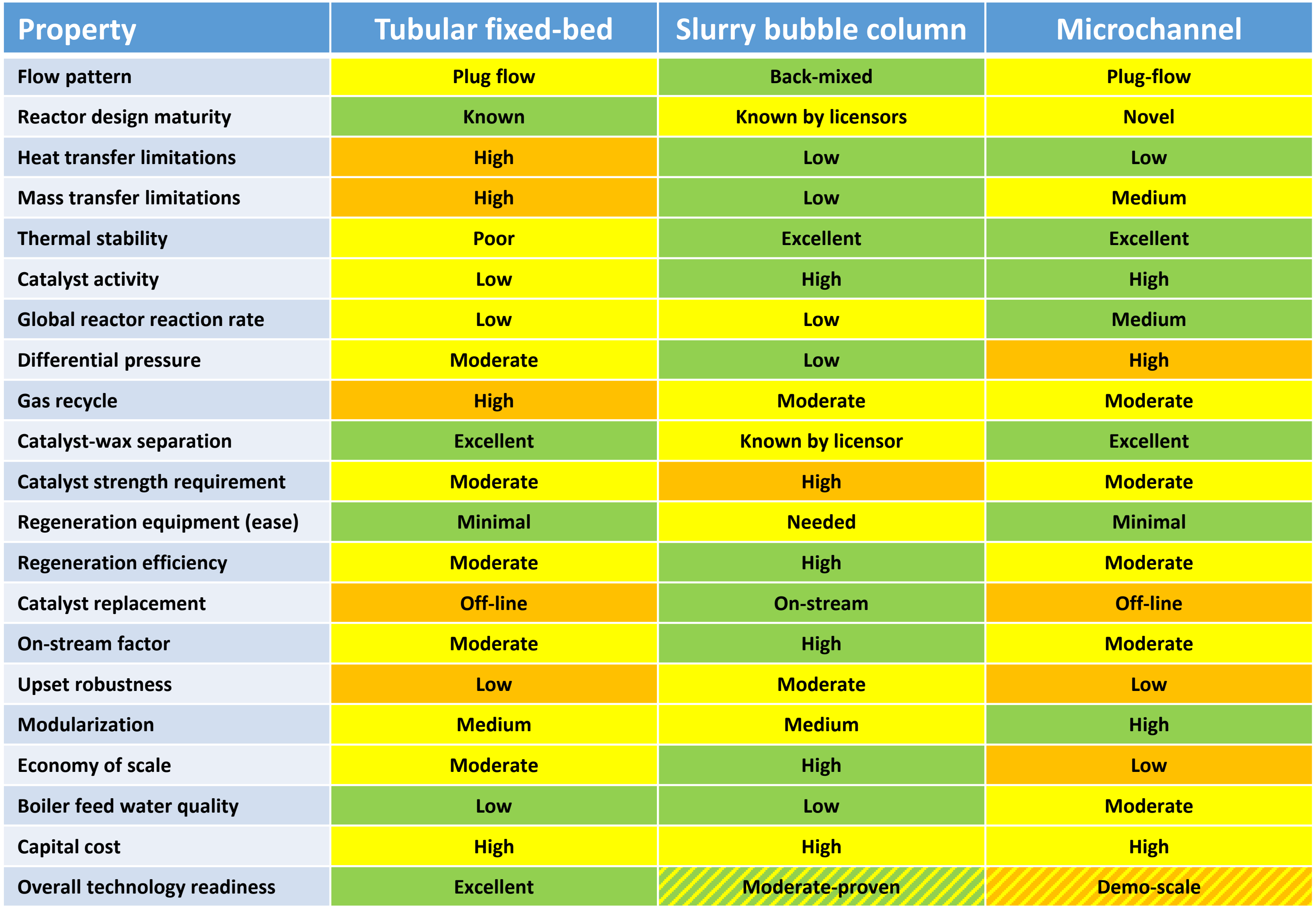
Adapted and modified from Velocys

Velocys Microchannel FT Reactor Score Card



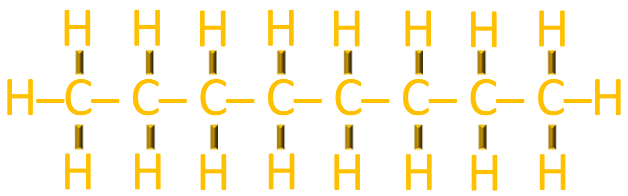
Property	Tubular Fixed Bed	Slurry Bubble Column	Velocys Microchannel
Flow Patterns	Plug flow	Well-mixed	Plug flow
Reactor Scale-up Methodology	Easy/known	Not well-known	Easy/known
Heat Transfer Limitations	Very high	Low	Low
Mass Transfer Limitations	High	Low	Medium
Thermal Stability	Poor	Excellent	Excellent
Catalyst Reaction Rate	Low	Moderate	Very High
Reactor Volumetric Production	Low	Low	High
Differential Pressure	Moderate	Low	Moderate
Gas Recycle Requirements	High	Moderate	Low
Catalyst Wax Separation	Excellent	Problematic/Difficult	Excellent
Catalyst Strength Requirement	Low	High	Low
Regeneration Equipment	Minimal	Significant	Minimal
Regeneration Ease	Difficult	Complicated	Simple
Catalyst Replacement	Offline-slow	On-stream	Offline-rapid
On-stream Factor	Low	High	High
Feed Poisoning	Local	Global	Somewhat Local
Upset Robustness	Low	Generally Good	High
Shutdown Robustness	Good	Poor	Excellent
Modularization	Low	Low	High
Mass Manufacturing Economies	Low-Medium	Poor	Excellent
Boiler Feed Water Quality	Low	Low	Moderate
Capital Cost per BPD	High	Low (large plants)	Low (distributed plants)

Rytter’s provisional FT reactor scorecard



Property	Tubular fixed-bed	Slurry bubble column	Microchannel
Flow pattern	Plug flow	Back-mixed	Plug-flow
Reactor design maturity	Known	Known by licensors	Novel
Heat transfer limitations	High	Low	Low
Mass transfer limitations	High	Low	Medium
Thermal stability	Poor	Excellent	Excellent
Catalyst activity	Low	High	High
Global reactor reaction rate	Low	Low	Medium
Differential pressure	Moderate	Low	High
Gas recycle	High	Moderate	Moderate
Catalyst-wax separation	Excellent	Known by licensor	Excellent
Catalyst strength requirement	Moderate	High	Moderate
Regeneration equipment (ease)	Minimal	Needed	Minimal
Regeneration efficiency	Moderate	High	Moderate
Catalyst replacement	Off-line	On-stream	Off-line
On-stream factor	Moderate	High	Moderate
Upset robustness	Low	Moderate	Low
Modularization	Medium	Medium	High
Economy of scale	Moderate	High	Low
Boiler feed water quality	Low	Low	Moderate
Capital cost	High	High	High
Overall technology readiness	Excellent	Moderate-proven	Demo-scale

The issue of the H_2/CO ratio



$$\begin{array}{cccccccccc} & H & H & H & H & H & H & H & H & \\ & | & | & | & | & | & | & | & | & \\ H- & C- & C- & C- & C- & C- & C- & C- & C & -H \\ & | & | & | & | & | & | & | & | & \\ & H & H & H & H & H & H & H & H & \end{array}$$

C_8H_{18} H/C = 2.25

$17\ H_2 + 8\ CO \rightarrow C_8H_{18} + 8\ H_2O$ $H_2/CO = 2.125$

- The H_2/CO consumption ratio is ca. 2.1
  - Feed to the FT reactor should, however, be significantly lower than 2.
- Composition of the syngas depends heavily on the gasification technology and operation
- The syngas composition needs to be predictable within reasonable ranges.

What has been reported for syngas composition ?

Tech-nology	Cond-itions	CO	H_2	H_2/CO	CO_2	CH_4	C_2-C_5	H_2S	N_2	Comment/ reference
Entrained-flow										
Chemrec	Air	8-12	10-15		15-17	0.2-1			55-65	[58,69]
	O_2	30	43	1.4	27	1		1.4	-	25–40 ppm COS
Choren	O_2	35-40	35-40		balance	small			small	[70]
KTI/Lurgi	Enr.air	50	27	0.54	14				6	[71]
UHDE		>85 (CO + H_2)			6-8	<0.1				[R7]
Fluidized-bed										
Cutec	Enr.air	22	31.6	1.4	33.6	7.9	1.8		3	[72]
ECN	Air	29	31	1.1	20	14	5			[61] 45 g/m^3 tar
Enerkem	O_2	20-24	20-24		30-35	8-12	10-20			[73]
Foster Wheeler	Air	15.5-17.5	10-12		14-17	5-7			45-50	Värnamo plant [74]
Güssing	15wt% H_2O	29.1	37.7	1.30	19.6	10.4	3.2		0.5-0.7	Tar free [55]
Fixed-bed or moving bed										
Cortus	Steam	14.9	70.3	4.7	22.9	1.8				[75]
		16.2	60.6	3.6	21.8	1.4				
Blue tower	Steam	20	50	2.5	25	5				[76]
Plasma										
Westing-house	23wt% H_2O	67.5	26.6	0.39	5.9					N_2 free basis [77]

From: Erling Rytter, Esther Ochoa-Fernández and Adil Fahmi, *Biomass-to-Liquids by the Fischer-Tropsch Process*

In: *Catalytic Process Development for Renewable Materials*, P. Imhof and J.C. van der Waal (Eds.), Wiley, 2013.

The compositional gap

Compound	Typical entrained –flow raw syngas composition	FT make-up gas specification
H_2	19 mol%	61 mol%
CO	58 mol%	32 mol%
CO_2	20 mol%	< 10 mol% total inerts
CH_4	0 mol%	
N_2	4 mol%	
NO_x	0 ppm	10 ppb
NH_3	20 ppm	1 ppm
HCN	0 ppm	10 ppb
H_2S	170 ppm	< 10 ppb sulfur
COS	20 ppm	

Add hydrogen

Remove CO_2

Once-through

Purification

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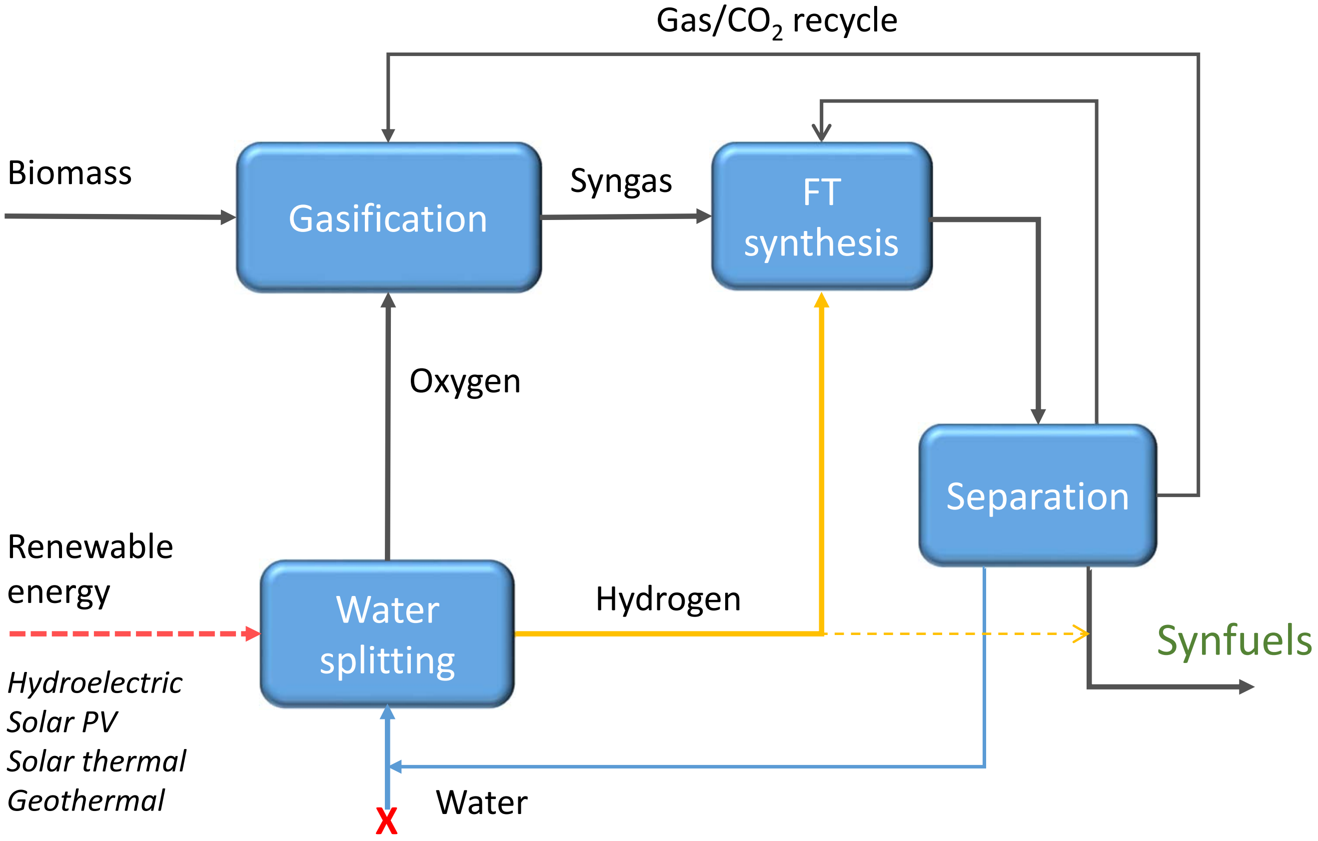
Enhanced energy efficiency in fuel synthesis from biomass



Gas/CO_2 recycle

Biomass

Gasification

Syngas

FT synthesis

Oxygen

Separation

Renewable energy

Hydroelectric
Solar PV
Solar thermal
Geothermal

Water splitting

Hydrogen

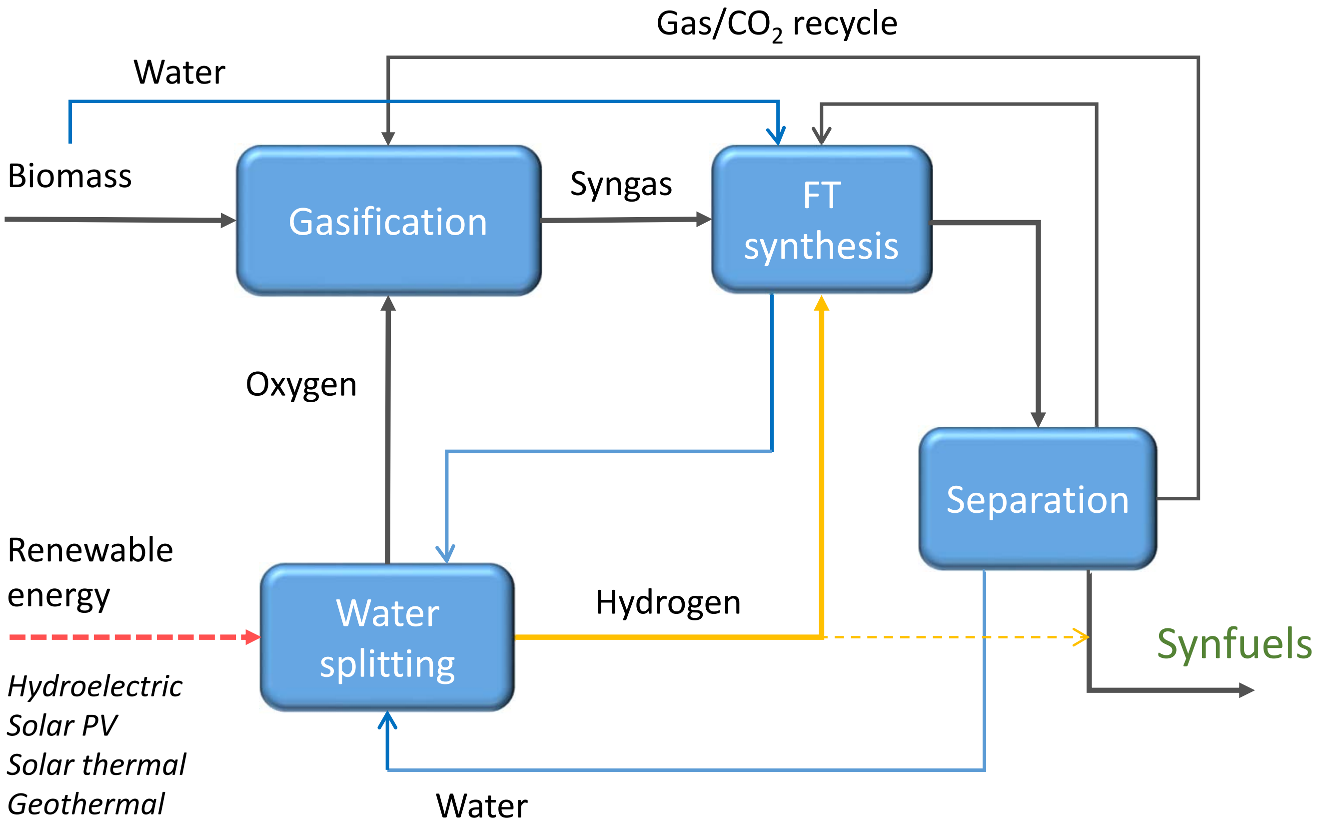
Synfuels

X

Water

Enhanced energy efficiency in fuel synthesis from biomass

Conceptual water management



Gas/CO_2 recycle

Water

Biomass

Gasification

Syngas

FT synthesis

Oxygen

Separation

Renewable energy

Hydroelectric
Solar PV
Solar thermal
Geothermal

Water splitting

Hydrogen

Synfuels

Water

Are efficiencies acceptable ?

	Arlanda 1 (Arlanda 2)	NREL 1	NREL 2	Statoil 1	Statoil 2	Statoil 3
Process conditions						
Feed LHV (MW_{th})	611(298)	417*	417*	790	559	493
Biomass	Grot and logs	Corn stover	Corn stover	Hard wood chips	Hard wood chips	Hard wood chips
Drying/humidity	50→20 %	25→10 %	25→10 %	35 %	35→15 %	35→7 %
Pretreatment**	-	-	-	-	Torrefaction	Pyrolysis
Gasifier feed**	30-50 mm	6 mm	1 mm	3-5 cm	0.1 mm	Liquid
Gasifier type	Bubbling fluidized-bed	Bubbling fluidized-bed	Entrained-flow	Circulating fluidized-bed	Entrained-flow	Entrained-flow
Gasifier design	Carbona	GTI	Texaco	Foster Wheeler/ VTT	Siemens	Siemens
Pressure/ temperature	10-20 bar 850-950 °C	28 bar 870 °C	28 bar 1300 °C	10 bar 865 °C	35 bar 1500 °C	35 bar 1500 °C
Syngas conditioning*** **CO_2 removal**	Tar reformer Rectisol	Tar reformer MDEA	MDEA	Tar reformer Water wash	Water wash	Water wash
FT-technology	Slurry Co-catalyst	Reactor n.a. Co-catalyst	Reactor n.a. Co-catalyst	Slurry Co-catalyst	Slurry Co-catalyst	Slurry Co-catalyst
FT-conditions****	n.a.	25 bar 200 °C 40 % conv.	25 bar 200 °C 40 % conv.	20 bar 226 °C 60 % conv.	20 bar 226 °C 60 % conv.	20 bar 226 °C 60 % conv.
Efficiencies						
Efficiency reported	44 (46)	43	53	26	29	37
Efficiency calculated*	45 (46)	43	54	**27**	**27**	**33**
Carbon eff. reported	n.a.	39	50	-	-	42
Carbon eff. calc.*	46 (47)	39	50	**24**	**33**	**38**

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In: *Catalytic Process Development for Renewable Materials*, P. Imhof and J.C. van der Waal (Eds.), Wiley, 2013.

Recommendations

- Select cobalt catalyst
- Select slurry reactor

but most importantly:

- Select gasification technology compatible with FTS
- Develop an integrated and optimized process design
    - Basic flow-sheet
    - Energy efficiency
    - Carbon efficiency
    - Water management
- Consider hydrogen added from other energy sources
    - Water electrolysis most realistic in short term