Centre for Catalysis Research

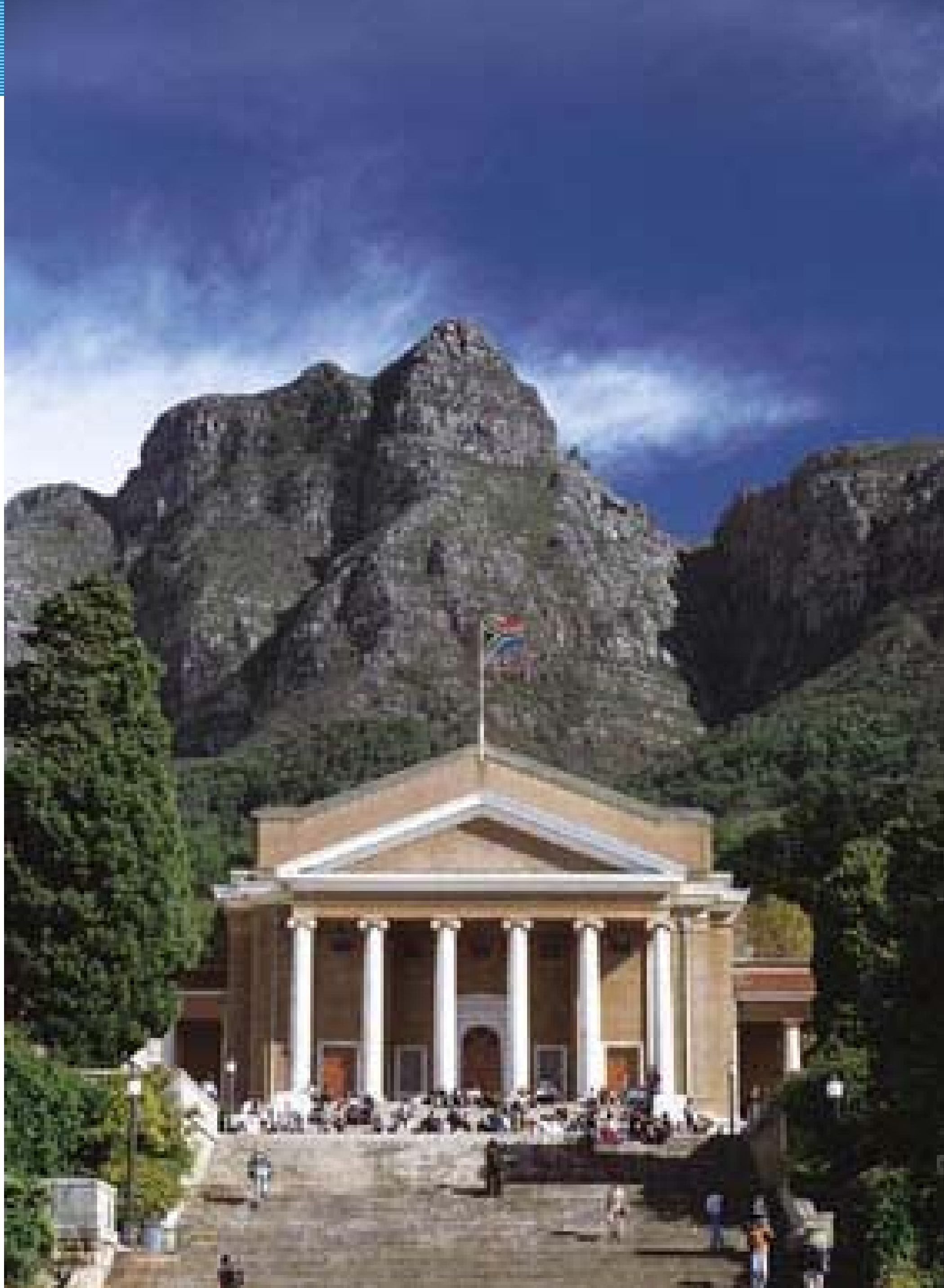
Department of Chemical Engineering
University of Cape Town • Rondebosch 7701
South Africa

Fischer-Tropsch synthesis
Reaction pathway
Reactors

Michael Claeys

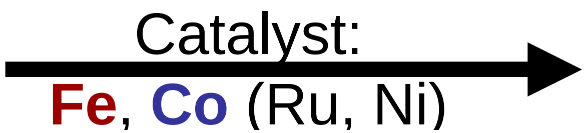
Eric van Steen

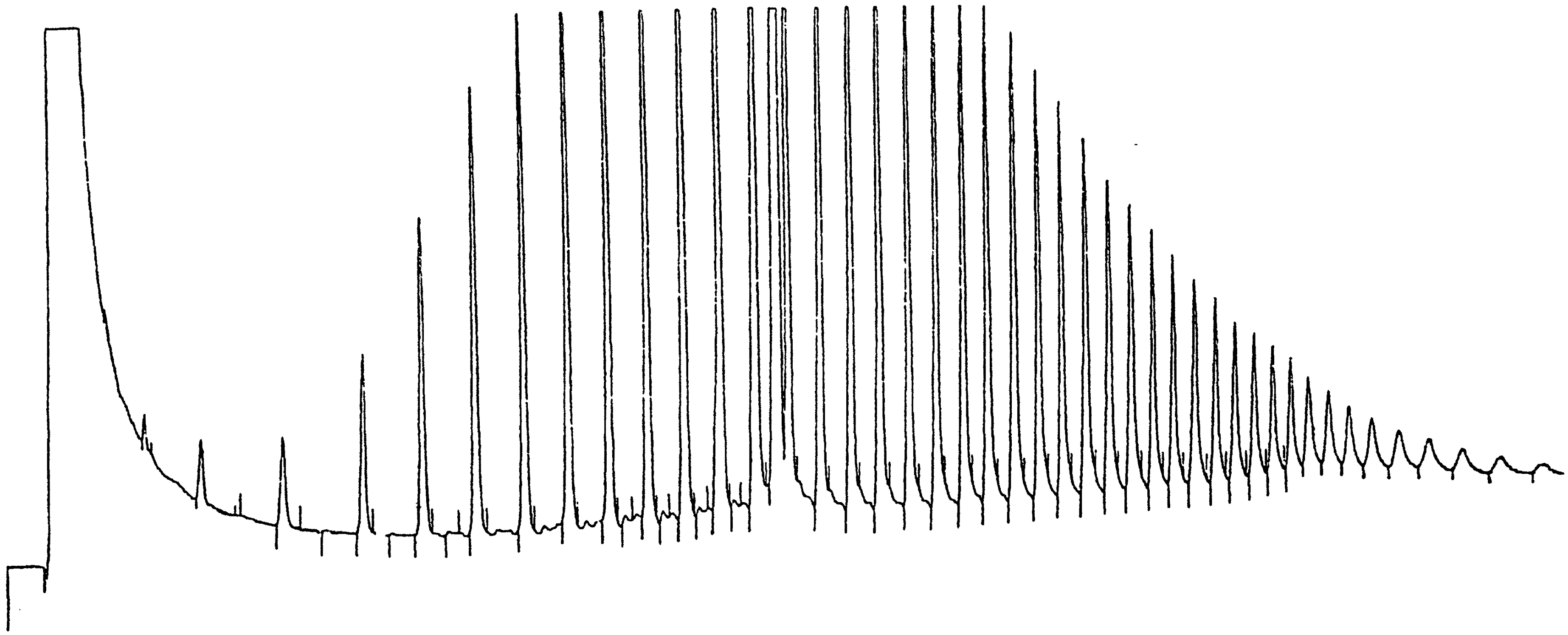
1. Mechanistic ideas
2. Fischer-Tropsch synthesis – a polymerization reaction
3. Re-adsorption of reactive product compounds
   a. reaction kinetic model
   b. diffusion model
4. Reactors and processes



Fischer-Tropsch synthesis

Synthesis gas





F.Fischer, H. Tropsch, *Brennstoff-Chem.* **7** (1926), 97

Products of Fischer-Tropsch synthesis

n-Olefins

- mainly α-olefins
- olefins with internal double bonds

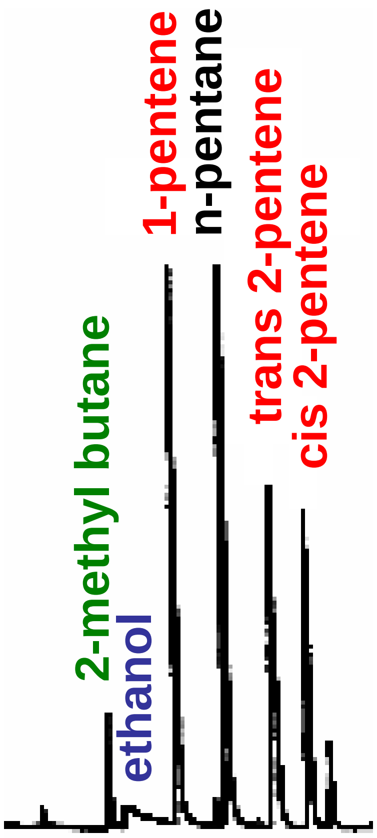
n-Paraffins

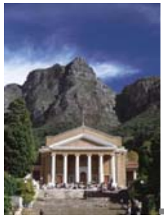
Oxygenates

- alcohols, aldehydes
- ketones

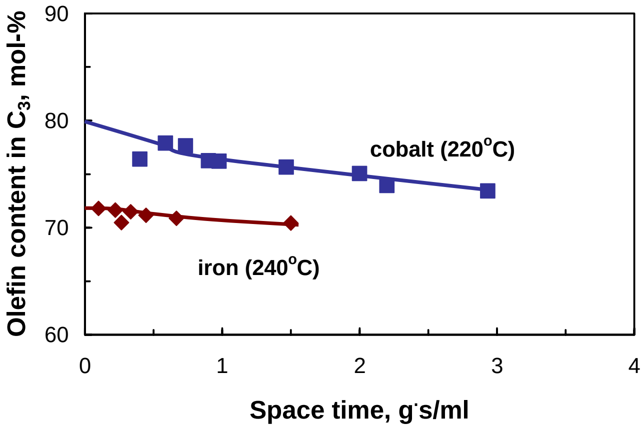
branched compounds

- olefins/paraffins/oxygenates

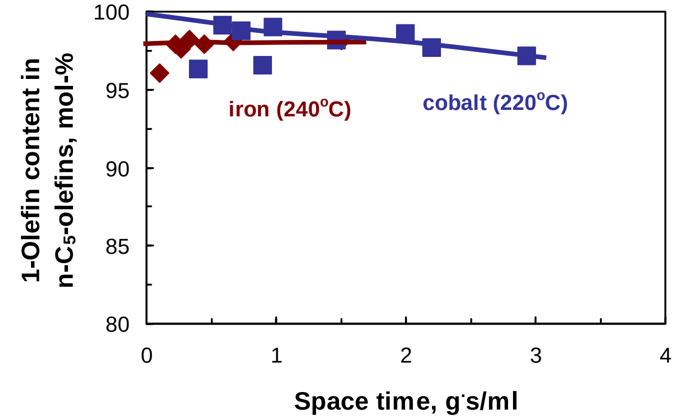




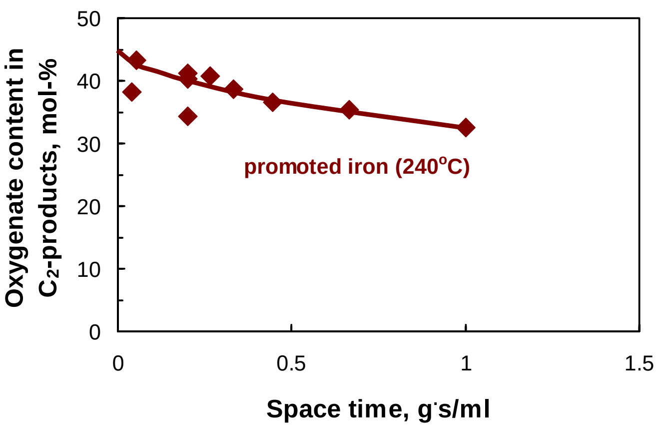
Product formation in Fischer-Tropsch synthesis



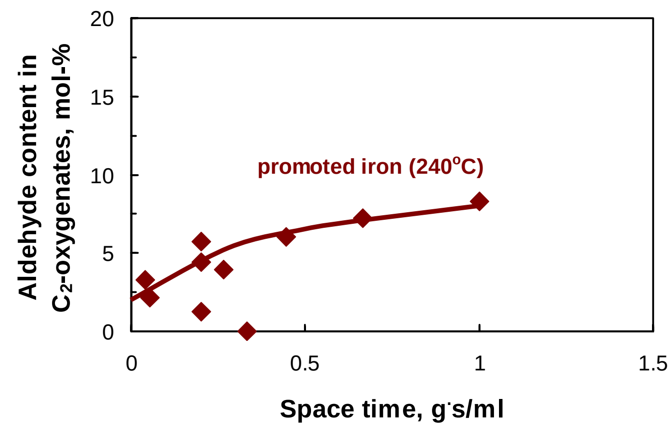
Primary formation of **olefins and paraffins**



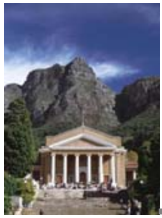
Most olefins are primarily **α-olefins**



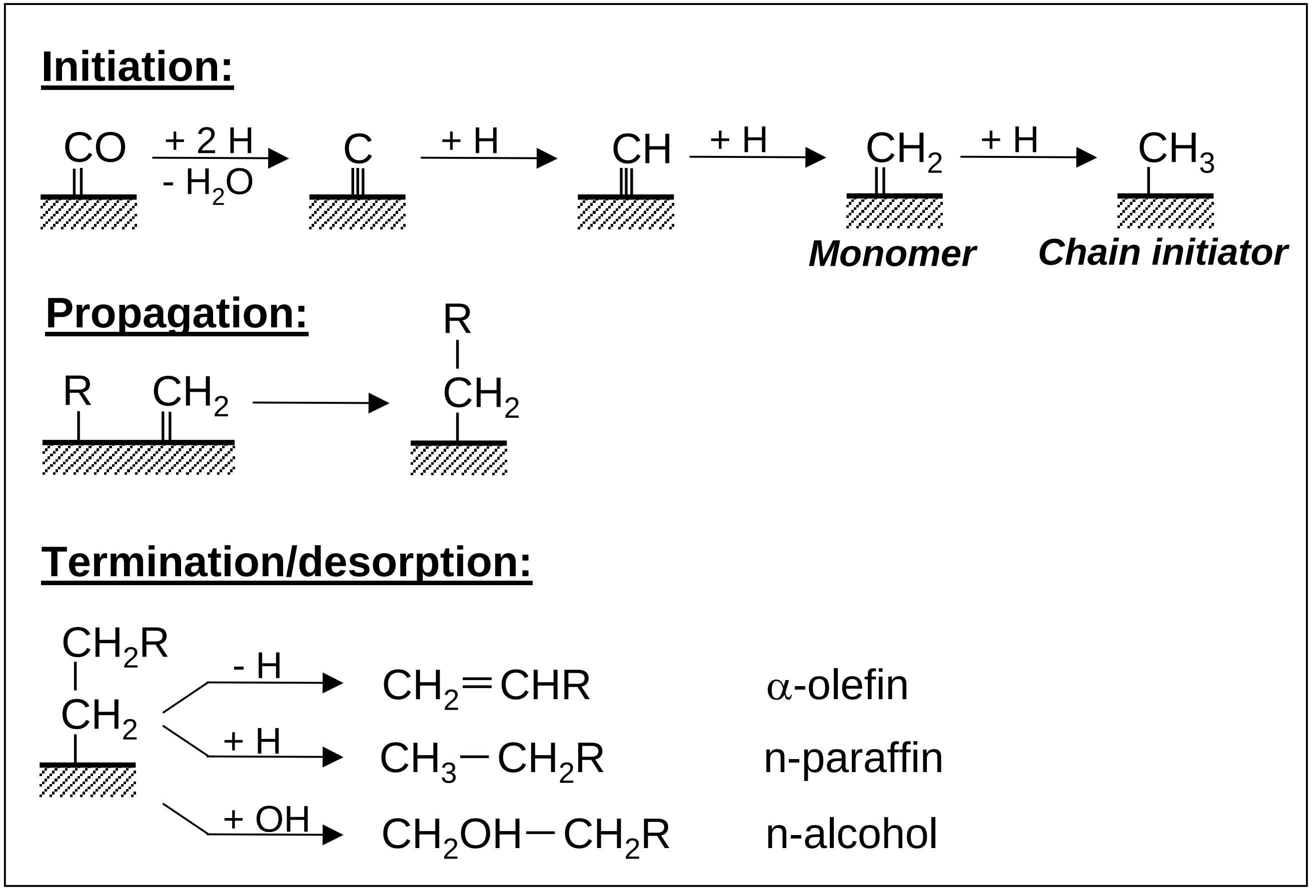
Primary formation of **alcohols/aldehydes**

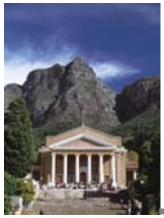


Most oxygenates are primarily **alcohols**



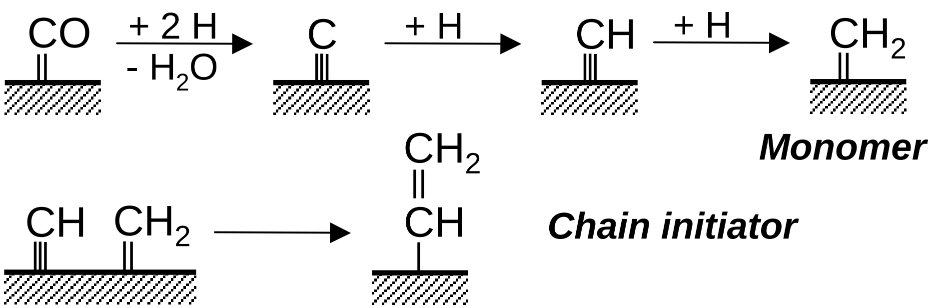
Mechanistic ideas:
"Modern surface carbide theory"



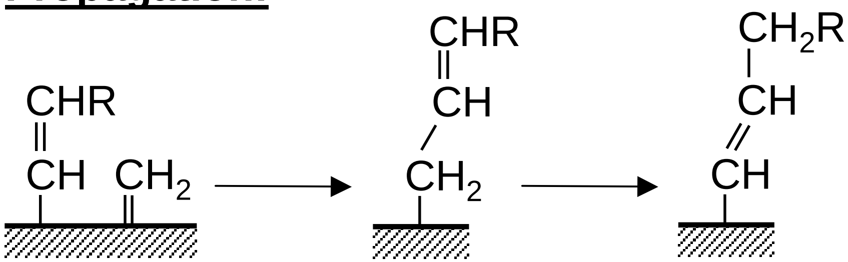


Mechanistic ideas: "Alkylidene mechanism

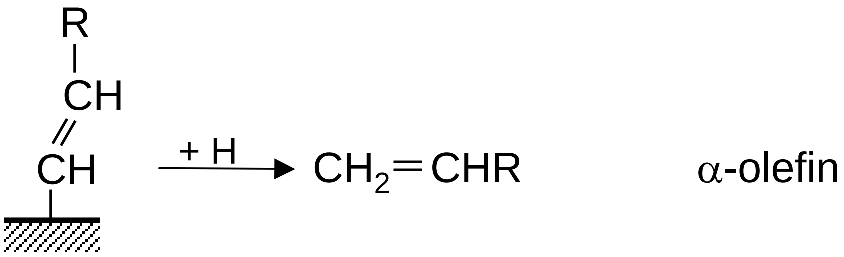
Initiation:

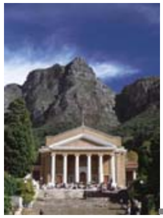


Propagation:

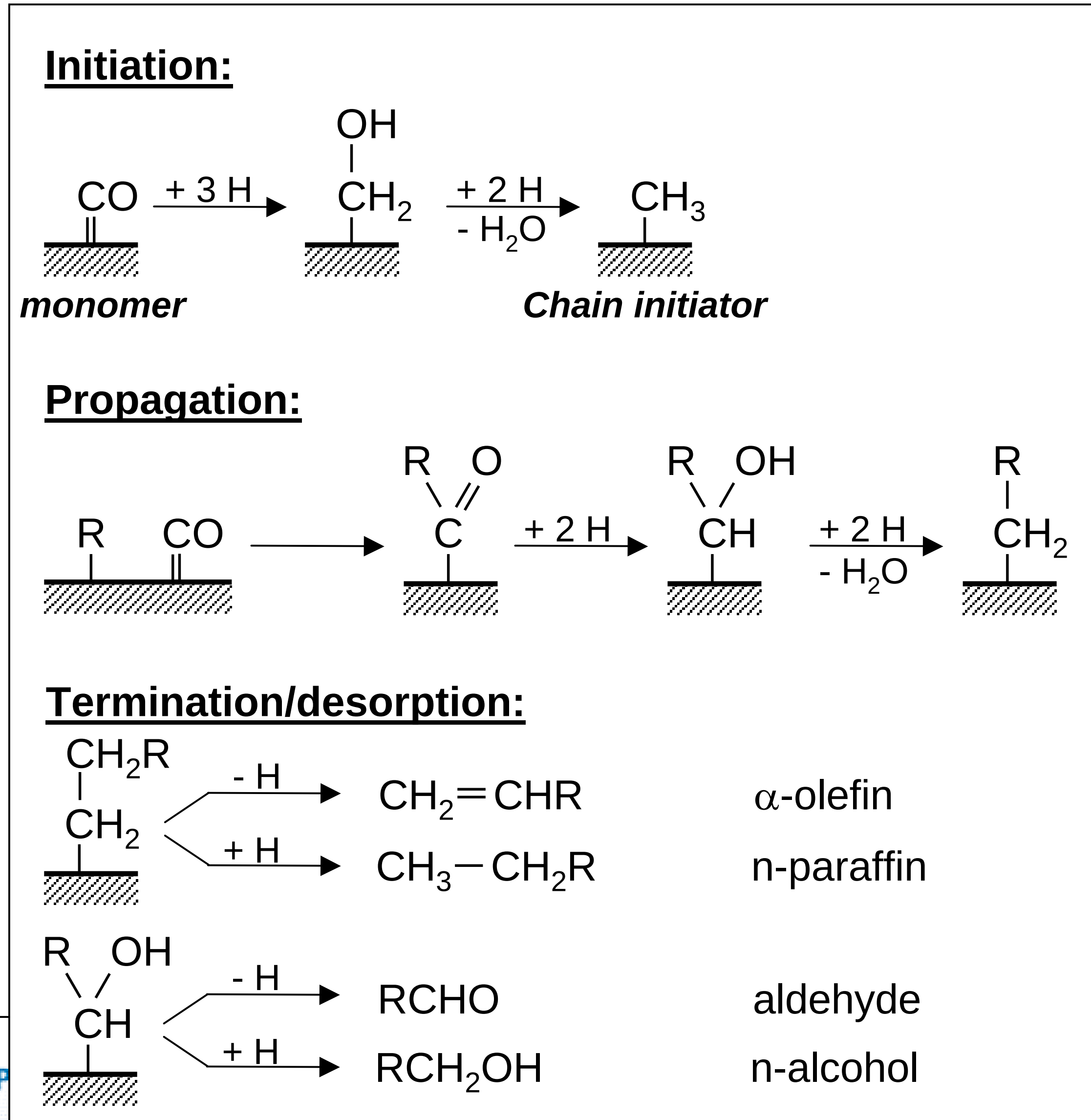


Termination/desorption:



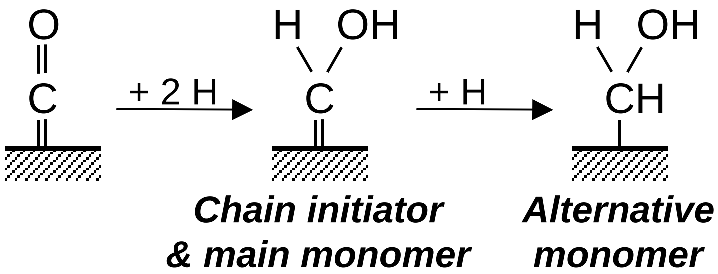


Mechanistic ideas: “CO-insertion mechanism”

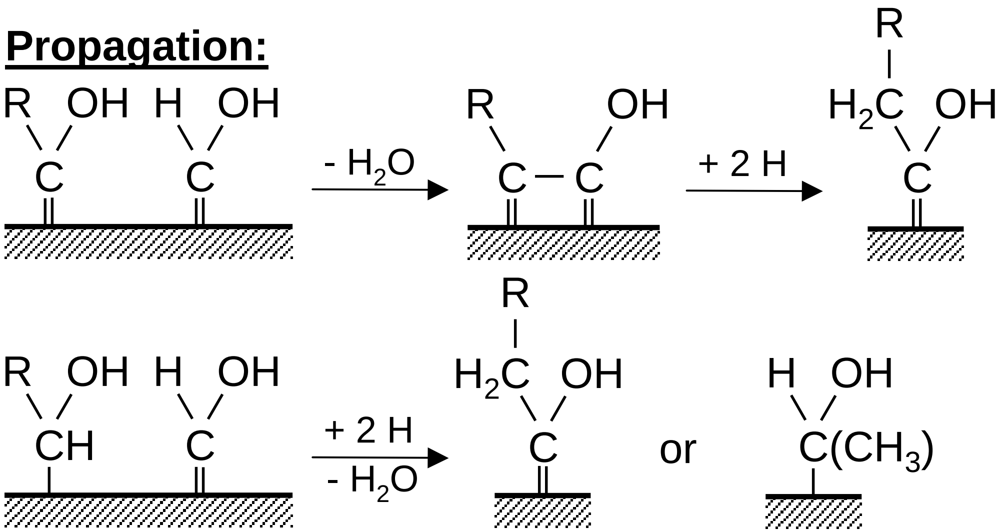


Mechanistic ideas: "Enol mechanism"

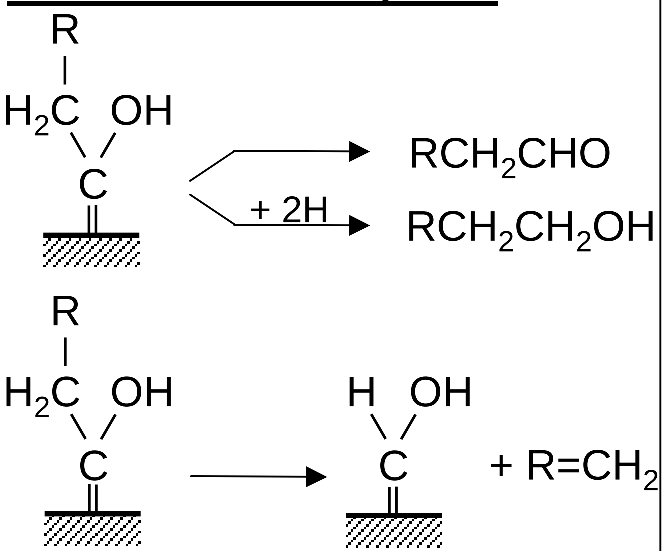
Initiation:

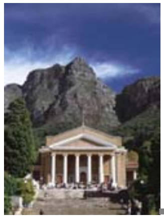


Propagation:

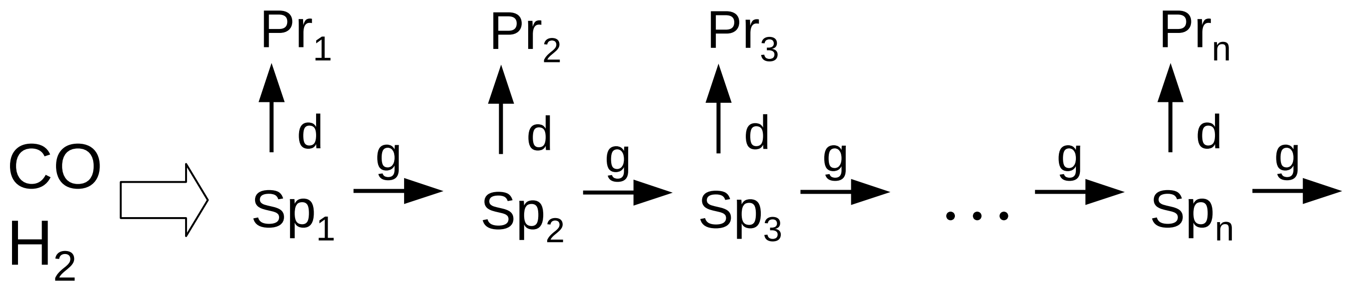


Termination/desorption:



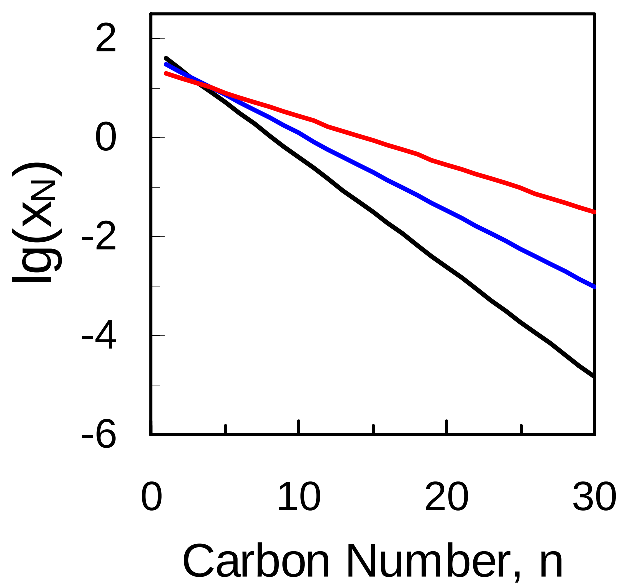


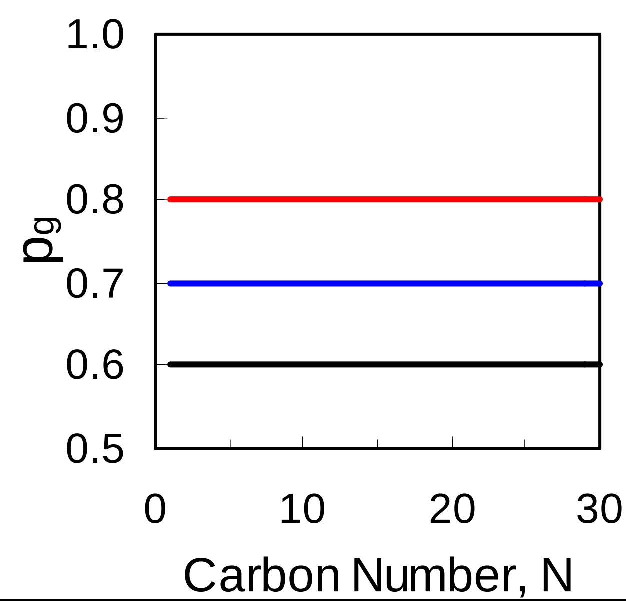
Fischer-Tropsch synthesis: polymerization reaction



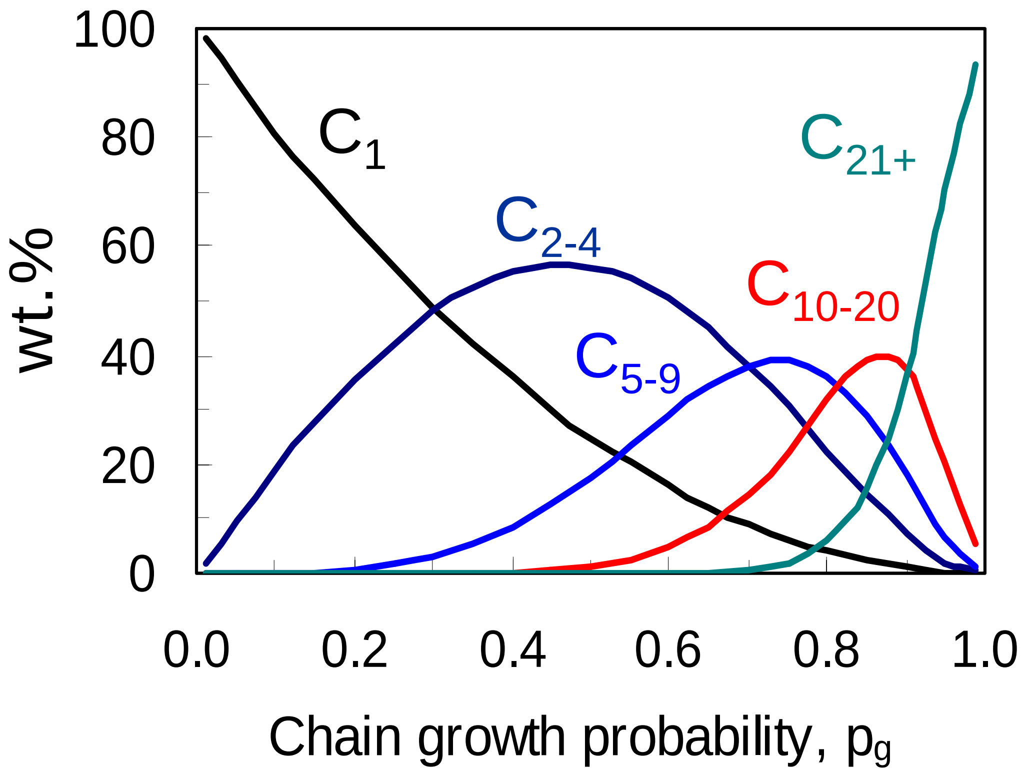
Chain growth probability $p_g = \frac{r_g}{r_g + r_d}$

ASF-kinetics $x_n = (1 - p_g) \cdot p_g^{(n-1)}$



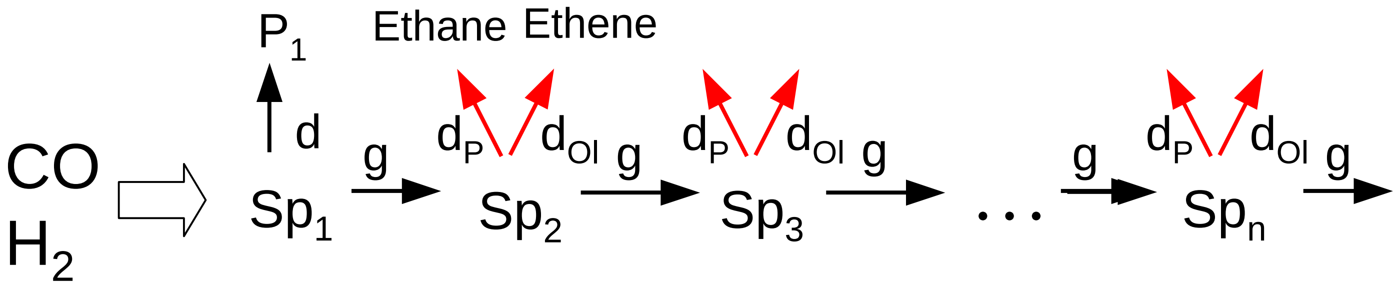


Constraint due to ASF-distribution

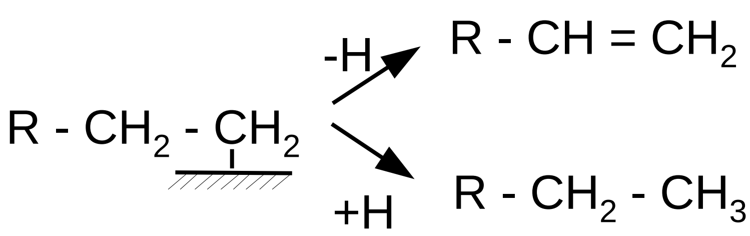


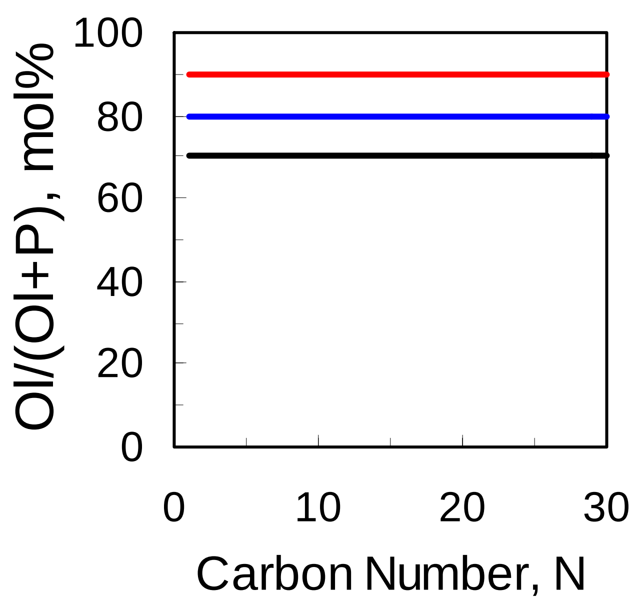
(after M. Dry, 1990)

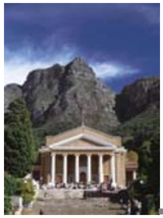
Ideal chain growth desorption as olefin and paraffin



Desorption of alkyl surface species:

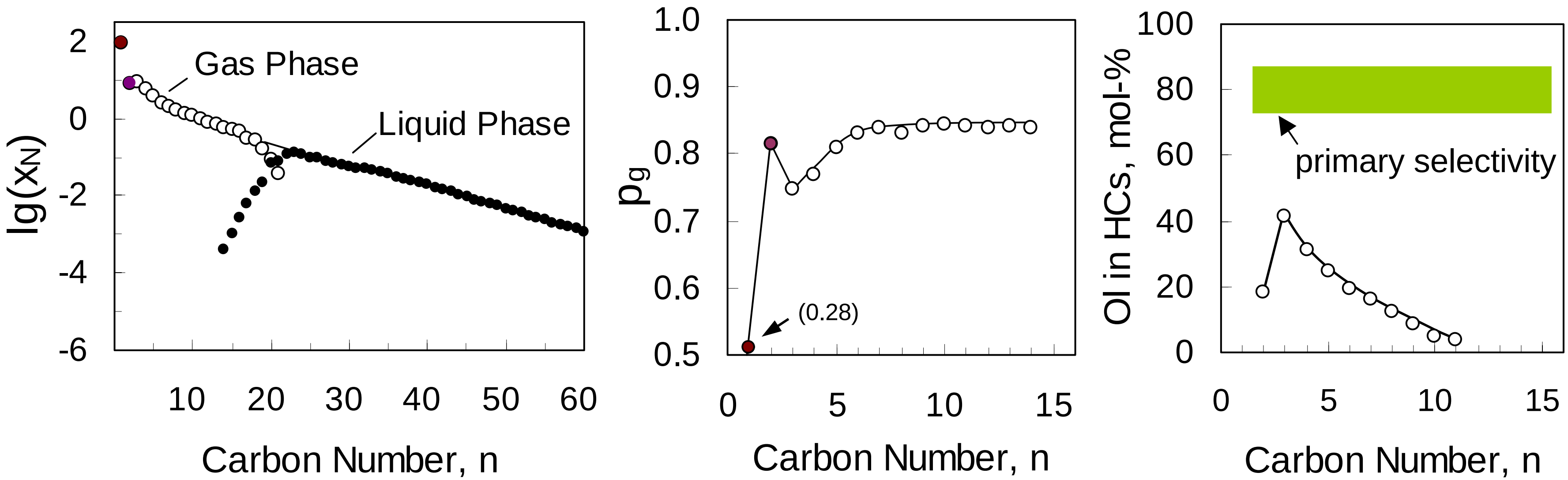






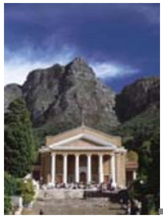
Real product distribution desorption as olefin and paraffin

(Reaction conditions: $CoZrRu\text{-}SiO_2$, T=190°C, p_{H2}=5.1 bar, p_{CO}=2.2 bar, p_{H2O}=1.1 bar)

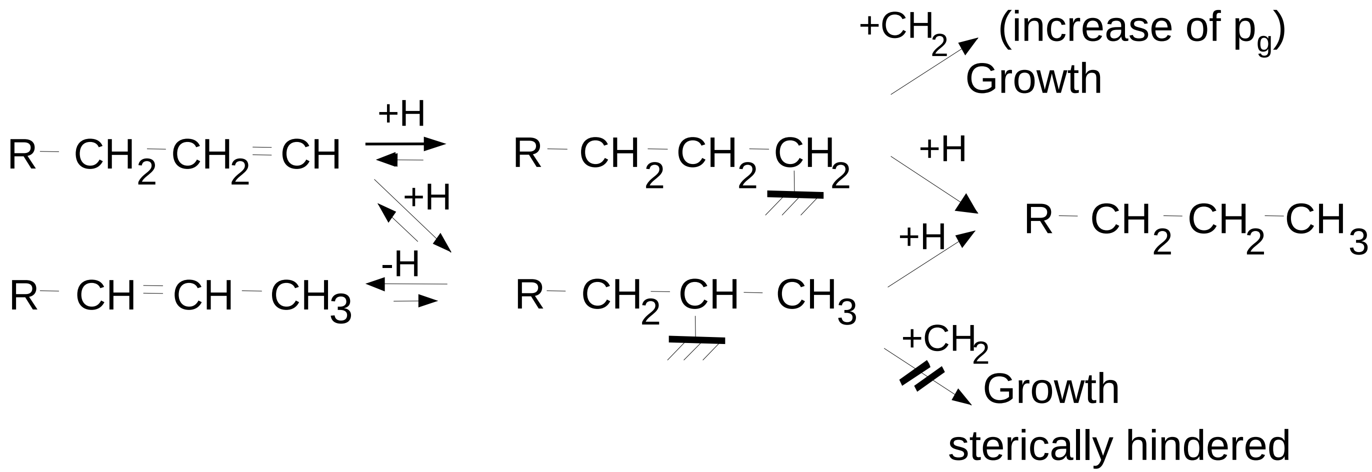


Deviations from ideal kinetics: "non ASF-distributions"

- Relatively **high methane** selectivity
- **Anomaly in C_2**
- Curvature in distribution at low n, chain length dependent p_g
- Chain length dependent olefin content



Secondary olefin reactions

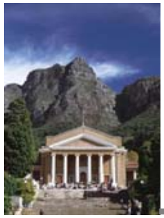


(Schulz et al., 1977 and 1996)

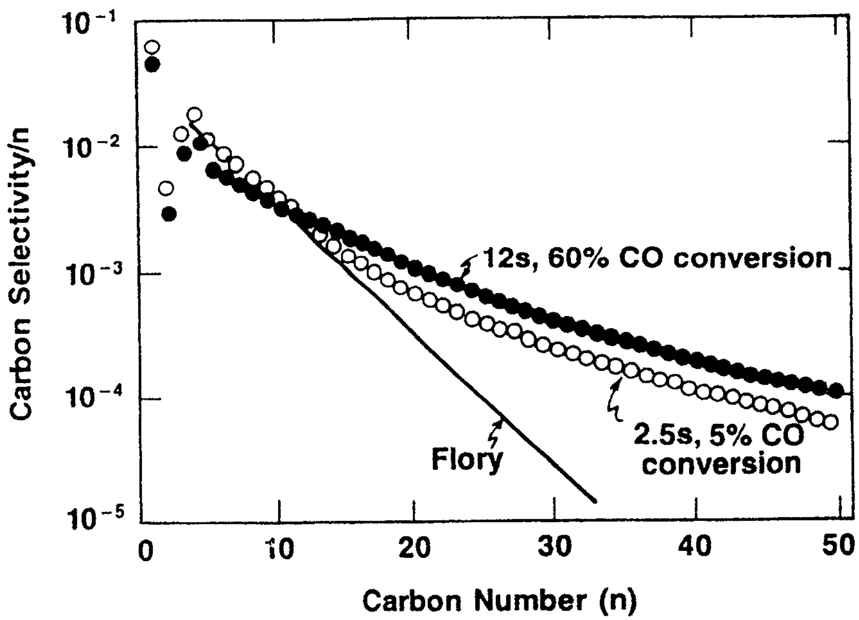
Known reactions

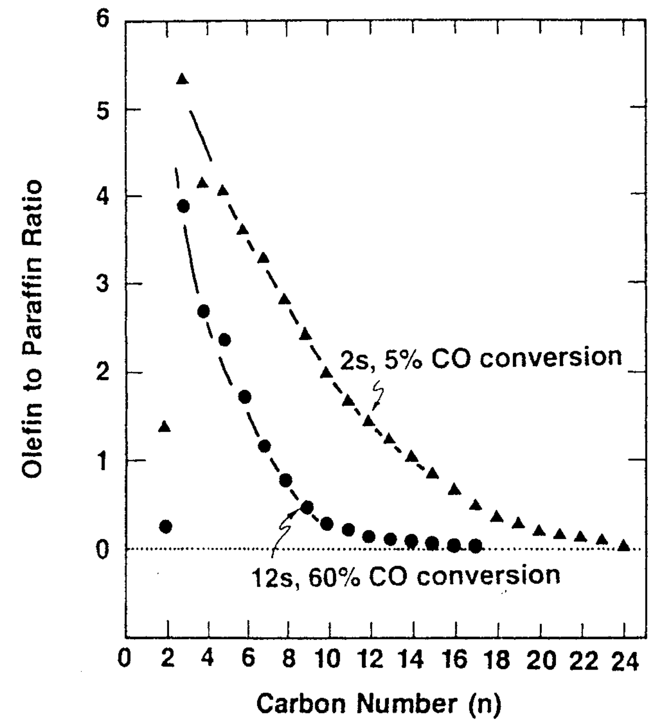
- Hydrogenation
- Incorporation
- Double bond shift
- (Hydroformylation)
- (Hydrogenolysis)

Extent and selectivity of secondary olefin reactions determine product distribution



Impact of secondary olefin reactions on chain growth

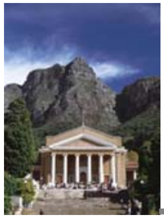




Bed residence time effects on carbon number distributions and α-olefin to n-paraffin ratio

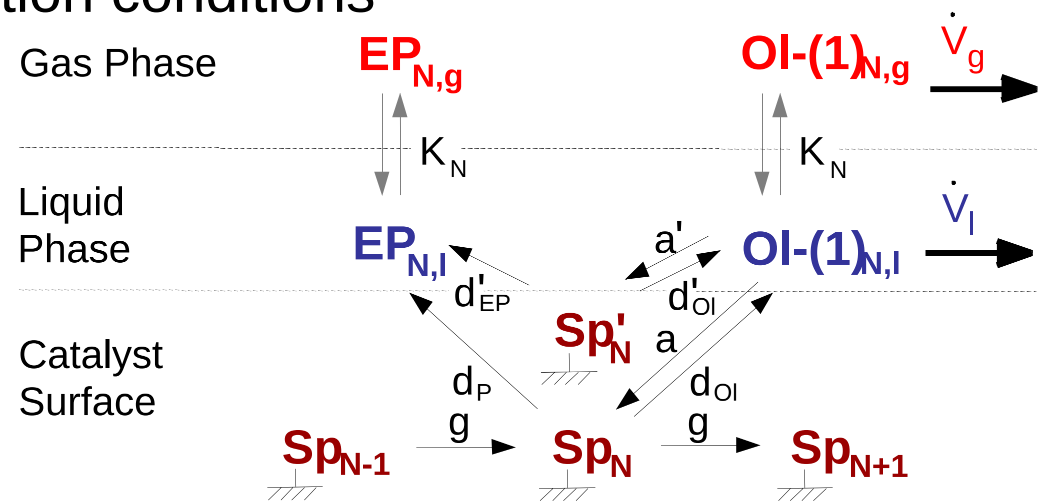
(reaction conditions: 1.2% Ru/TiO$_2$, T=203°C, H$_2$/CO$_{in}$=2.1, p$_{tot}$=6 bar, 5-60% conversion, Fixed bed reactor)

(Iglesia et al., 1991)



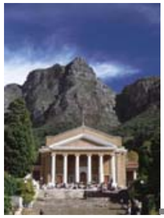
Incorporating secondary olefin reactions in Fischer-Tropsch model

Fischer-Tropsch products are both vapour and liquid products under reaction conditions



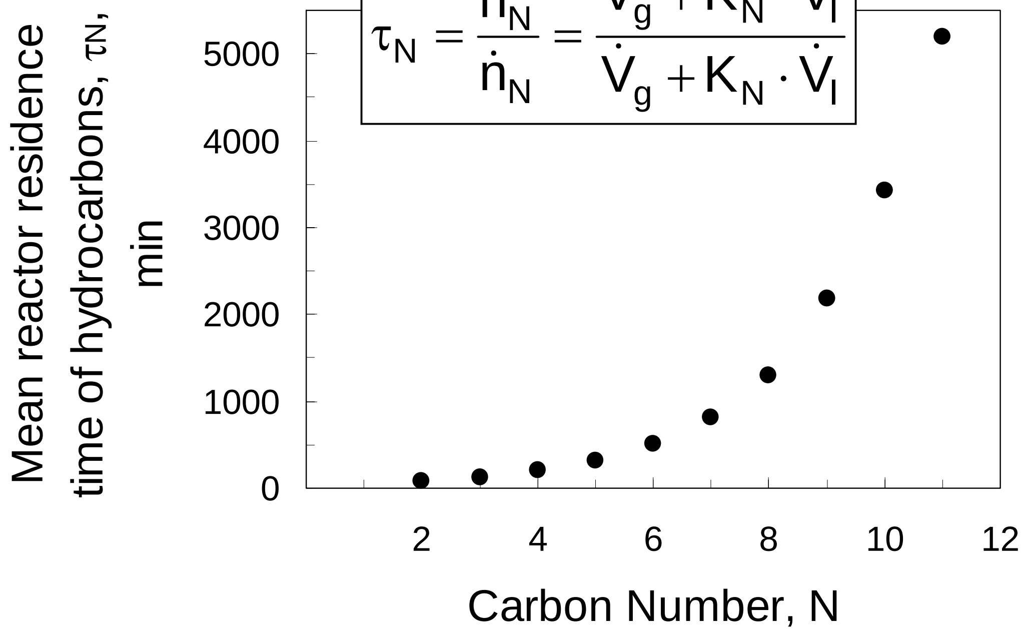
Schulz & Claeys, 1999

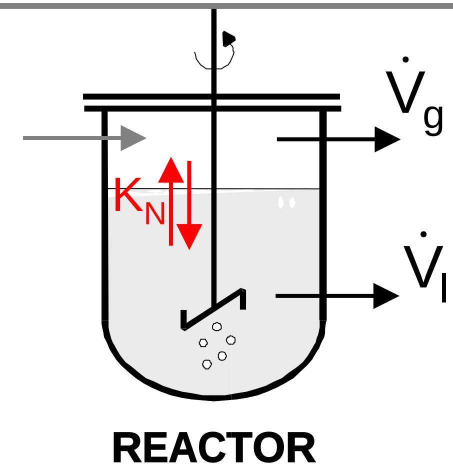
- Desorption as linear α-olefin Ol-(1) and non-reactive end product EP
- Readsorption as species Sp or Sp'; Sp' doesn't participate in chain growth
- All rate constants are assumed carbon number independent (except $k_{a,2}$)
- Thermodynamic equilibrium between gas and liquid phase (carbon number dependent)
- No effects of diffusional limitations or concentration gradients
- Steady state conversion, convective product removal via gas and liquid phase



Distribution over liquid and gas phase

$$\tau_N = \frac{n_N}{\dot{n}_N} = \frac{V_g + K_N \cdot V_l}{\dot{V}_g + K_N \cdot \dot{V}_l}$$





Partition coefficient K_N:

$$K_N = \frac{c_{l,N}}{c_{g,N}} = K_2 \cdot b^{(N-2)}$$

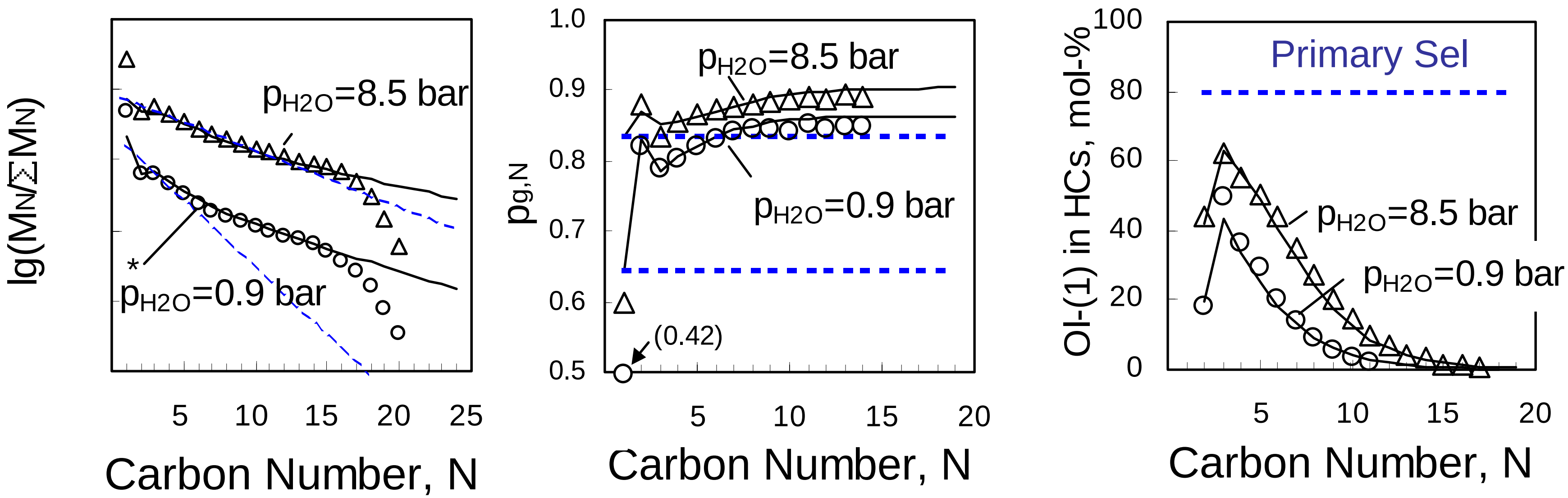
(***CoZrRu-SiO$_2$***, *T=190°C, p_{H2}=5.1 bar, p_{CO}=2.2 bar, p_{H2O}=1.0 bar*

V_g=210 ml, V_l=270 ml, $\dot{V}_g$=5.38 ml/min, $\dot{V}_l$=6.28·10^{-4} ml/min)

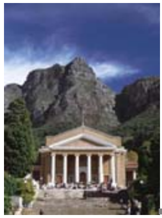
T=190ºC: K_2=1.91; **b=1.53**

Rate of convective removal of products depends on removal of gas and liquid phase and and is therefore carbon number dependent

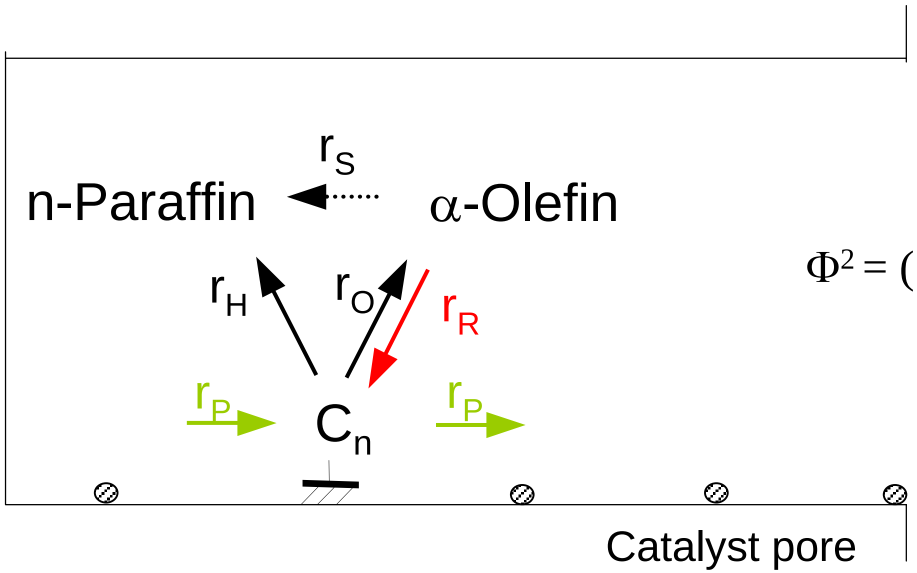
Comparison of extended model with real product distributions



(***CoZrRu-SiO$_2$***, *T=190°C, p_{H2}=5.8 bar, p_{CO}=2.9 bar, p_{H2O}=varied)*



Diffusion enhanced olefin re-adsorption



Diffusion / Reaction

$$\Phi^2 = (k_R/D_n) \cdot \mathbf{(L^2 \cdot \varepsilon \cdot (site\ density) / R_P)}$$

↑

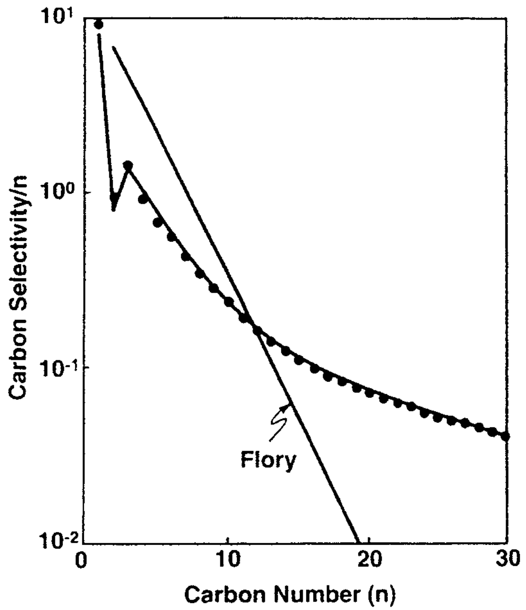
Property of Catalyst (χ)

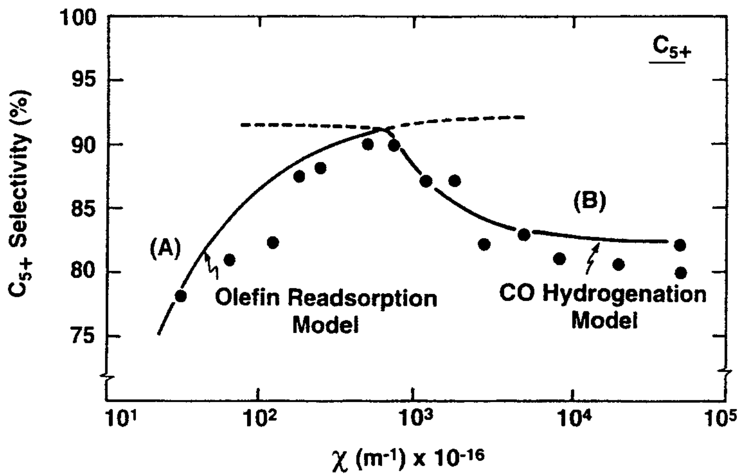
(Iglesia et al., 1991)

Assumptions:

- Product desorption as paraffin or α-olefin only
- Product transport limitations in liquid filled pores of catalyst
  ⇒ increase in local olefin concentration / residence time inside liquid filled pores
  ⇒ diffusion enhanced olefin readsorption: $\mathbf{D_n \propto e^{-0.3n}}$
- All rate constant assumed carbon number independent (except C_2: $k_{R,2}=10k_{R,n}$)
- r_s negligible at CO conversion >5% and p_{total}>5 bar (inhibition by CO and H_2O)

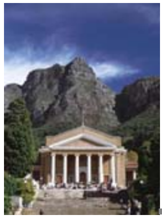
Diffusion enhanced olefin re-adsorption





(Reaction conditions: Cobalt catalysts, T=200°C, p_{total}=20 bar, H_2/CO=2.1, X_{CO}~60%)
(Iglesia et al., 1991, 1993)

- Complete description of Fischer-Tropsch reaction in fixed bed reactors for Cobalt and Ruthenium catalysts, H_2/CO~2
- Non-ASF distributions and olefin/paraffin ratios caused by different product diffusivities
- C5+ selectivity dependent on catalyst properties (χ)



Reactors for Fischer-Tropsch synthesis

Fischer-Tropsch synthesis is highly exothermic
(ca. 160 kJ/mol of CO converted)

Heat removal essential

<u>Objective</u>

Diesel production $\rightarrow$ maximize wax formation

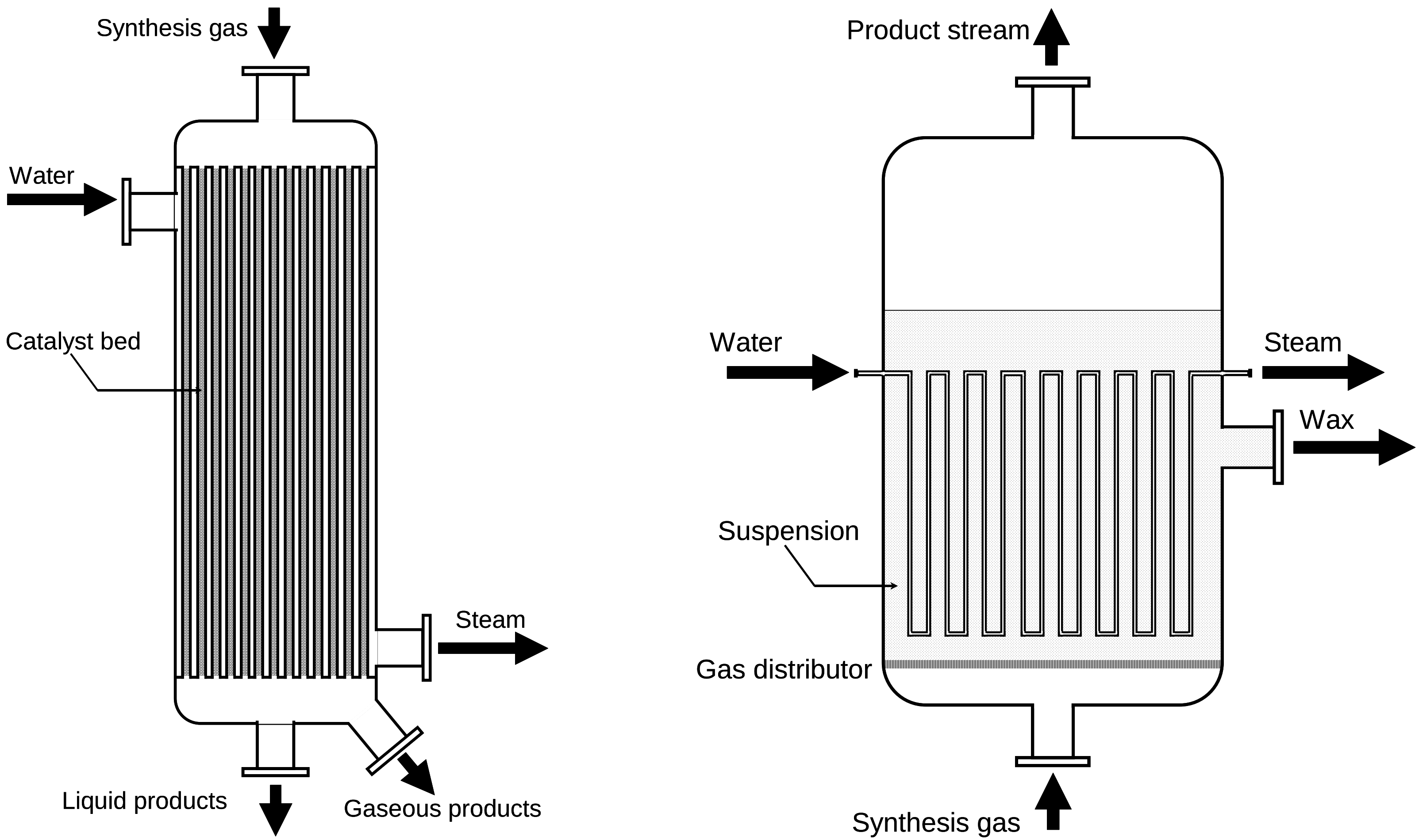
hydrocracking of wax to diesel

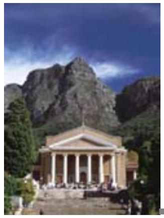
Cobalt (200-220^{o}C) or iron-based (240-260^{o}C) catalyst

Chemicals (olefins)/petrol production

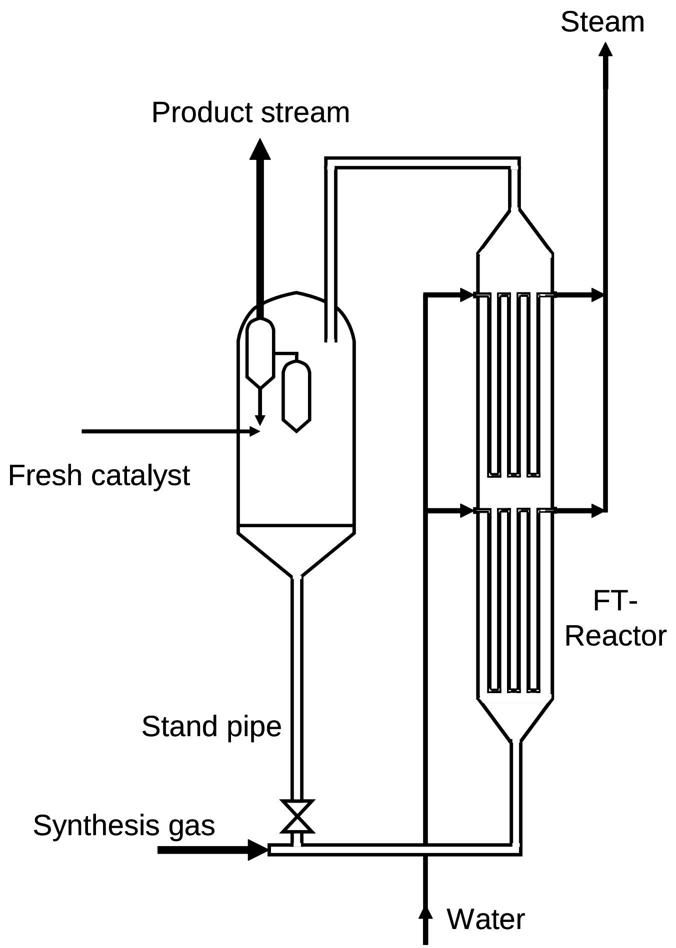
Fused iron catalyst (300-350^{o}C)

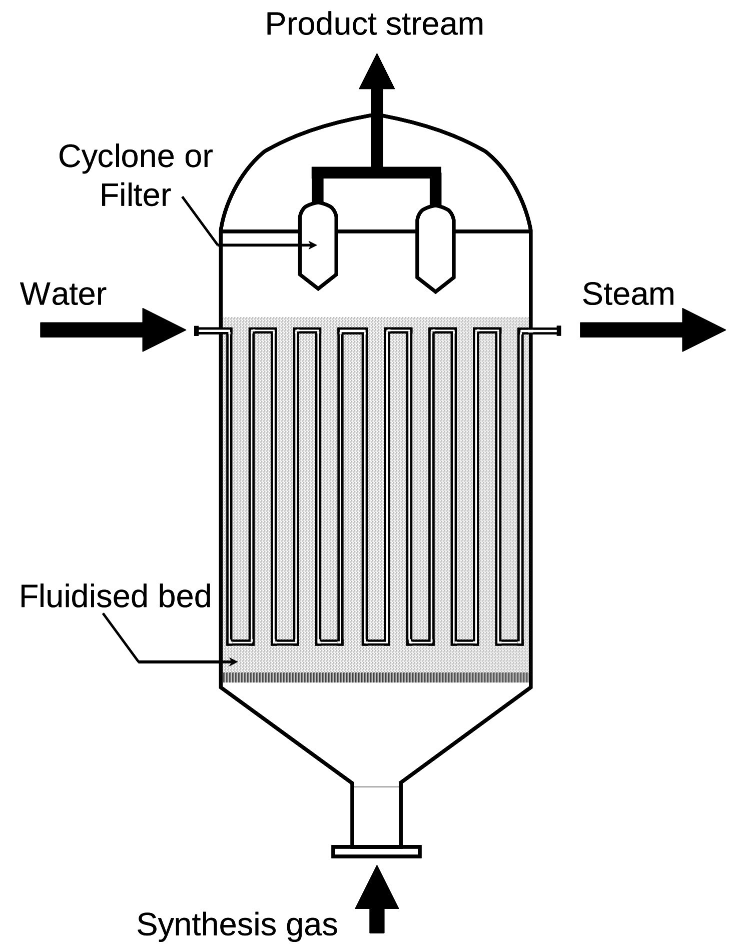
Reactors for Fischer-Tropsch synthesis

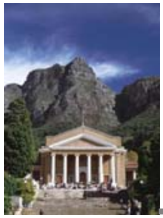




Reactors for Fischer-Tropsch synthesis







Concluding remarks

Main primary products of Fischer-Tropsch synthesis:

linear α-olefins
paraffins
(alcohols)

Mechanism: more than one single mechanism in operation
debate on the importance of the various mechanisms still ongoing

Fischer-Tropsch synthesis = polymerization reaction
constraints in the product formation
maximum liquid productivity by re-adsorption and re-incorporation of reactive product compounds

Reactors for Fischer-Tropsch synthesis
Heat removal primary concern