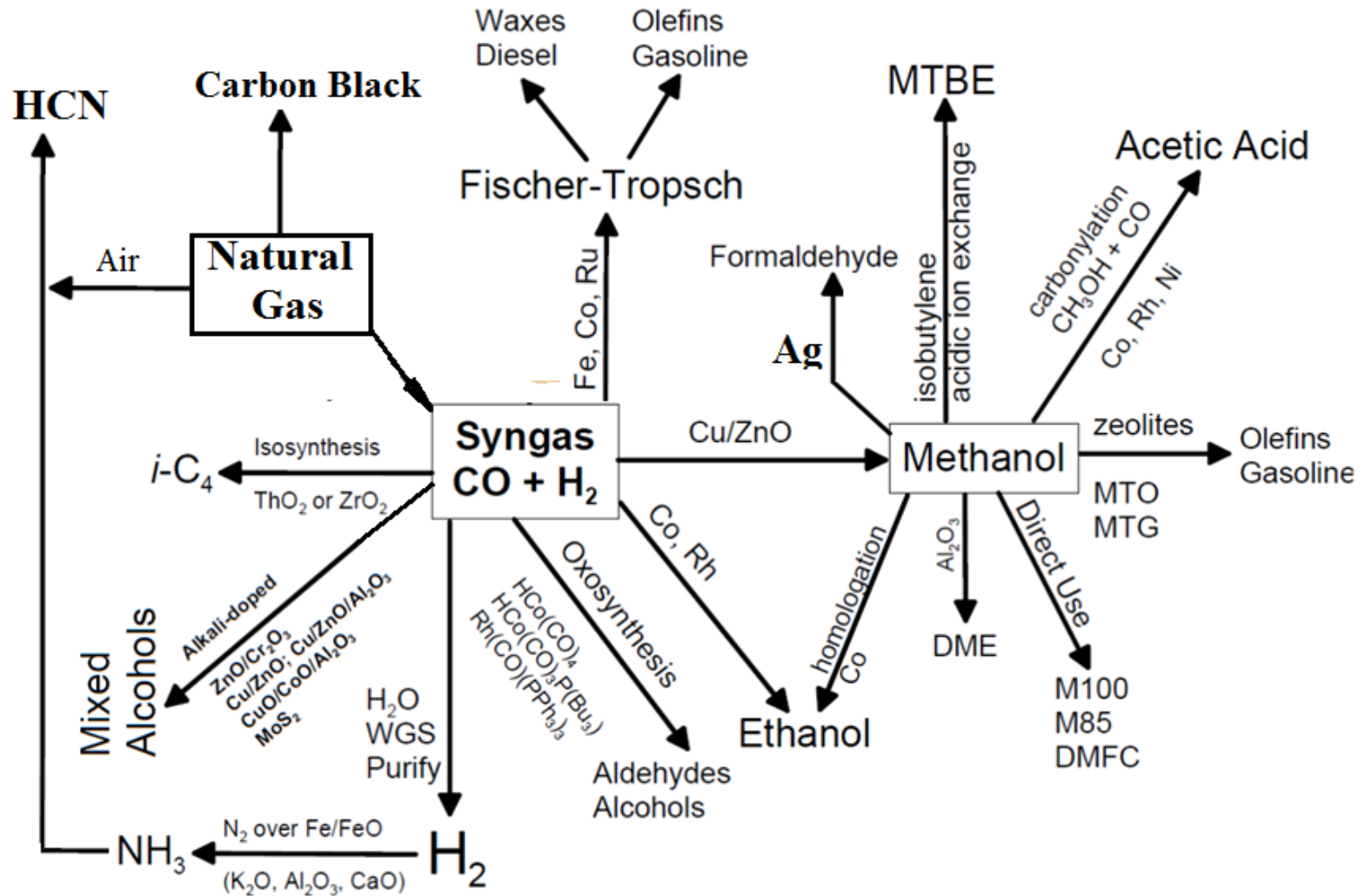


Petrochemical Technology

Chemicals from SynGas

Chemicals from Natural Gas



Fisher-Tropsch Synthesis (FTS)

Fischer-Tropsch (FT) synthesis, named after the original German inventors, Franz Fischer and Hans Tropsch in the 1920s.

- Developed during WW II in order to satisfy the demand for fuel with the abundant coal supply.
- High pressure hydrogenation of CO over metal or transition metal carbide catalysts.
- The process leads to oligomer like large saturated and mostly unbranched alkanes, as well as some oxygenates.
- Fe, Co and Ru are the most widely use catalysts.
- Alkali metal oxide promoters seem essential for good catalytic performance.
- The two main catalytic functions are
 - *CO bond activation and dissociation*
 - *Formation of C-C and C-H bonds*

Fischer-Tropsch synthesis (FTS) is the heart of the **Gas-to-Liquid (GTL)** technology as it is the process by which synthesis gas (or syngas, a mixture of carbon monoxide and hydrogen) can be converted into ultra-clean fuels and value added chemicals.

Depending on the source of the syngas, the technology is often referred to as coal-to-liquids (CTL) and/or gas-to-liquids (GTL). Examples of current operating CTL plants include Sasol's Sasolburg I and II plants, and an example of a GTL FT process is Shell's plant in Bintulu, Malaysia. Several world-class GTL and CTL plants are currently at various stages of engineering, construction, and production in Nigeria, Qatar and China, and most recently in the United States as well.

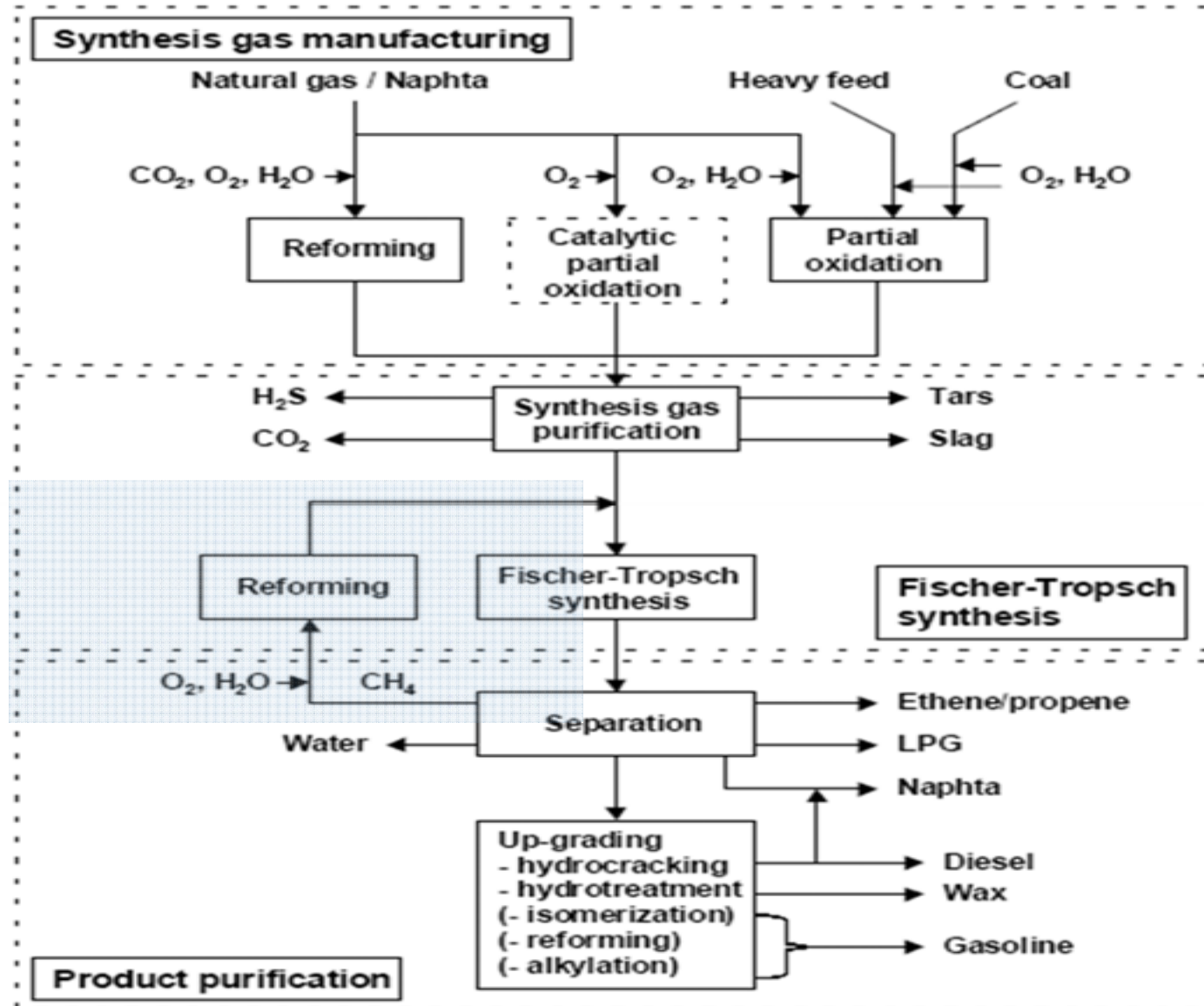
Fischer-Tropsch Process has three main processing steps, all of which are commercially proven:

STEP-1: SynGas generation – 50+% of the total cost

STEP-2: F-T conversion – 25-35% of the total cost

STEP-3: Product upgrading – 15-25% of the total cost

Overall FT Process scheme

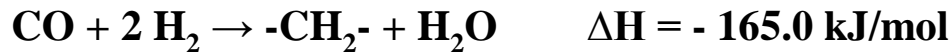


FTS Chemistry

FTS has long been recognized as a polymerization reaction with the basic steps of:

- Reactant (CO) adsorption on the catalyst surface
- Chain initiation by CO dissociation followed by hydrogenation
- Chain growth by insertion of additional CO molecules followed by hydrogenation
- Chain termination
- Product desorption from catalyst surface

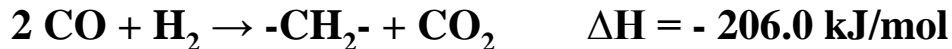
The following is the F-TS reaction:



With Fe catalyst WGS reaction occurs



So, the net overall F-TS reaction is



The required H_2/CO ratio for the cobalt catalyst is 2.15 but since the Fe catalyst performs WGS in addition to the F-T reaction, the H_2/CO ratio can be slightly lower.

Specific FTS products are synthesized according to the following reactions:

<i>Main reactions</i>		
Alkanes	$n \text{ CO} + (2n + 1) \text{ H}_2 \rightarrow$	$\text{C}_n \text{ H}_{2n+2} + n \text{ H}_2\text{O}$
Alkenes	$n \text{ CO} + 2n \text{ H}_2 \rightarrow$	$\text{C}_n \text{ H}_{2n} + n \text{ H}_2\text{O}$
Water-gas shift	$\text{CO} + \text{H}_2\text{O} \rightleftharpoons$	$\text{CO}_2 + \text{H}_2$
<i>Side reactions</i>		
Alcohols	$n \text{ CO} + 2n \text{ H}_2 \rightarrow$	$\text{H}(-\text{CH}_2-)_n\text{OH} + (n-1) \text{ H}_2\text{O}$
Boudouard reaction	$2 \text{ CO} \rightarrow$	$\text{C} + \text{CO}_2$

Product	Reactions	H ₂ /CO usage ratio
CH ₄	$\text{CO} + 3 \text{ H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$	3
C ₂ H ₆	$2 \text{ CO} + 5 \text{ H}_2 \rightarrow \text{C}_2\text{H}_6 + 2 \text{ H}_2\text{O}$	2.5
Alkanes	$n \text{ CO} + (2n+1) \text{ H}_2 \rightarrow \text{C}_n \text{ H}_{(2n+2)} + n \text{ H}_2\text{O}$	$(2n+1)/n$
Alkenes	$n \text{ CO} + 2n \text{ H}_2 \rightarrow \text{C}_n \text{ H}_{2n} + n \text{ H}_2\text{O}$	2
Alcohols	$n \text{ CO} + 2n \text{ H}_2 \rightarrow \text{C}_n \text{ H}_{(2n+1)} \text{ OH} + (n-1) \text{ H}_2\text{O}$	2

Catalysts

Group VIII transition metal oxides are generally regarded as good CO hydrogenation catalysts. The earliest catalysts used for FTS were Fe and Co.

Order of activity: **Ru>Fe>Ni>Co>Rh>Pd>Pt**

Ni is basically a methanation catalyst and does not have the broad selectivity of other FT catalysts.

Ru has very high activity and quite high selectivity for producing high molecular weight products at low temperatures.

Fe is also very active and has WGS activity.

Co tends to have a longer lifetime than Fe and does not have WGS activity, which leads to improved carbon conversion to products as CO₂ is not formed.

Although **Ru is the most active FTS catalyst, it is 3×10^5 times more expensive than Fe, which is by far the least expensive FT catalyst of all these metals. Co catalysts are 230 times more expensive than Fe but are still an alternative to Fe catalysts for FTS because they demonstrate activity at lower synthesis pressures, so higher catalyst costs can be offset by lower operating costs.**

Catalysts: Gas cleanliness requirements

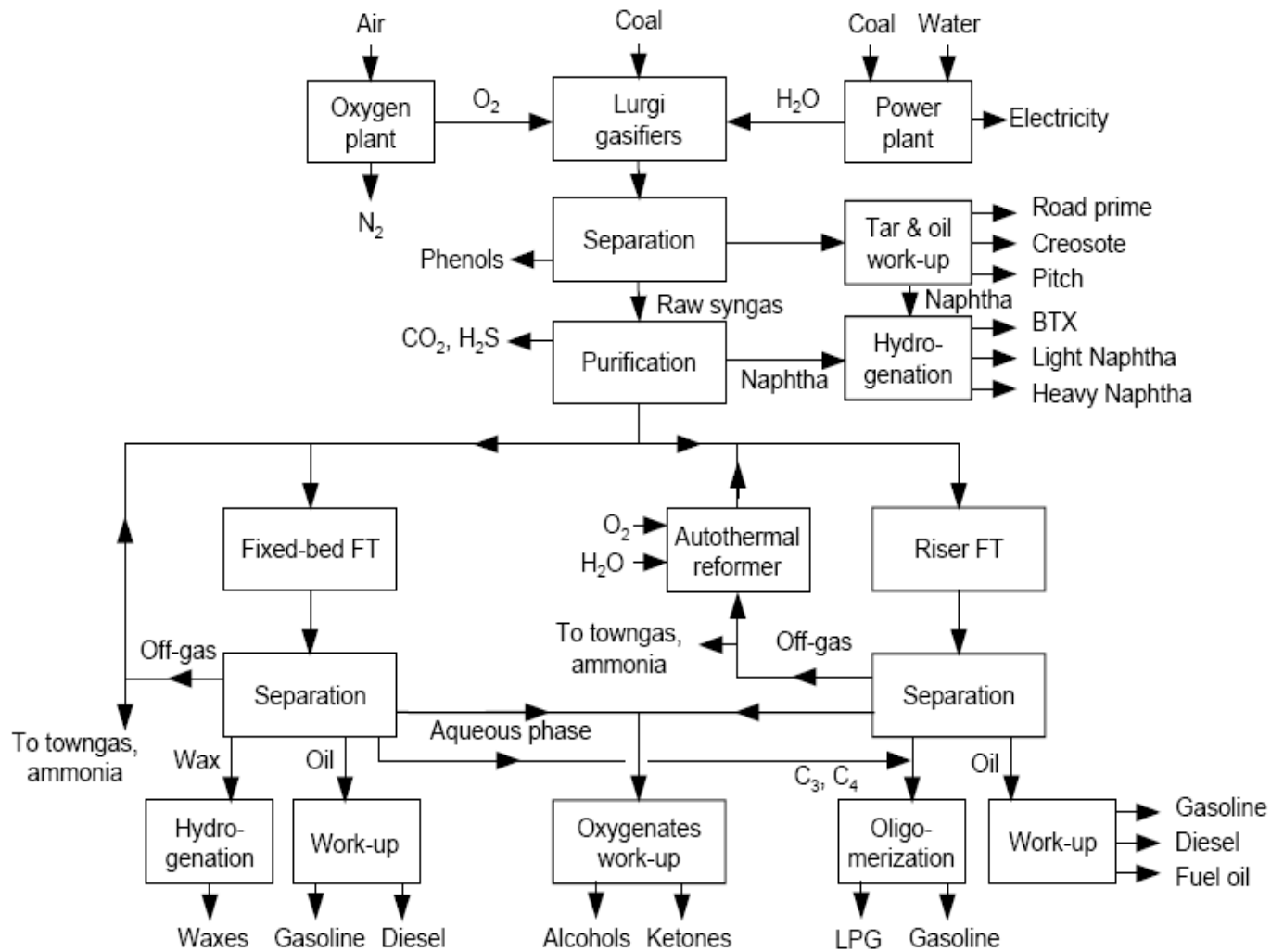
FT S catalysts can lose activity as a result of (1) Conversion of the active metal site to an inactive oxide site (2) sintering (3) loss of active area by carbon deposition and (4) chemical poisoning.

Some of these mechanisms are unavoidable and others can be prevented or minimized by insuring that the impurity levels in the incident syngas are acceptable for the given process.

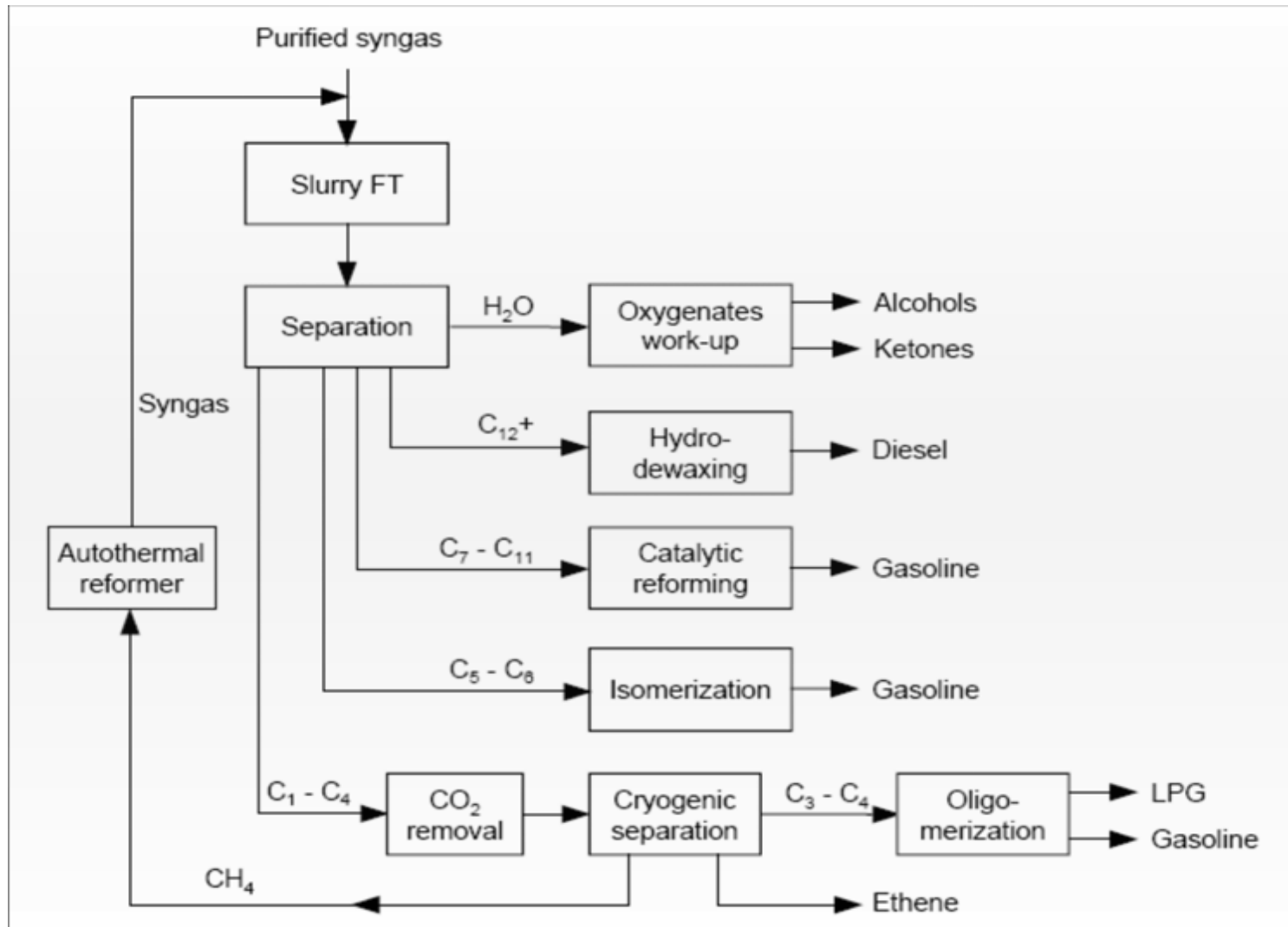
Impurity	Tolerance level
Sulfur	0.2 ppm, 1 ppmv, 60 ppb
Halides	10 ppb
Nitrogen	10 ppmv NH ₃ 0.2 ppmv NO _x 10 ppb HCN

There are differing points of view regarding sulfur levels but in general, the sulfur content of the syngas should be minimized according to economics.

Sasol I flow scheme

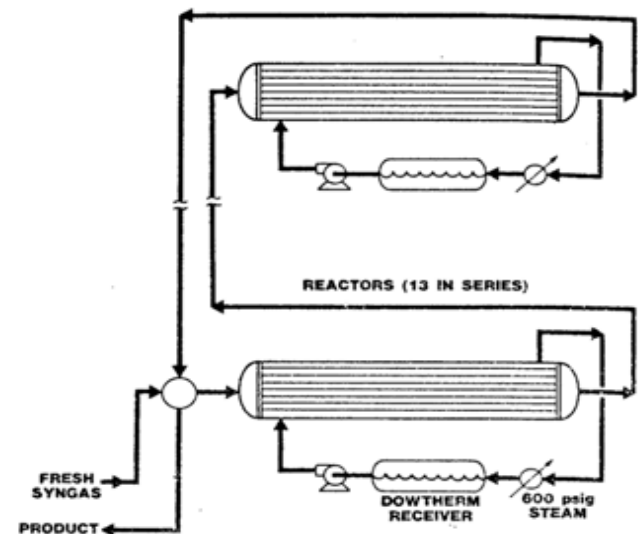
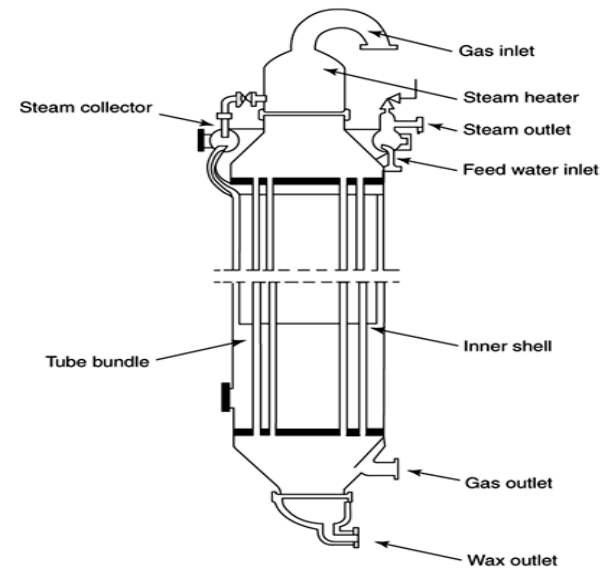


Sasol II & III flow scheme



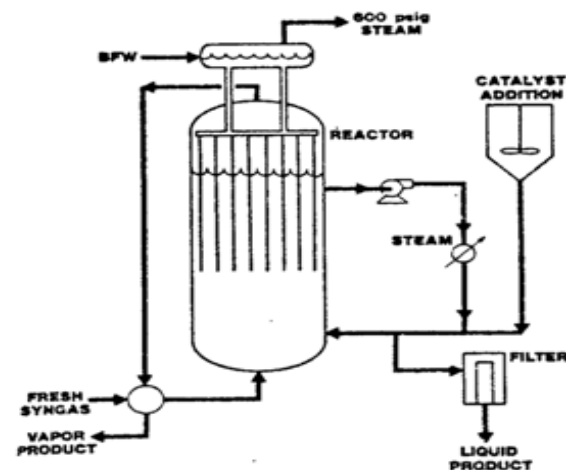
Fixed bed reactor

- Removal of the heat of reaction and achieving constant temperature over the entire catalyst bed are challenging.
- Catalyst is placed in tubes with small diameter.
- High space velocity (250 h^{-1}) and high recycle result in SV of 500 h^{-1} for new feed.
- $T = 493\text{--}523 \text{ K}$, $p = 2.7 \text{ MPa}$, lifetime up to 350 days.
- High wax production
- Improving the isothermicity by *high recycle ratio (up to 20/1) large empty reactor volume tube wall reactors*

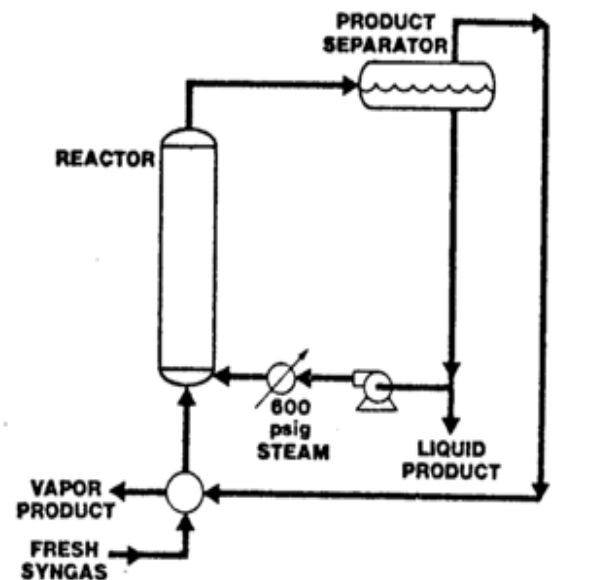
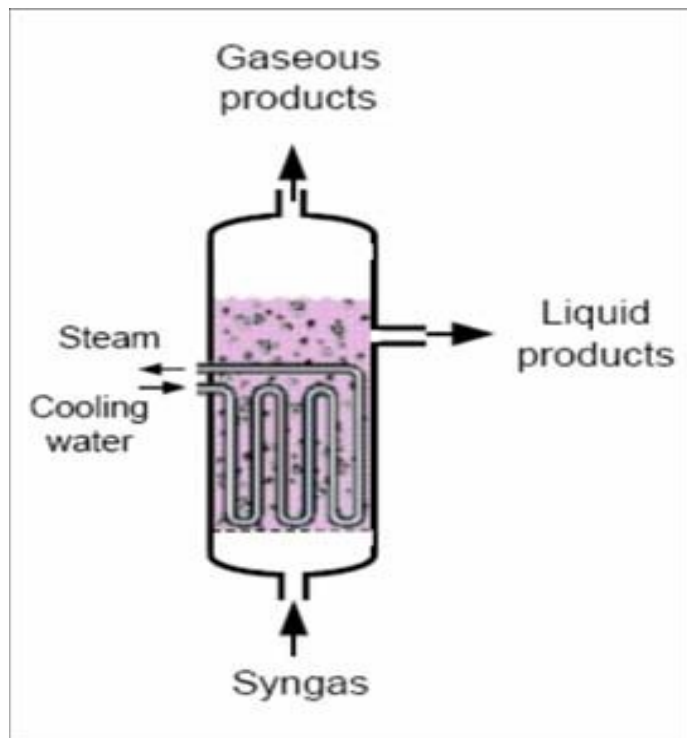


Slurry reactors

- Gas is passed through suspension of small catalyst particles in a liquid with low vapor pressure (high boiling waxes)
- Low reaction temperature
- High wax selectivity
- Most flexible design



Slurry reactor



Ebullating bed reactor

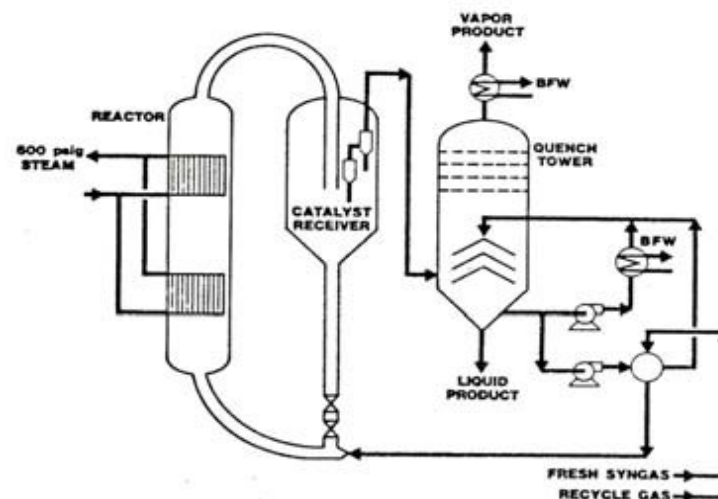
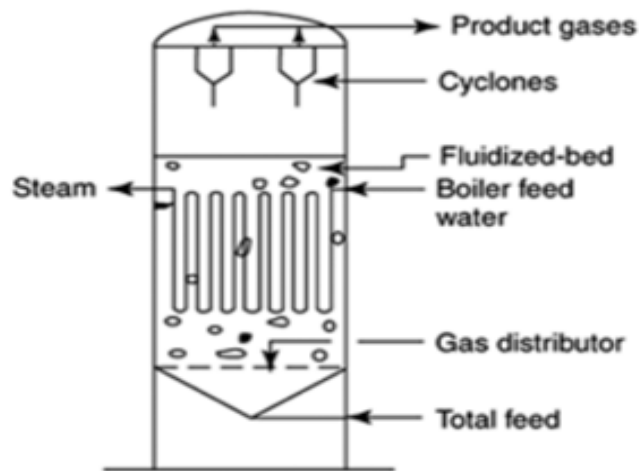
Fluidized bed reactors

•Fixed fluidized bed reactors

- $T = 593 \text{ K}$, $p = 2.7 \text{ MPa}$
 - high gas velocity, LHSV = 2000-3000
 - 1.5 recycle ratio
 - High yields, high throughput, good temperature control

•Moving fluidized bed

- $T = 593 - 633 \text{ K}$, $p = 2.7 \text{ MPa}$
 - Kellog and Sasol Synthol design
 - Catalyst lasts about 40 days and is replaced.



Entrained bed reactor

Comparison of Reactors

Activity

Using standard catalysts (size typical for the process)
the sequence in the space-time yields is

slurry < fixed bed < fluidized bed reactor

using identical catalysts

slurry < fluidized bed < fixed bed reactor

Selectivity

Waxes Gasoline

Light products

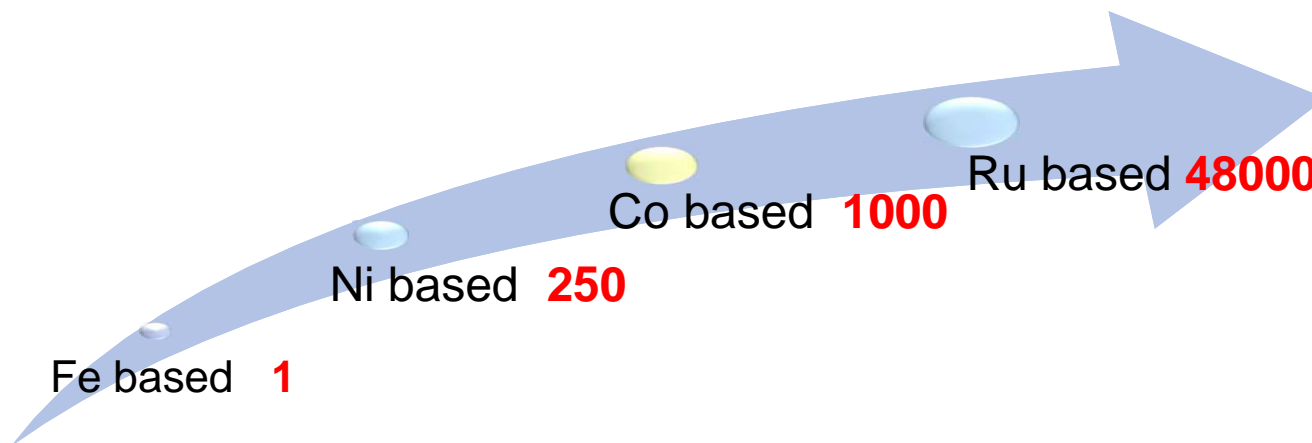
High yields in
isothermal fixed bed and slurry reactors
fluidized bed and slurry reactors
fluidized bed reactors

FT Product distribution in various reactors

	Multi-tubular fixed-bed reactor	Riser reactor	Slurry reactor
Conditions			
Inlet T (K)	496	593	533
Outlet T (K)	509	598	538
Pressure (bar)	25	23	15
H ₂ /CO feed ratio	1.7	2.54	0.68*
Conversion (%)	60 – 66	85	87
Products (wt%)			
CH ₄	2.0	10.0	6.8
C ₂ H ₄	0.1	4.0	1.6
C ₂ H ₆	1.8	4.0	2.8
C ₃ H ₆	2.7	12.0	7.5
C ₃ H ₈	1.7	1.7	1.8
C ₄ H ₈	2.8	9.4	6.2
C ₄ H ₁₀	1.7	1.9	1.8
C ₅ – C ₁₁ (gasoline)	18.0	40.0	18.6
C ₁₂ – C ₁₈ (diesel)	14.0	7.0	14.3
C ₁₉ ⁺ (waxes)	52.0	4.0	37.6
Oxygenates	3.2	6.0	1.0

Catalysts

Possible catalyst cost basis



Influence of promoters and support on precipitated Fe catalysts

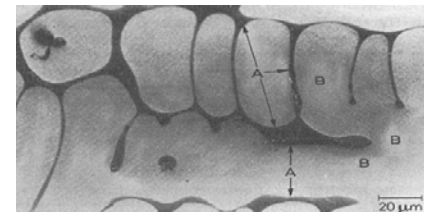
- For Fe, promoters (alkali metal) are essential to obtain high basicity and to stabilize high specific metal surface areas.
- Highly electronegative anions decrease the activity (Br^- , Cl^- , SO_4^{2-} , S^{2-})
- The effect of alkali metals on the activity of an Fe-Cu-SiO₂ catalyst decreases in the sequence
 $\text{K} > \text{Rb} > \text{Na} > \text{Li}$ (100, 90, 50, 40)
- The wax selectivity increases in the sequence
 $\text{Li} < \text{Na} < \text{K} < \text{Rb}$

The relatively low activity of Rb promoted samples is due to the high wax selectivity (diffusion problems).

- The higher the alkali level the higher the shift to longer chains.
- Addition of Cu enhances the reducibility and increases the activity for a given degree of reduction.
- SiO₂ is the best support.

Fused iron catalysts

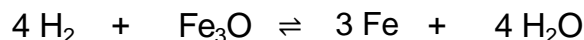
- Iron oxide should contain small impurities of SiO₂, TiO₂, MgO and Al₂O₃; mill scale from steel works is used, electrically fused with the desired amount of promoters, particles are crushed and fractionated
- Before loading the catalyst is reduced in H₂ (FFB reactor)
- Microscopic investigation of the particles reveals that only the very outside skin is Fe₂O₃
- Small occlusions of alkali silicates are present; their size increases towards the center of the particle.
- Little of the structural promoter is present in the silicate inclusions, most of it is in solid solution with the magnetite phase.



Strong heterogeneity of the catalyst - redistribution of Fe during reduction

Promoters and physical properties of fused Fe catalysts

- After reduction, metallic Fe is finely dispersed between promoter particles. The metal surface area increases with the concentration of the promoter.
- H₂O has a strong inhibiting effect. Insignificant reduction in the presence of 20% water



- The higher the charge/radius ratio of the metal cation the higher is the resulting specific surface area.

Al₂O₃, TiO₂, Cr₂O₃ increase spec. surface area strongly

MnO, Li₂O, CaO

little influence

Na₂O, K₂O

negative effect

- The catalyst becomes more basic as the alkali content increases. Pre- reduction of fused Fe to obtain reasonable surface areas, the reduction temperature is between 623 - 723 K with H₂ as reducing agent
- Increase of the hydrogen space-velocity increases the rate of reduction corresponding to a higher final spec. surface area.
- Pores smaller than 5 nm do not exist, the average pore size is 30 nm.

Co based catalysts

- Promoted with small amounts of noble metals
 - Decrease reduction temperature
 - Increase activity
- Transition metal oxides are added to improve wax selectivity
- Catalyst are able to operate at lower pressure (1 – 10 bar)
- Yield less olefins and oxygenated products.
- Catalytic activity is directly proportional to concentration of Co available.

Ruthenium based catalysts

- Activity at lower temperatures better than with conventional FT catalysts.
- At high temperatures excellent methanation catalyst.
- At low temperatures & high pressures large amounts of very high molecular mass waxes (low in oxygen)
- Most active when pure, promoters do not have positive effects.
- However, even under conditions of high wax yields – high methanation activity (~10 %)
- Supported catalysts contain approximately 5 % Ru
- At low conversions → Ru produces light hydrocarbons (high olefin and alcohol content)

Alternative catalysts

Ni based catalysts

- Good methanation catalysts
- Catalysts have too high hydrogenolysis activity.

Activity of other (supported) metal catalysts

- Maximum of activity is observed at moderate heats of adsorption of CO

Thank you