Synthesis Gas Utilization

The Fischer-Tropsch Process

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Alberta Innovates Technology Futures

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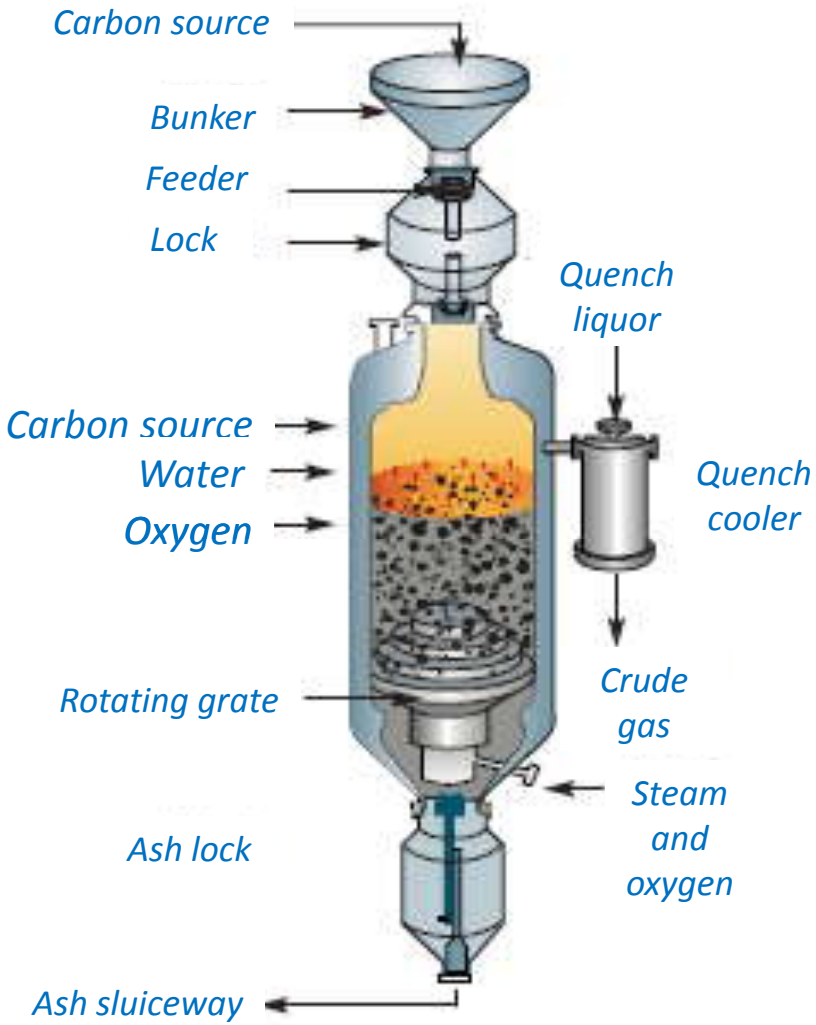
Sponsored by Alberta Plastics Recycling Association,
The Canadian Plastics Industry Association, and the American Chemistry Council
in conjunction with the annual conference of the Recycling Council of Alberta

Outline

- Syngas generation i.e. Gasification
- Syngas, a powerful reagent
- Syngas to Liquids
- Conclusions
- Questions

Gasification



Chemistry…

$C + H_2O \rightarrow CO + H_2$

$C + 0.5O_2 \rightarrow CO$

$CO + H_2O \Leftrightarrow CO_2 + H_2$

$CO + 3H_2 \rightarrow CH_4 + 2H_2O$

But also…

H_2S, COS, R-SH, R-S-S-R',

HCN, NH_3

Tars, volatile metals

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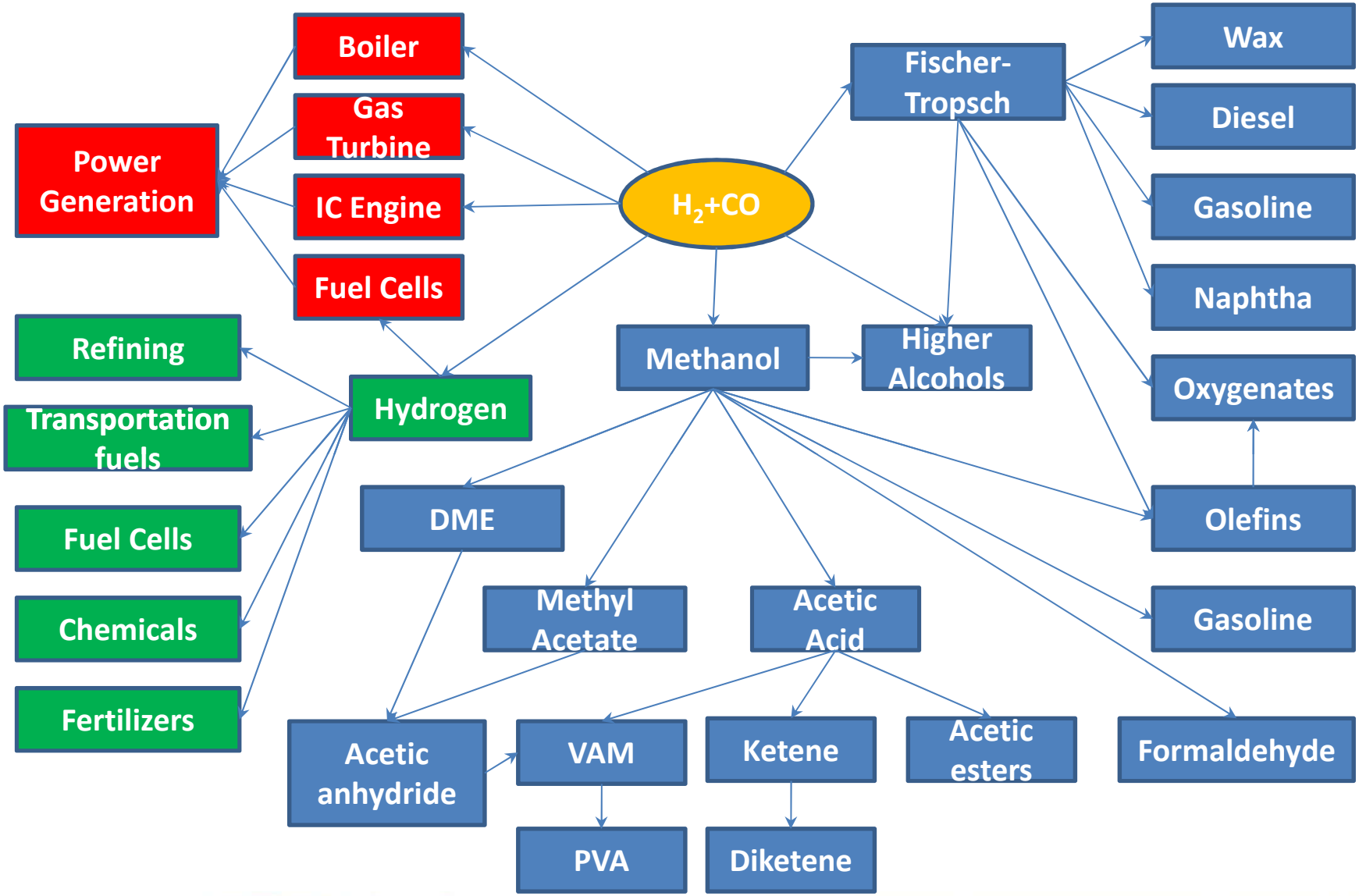
Collings, 2002

Syngas as building block



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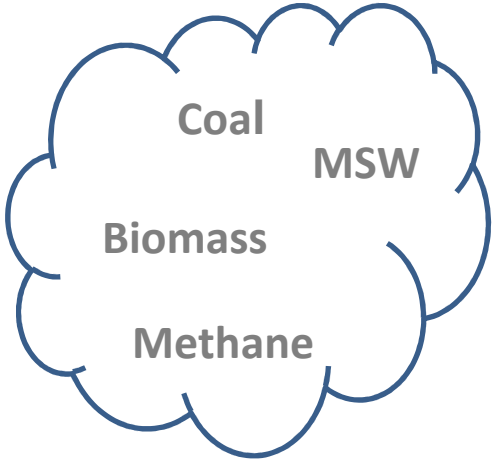
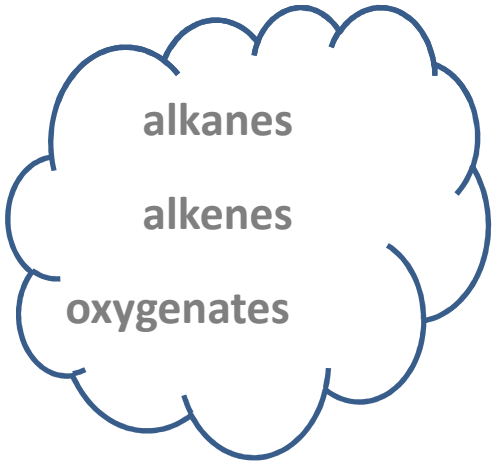
What is "Fischer-Tropsch"?

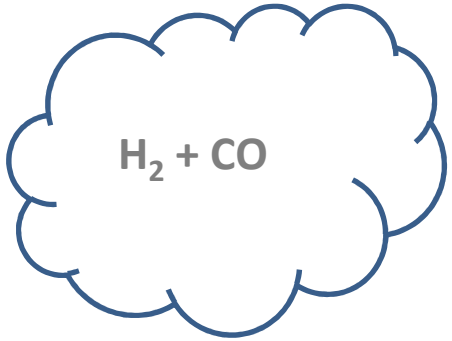
Catalytically mediated chemical process that….



…converts carbonaceous material



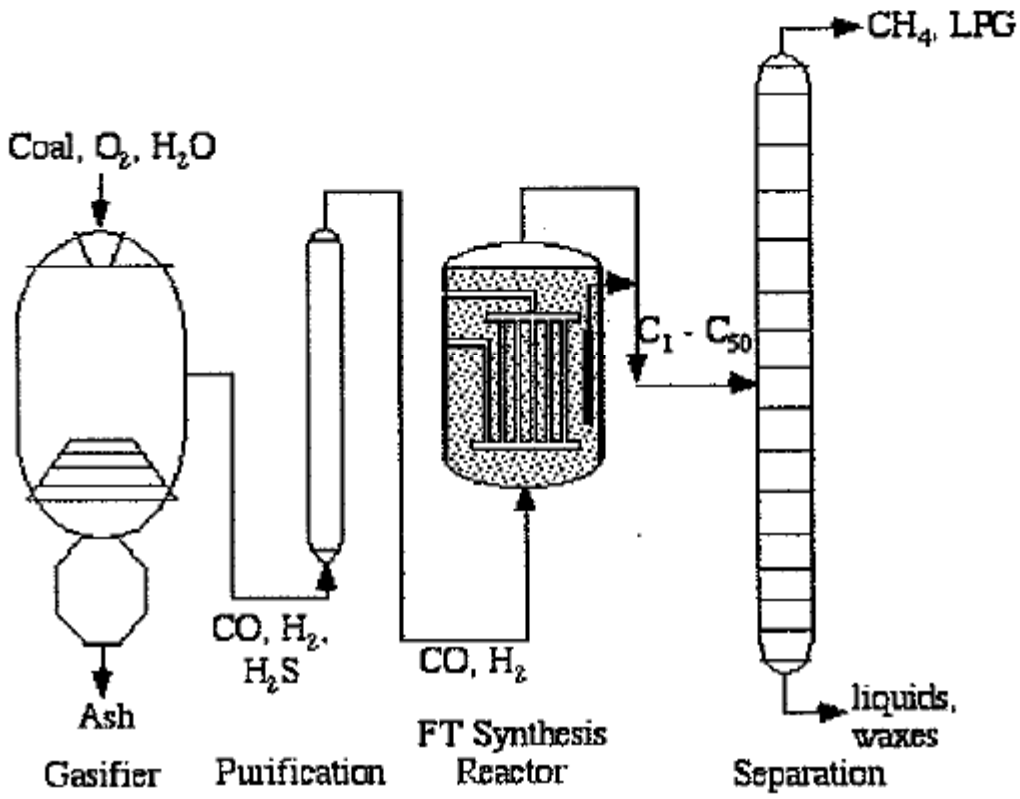
…into hydrocarbon products



…*via* "synthesis gas" (syngas)

Elements of "Fischer-Tropsch"

IB. Typical Simplified Coal to Liquids PFD
(BTL nearly identical)



$$Coal + O_2 + H_2O \rightarrow CO + H_2 \rightarrow -C-C-C-C- + H_2O$$

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Bartholomew and Hecker, 2009

Conditions

H_2/CO

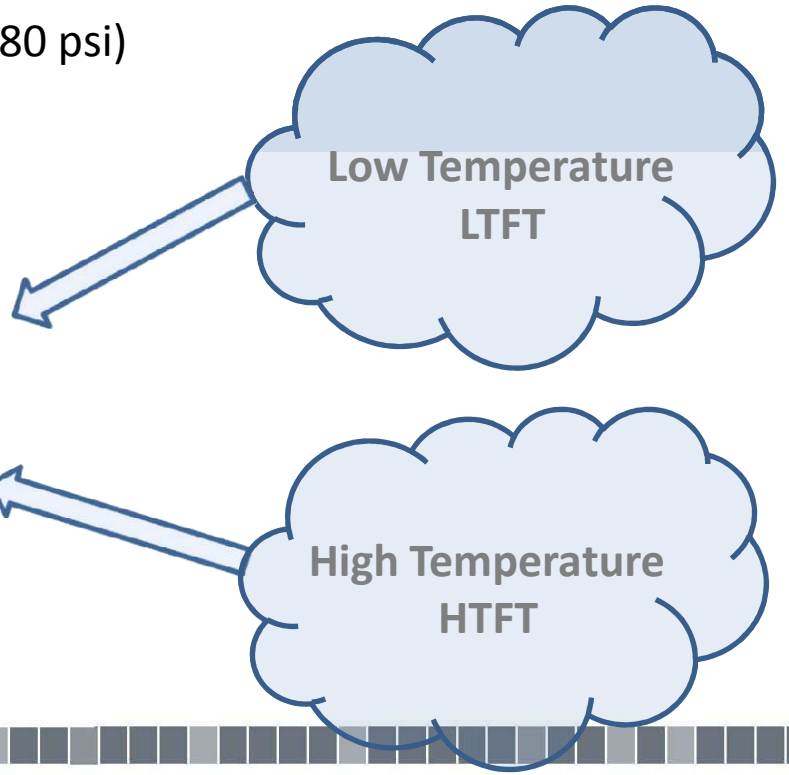
1.0 – 2.2

Pressure

20 – 40 bar (290 – 580 psi)

Temperature

1. 220°C – 240°C
2. 300°C – 350°C



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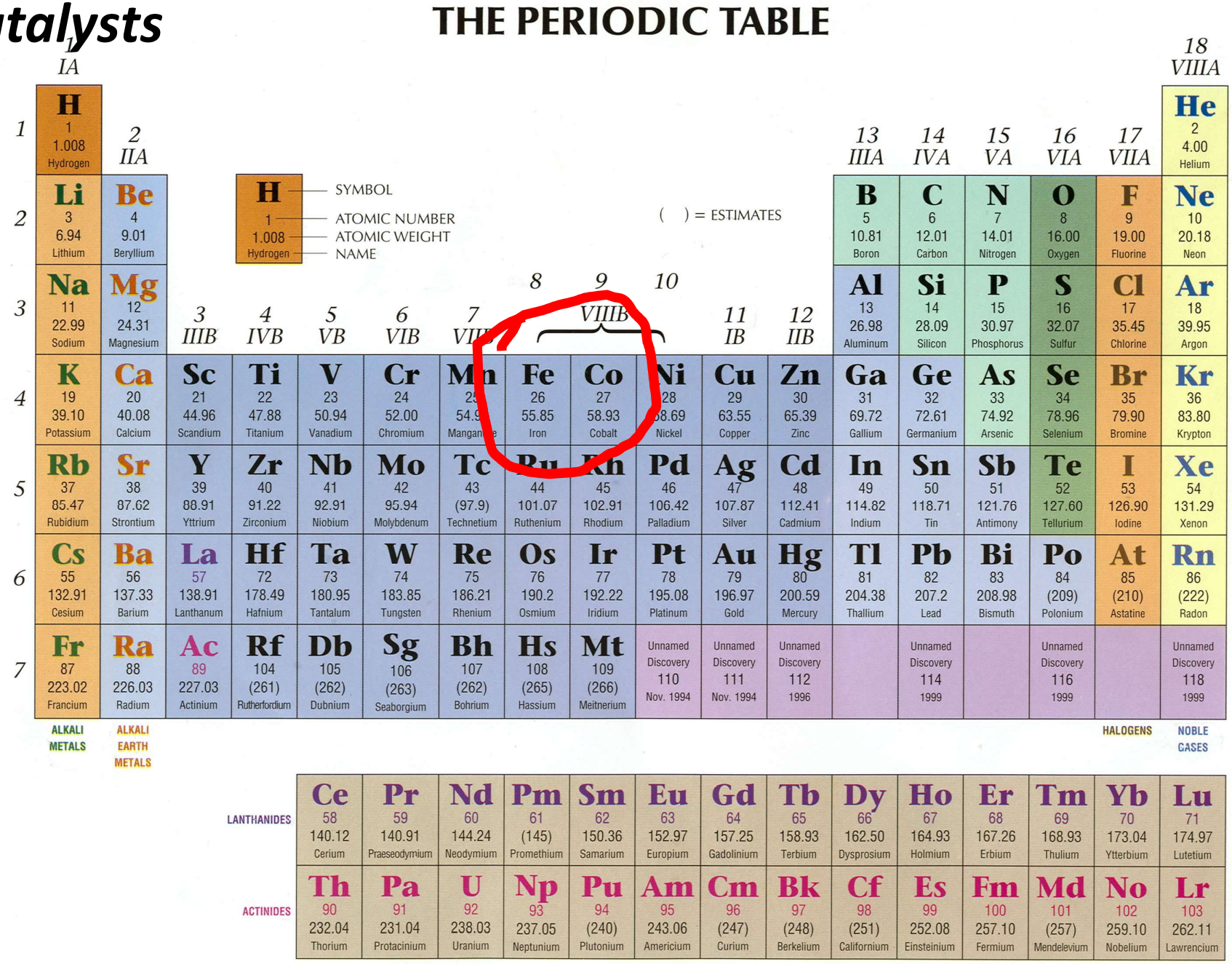
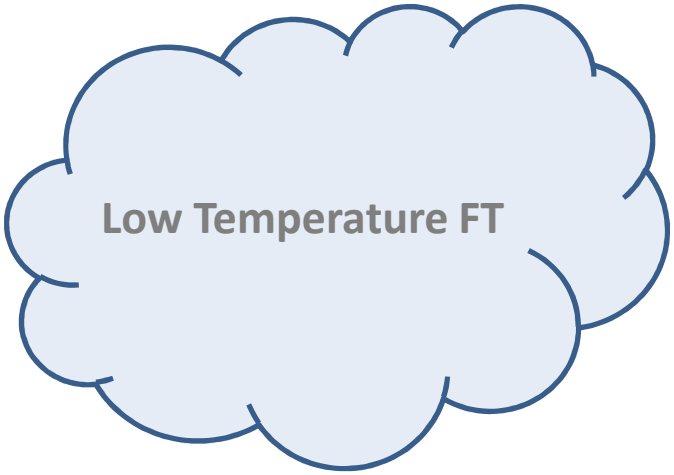
Catalysts

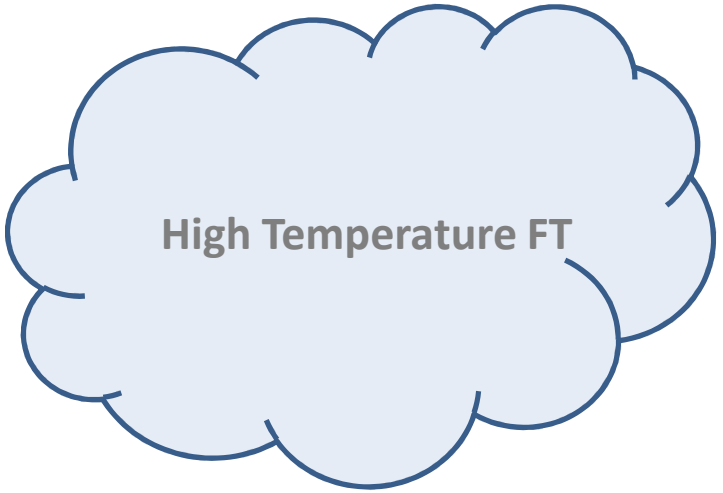

THE PERIODIC TABLE
1 IA
2 IIA
3 IIIB
4 IVB
5 VB
6 VIB
7 VIIB
8
9 VIIIB
10
11 IB
12 IIB
13 IIIA
14 IVA
15 VA
16 VIA
17 VIIA
18 VIIIA
H 1 1.008 Hydrogen
SYMBOL
ATOMIC NUMBER
ATOMIC WEIGHT
NAME
( ) = ESTIMATES
He 2 4.00 Helium
Li 3 6.94 Lithium
Be 4 9.01 Beryllium
B 5 10.81 Boron
C 6 12.01 Carbon
N 7 14.01 Nitrogen
O 8 16.00 Oxygen
F 9 19.00 Fluorine
Ne 10 20.18 Neon
Na 11 22.99 Sodium
Mg 12 24.31 Magnesium
Al 13 26.98 Aluminum
Si 14 28.09 Silicon
P 15 30.97 Phosphorus
S 16 32.07 Sulfur
Cl 17 35.45 Chlorine
Ar 18 39.95 Argon
K 19 39.10 Potassium
Ca 20 40.08 Calcium
Sc 21 44.96 Scandium
Ti 22 47.88 Titanium
V 23 50.94 Vanadium
Cr 24 52.00 Chromium
Fe 26 55.85 Iron
Co 27 58.93 Cobalt
Ni 28 Nickel
Cu 29 63.55 Copper
Zn 30 65.39 Zinc
Ga 31 69.72 Gallium
Ge 32 72.61 Germanium
As 33 74.92 Arsenic
Se 34 78.96 Selenium
Br 35 79.90 Bromine
Kr 36 83.80 Krypton
Rb 37 85.47 Rubidium
Sr 38 87.62 Strontium
Y 39 88.91 Yttrium
Zr 40 91.22 Zirconium
Nb 41 92.91 Niobium
Mo 42 95.94 Molybdenum
Tc 43 (97.9) Technetium
Ru 44 101.07 Ruthenium
Rh 45 102.91 Rhodium
Pd 46 106.42 Palladium
Ag 47 107.87 Silver
Cd 48 112.41 Cadmium
In 49 114.82 Indium
Sn 50 118.71 Tin
Sb 51 121.76 Antimony
Te 52 127.60 Tellurium
I 53 126.90 Iodine
Xe 54 131.29 Xenon
Cs 55 132.91 Cesium
Ba 56 137.33 Barium
La 57 138.91 Lanthanum
Hf 72 178.49 Hafnium
Ta 73 180.95 Tantalum
W 74 183.85 Tungsten
Re 75 186.21 Rhenium
Os 76 190.2 Osmium
Ir 77 192.22 Iridium
Pt 78 195.08 Platinum
Au 79 196.97 Gold
Hg 80 200.59 Mercury
Tl 81 204.38 Thallium
Pb 82 207.2 Lead
Bi 83 208.98 Bismuth
Po 84 (209) Polonium
At 85 (210) Astatine
Rn 86 (222) Radon
Fr 87 223.02 Francium
Ra 88 226.03 Radium
Ac 89 227.03 Actinium
Rf 104 (261) Rutherfordium
Db 105 (262) Dubnium
Sg 106 (263) Seaborgium
Bh 107 (262) Bohrium
Hs 108 (265) Hassium
Mt 109 (266) Meitnerium
Unnamed Discovery 110 Nov. 1994
Unnamed Discovery 111 Nov. 1994
Unnamed Discovery 112 1996
Unnamed Discovery 114 1999
Unnamed Discovery 116 1999
Unnamed Discovery 118 1999
ALKALI METALS
ALKALI EARTH METALS
HALOGENS
NOBLE GASES
LANTHANIDES
Ce 58 140.12 Cerium
Pr 59 140.91 Praseodymium
Nd 60 144.24 Neodymium
Pm 61 (145) Promethium
Sm 62 150.36 Samarium
Eu 63 152.97 Europium
Gd 64 157.25 Gadolinium
Tb 65 158.93 Terbium
Dy 66 162.50 Dysprosium
Ho 67 164.93 Holmium
Er 68 167.26 Erbium
Tm 69 168.93 Thulium
Yb 70 173.04 Ytterbium
Lu 71 174.97 Lutetium
ACTINIDES
Th 90 232.04 Thorium
Pa 91 231.04 Protacinium
U 92 238.03 Uranium
Np 93 237.05 Neptunium
Pu 94 (240) Plutonium
Am 95 243.06 Americium
Cm 96 (247) Curium
Bk 97 (248) Berkelium
Cf 98 (251) Californium
Es 99 252.08 Einsteinium
Fm 100 257.10 Fermium
Md 101 (257) Mendelevium
No 102 259.10 Nobelium
Lr 103 262.11 Lawrencium



Reactors
Fixed bed
Slurry

Catalysts
Precipitated Fe
Supported Co

H_2/CO
Precipitated Fe: 1 - 1.5
Supported Co: 2 – 2.2



Reactors
Circulating Fluidized Bed
Fixed Fluidized Bed

Catalysts
Fused Fe

H_2/CO
1.5

Table 1. Representative Generic Fischer–Tropsch Syncrude Compositions from Cobalt-based LTFT (Co-LTFT), Iron-based LTFT (Fe-LTFT) and Iron-based HTFT (Fe-HTFT) Synthesis

		syncrude composition (mass %) [(a),(b)]		
carbon range	compound class	Co-LTFT	Fe-LTFT	Fe-HTFT
	Oil and Gaseous Products			
C_1	paraffin	5.6	4.3	12.7
C_2	olefin	0.1	1.0	5.6
	paraffin	1.0	1.0	4.5
C_3–C_4	olefins	3.4	6.0	21.2
	paraffins	1.8	1.8	3.0
C_5–C_{10}	olefins	7.8	7.7	25.8
	paraffins	12.0	3.3	4.3
	aromatics	0	0	1.7
	oxygenates	0.2	1.3	1.6
C_{11}–C_{22}	olefins	1.1	5.7	4.8
	paraffins	20.8	13.5	0.9
	aromatics	0	0	0.8
	oxygenates	0	0.3	0.5
C_{22}+	olefins	0	0.7	1.6
	paraffins	44.6	49.2	0.4
	aromatics	0	0	0.7
	oxygenates	0	0	0.2
	Aqueous Product			
C_1–C_5	alcohols	1.4	3.9	4.5
	carbonyls	0	0	3.9
	carboxylic acids	0.2	0.3	1.3

Table 10

Typical composition of water soluble oxygenated products with iron catalysts

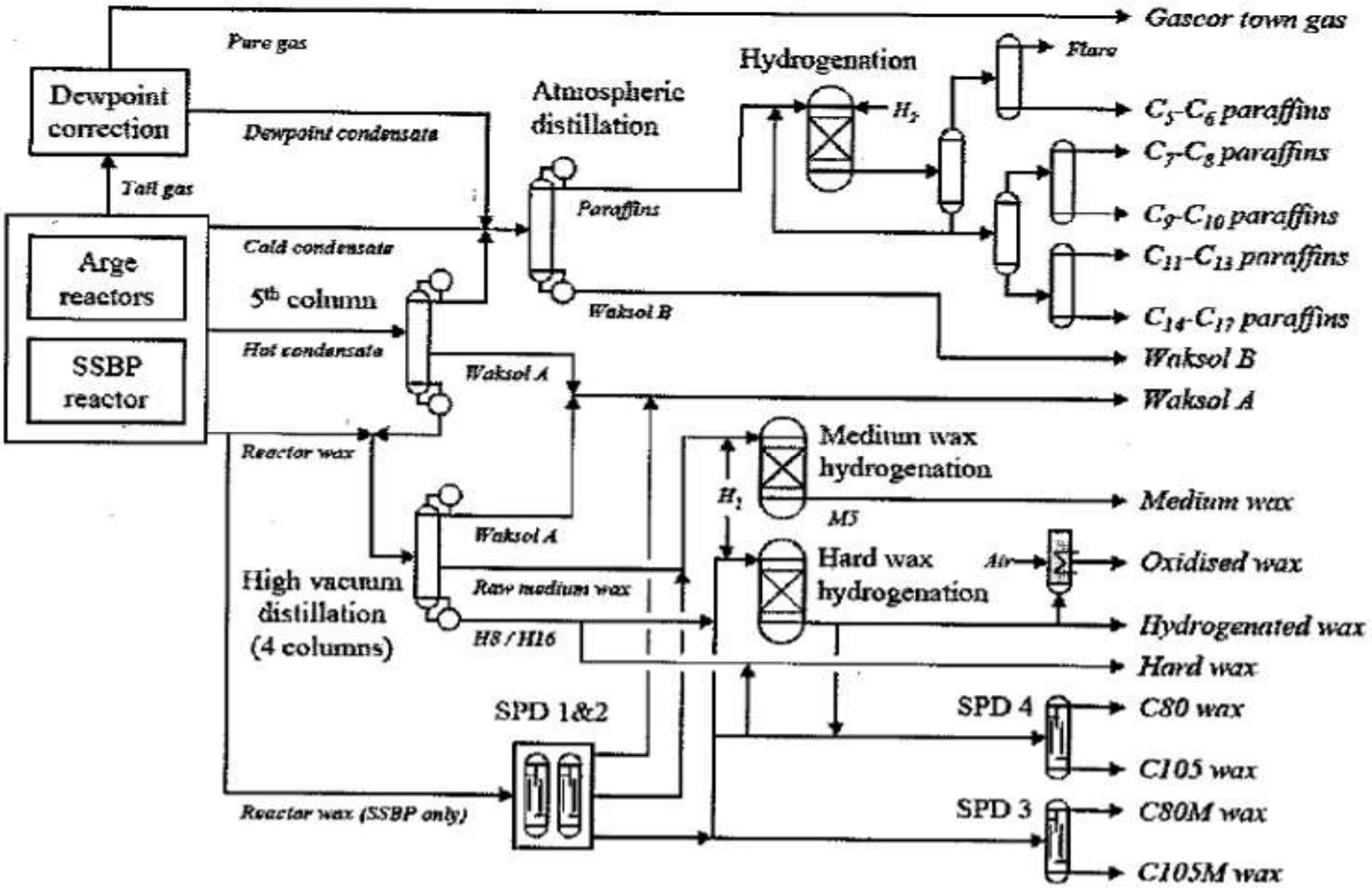
Compound	**LTFT[1] 230°C**	**HTFT[2] 340°C**
Non-acid chemicals	Mass%	
Ethanal (acetaldehyde)	0.5	2
Propanal	0.1	0.5
2 Propanone (acetone)	4	23
2 Butanone (MEK)	0.3	6
Methanol	24	0.5
Ethanol	45	40
1 Propanol	13	12
2 Propanol	1	5
1 Butanol	5	4
2 Butanol		1
2 Me 1 Propanol		1
Acids (mass % distribution)		
CH_3COOH		70
C_2H_5COOH		16
C_3H_7COOH		9
Acid content of water (mass %)	0.4	1.2

1 Precipitated iron catalyst

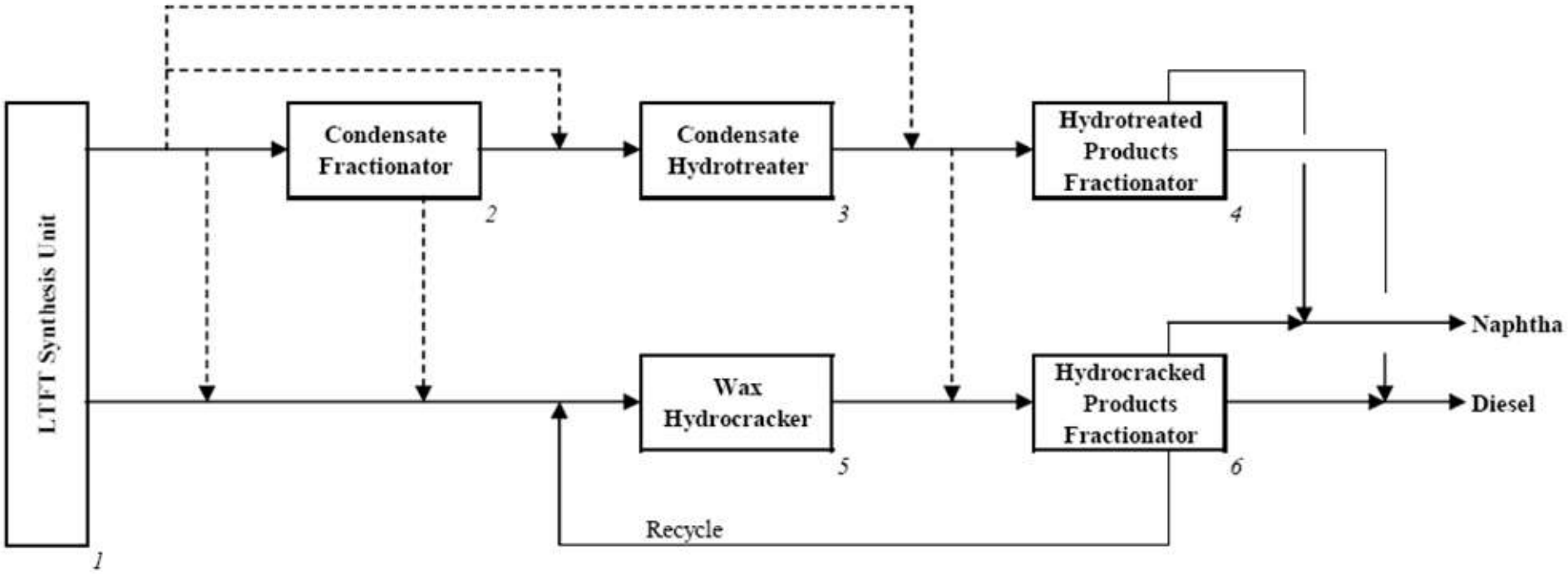
2 Fused iron catalyst

Steynberg and Dry, 2004

LT-FT Refinery: Chemicals

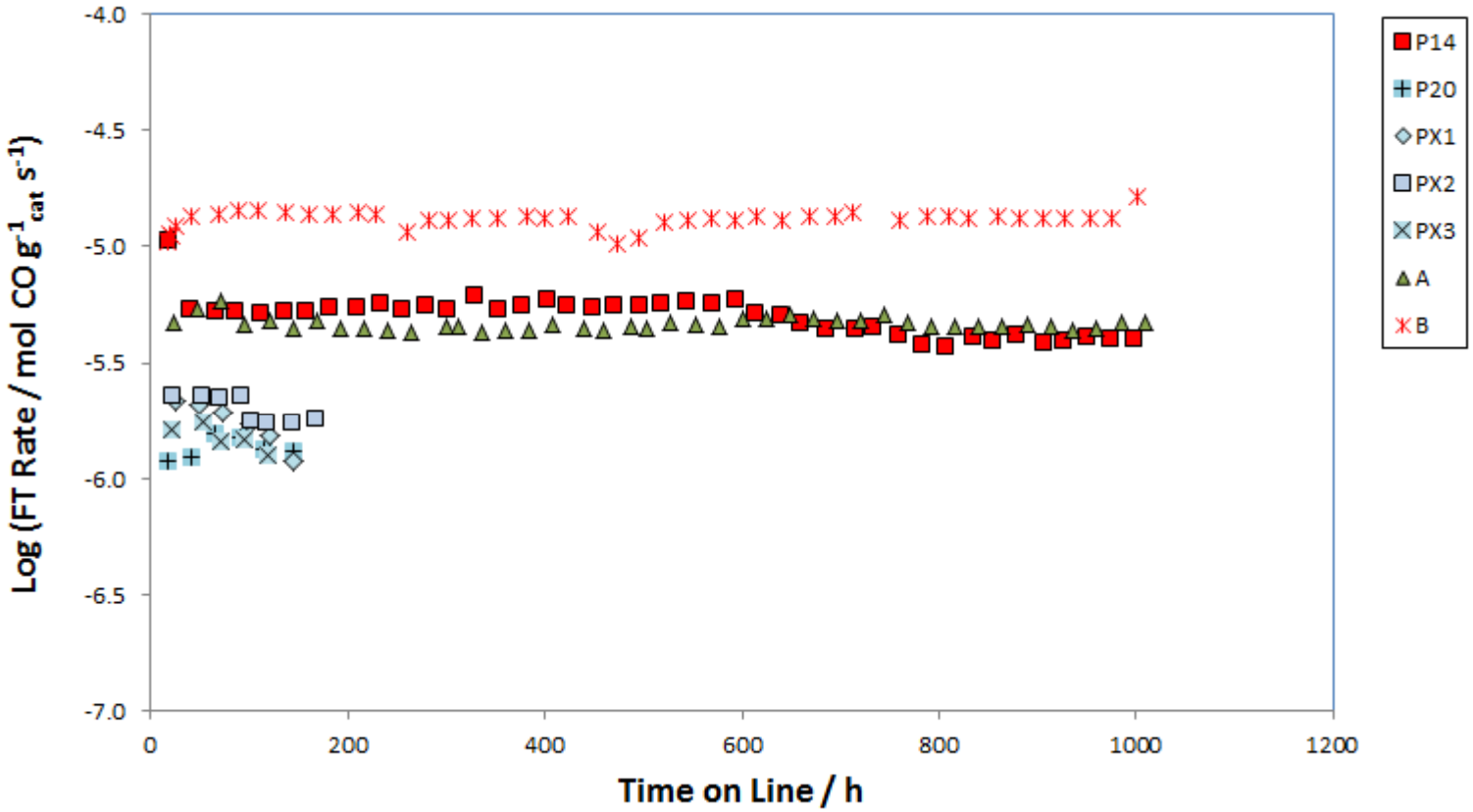


LT-FT Refinery: Diesel



Steynberg and Dry, 2004

Research and Development needs



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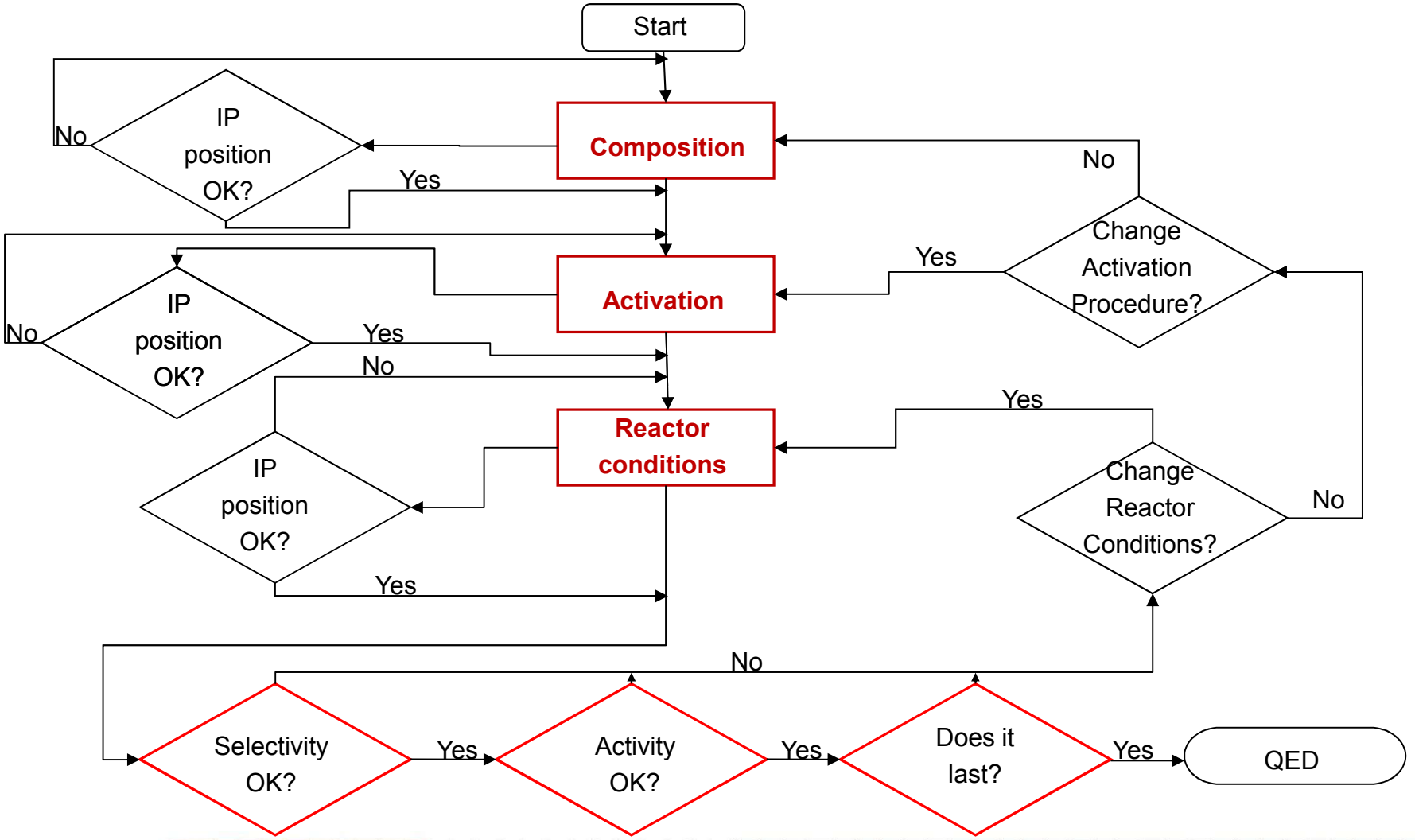
Research framework…



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Conclusions

- **Syngas, a powerful reagent**
- **FT is versatile, mitigates economic risk**
- **Research needs in FT catalyst improvement**

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Thank you!

Questions?

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