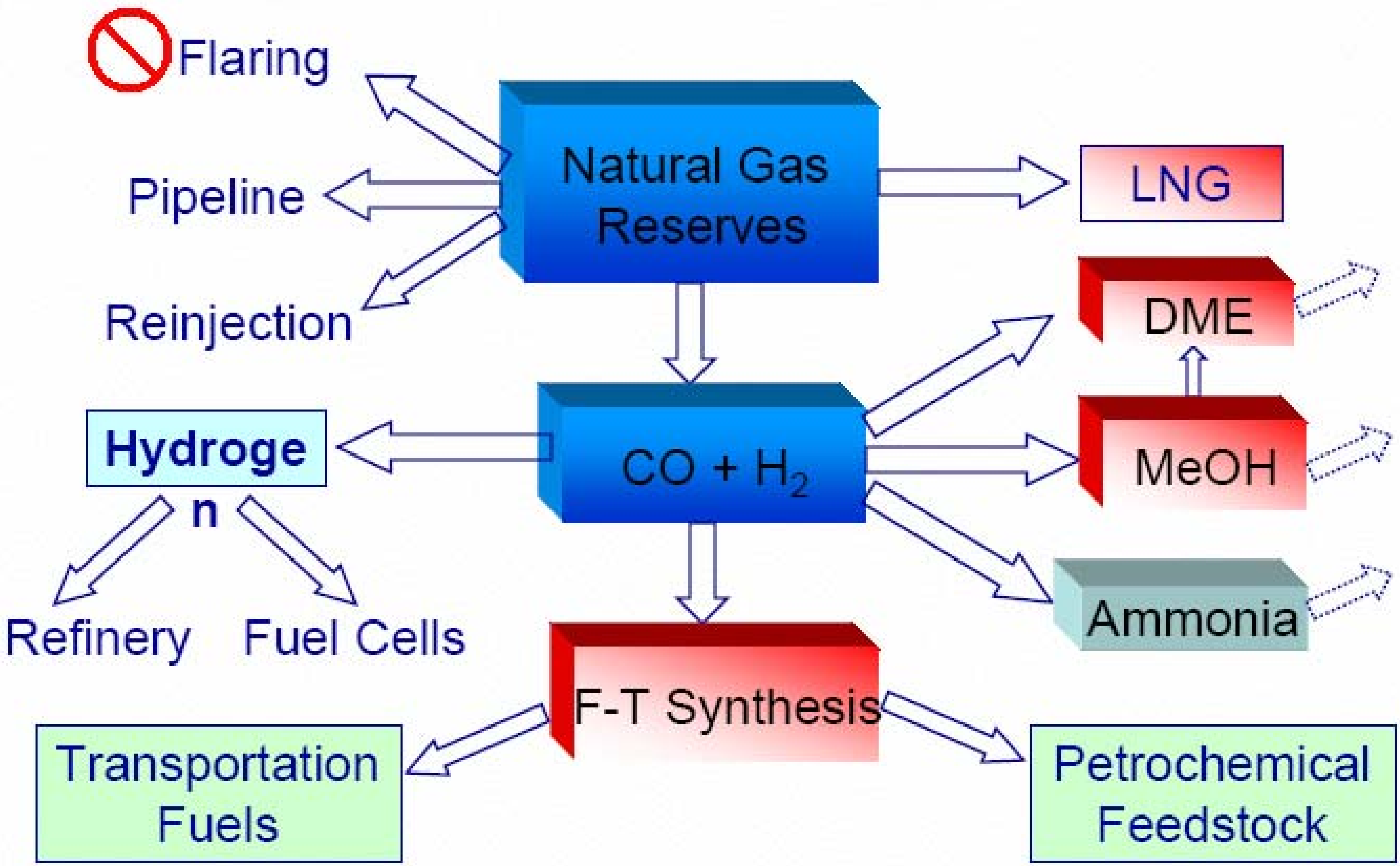


Flaring

Pipeline

Reinjection

Natural Gas Reserves

LNG

DME

MeOH

CO + H_2

Hydrogen

Refinery

Fuel Cells

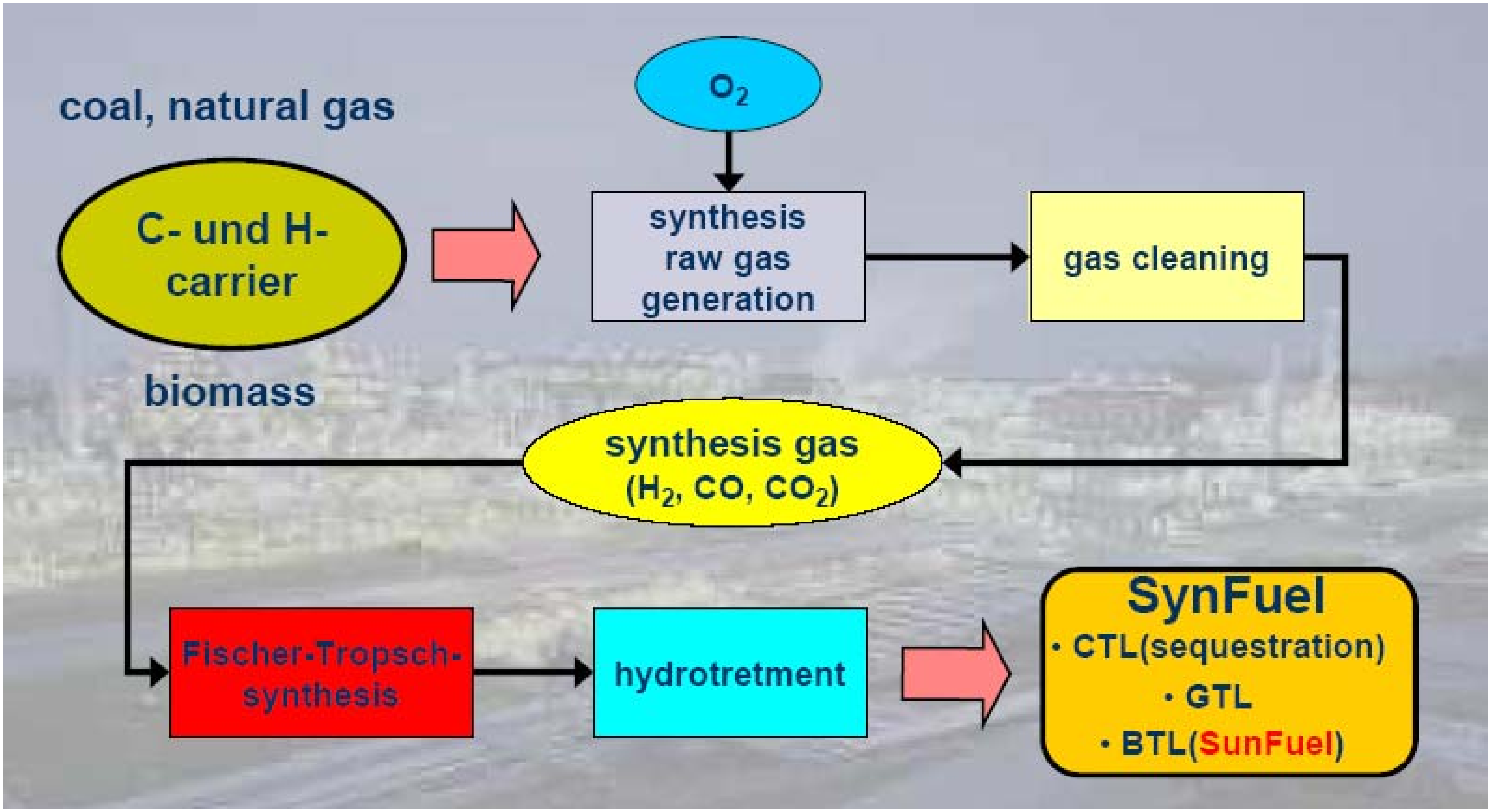
Ammonia

F-T Synthesis

Transportation Fuels

Petrochemical Feedstock

Gasification



coal, natural gas

C- und H-carrier

biomass

O_2

synthesis raw gas generation

gas cleaning

synthesis gas (H_2, CO, CO_2)

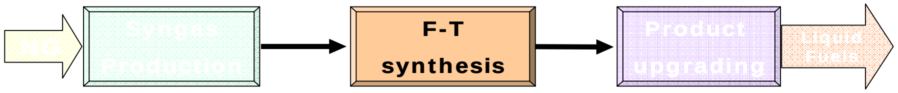
Fischer-Tropsch-synthesis

hydrotretment

SynFuel

- CTL(sequestration)
- GTL
- BTL(SunFuel)

Fischer-Tropsch Reaction



$nCO + 2nH_2 \rightarrow n(-CH_2-) + n\ H_2O \quad \Delta H = -167\ kJ/mole$

$CO + 3\ H_2 \rightarrow CH_4 + H_2O$	Methanation (ΔH=-206 kJ/mole)
$CO + H_2O \rightarrow CO_2 + H_2$	Water Gas Shift (ΔH=-41 kJ/mole)
$2CO \rightarrow C + CO_2$	Boudouard reaction (ΔH=-172 kJ/mole)
$H_2 + CO \rightarrow C + H_2O$	Coke formation (ΔH=-133 kJ/mole)

Main features of modern GTL-FT:

- Low temperature (200-240°C) and mid pressure (20-30 bar) to promote F-T over methanation reaction
- Active catalyst based on **IRON** or **COBALT**
- Production of high molecular weight linear waxes for further hydroprocessing step to optimize the overall liquid production, because it is impossible to produce directly a well defined range of products (i.e. middle distillates)

Fischer-Tropsch

Goal: production of liquid fuels or chemicals from gas

Also called: GTL

- political reasons (South Africa)
- remote gas fields (e.g., SMDS)

Main reactions	
Alkanes	$n\,CO + (2n+1)\,H_2 \rightarrow C_nH_{2n+2} + n\,H_2O$
Alkenes	$n\,CO + 2n\,H_2 \rightarrow C_nH_{2n} + n\,H_2O$
Water-gas shift	$CO + H_2O \rightleftarrows CO_2 + H_2$
Side reactions	
Alcohols	$n\,CO + 2n\,H_2 \rightarrow H(\text{-}CH_2\text{-})_nOH + (n\text{-}1)\,H_2O$
Boudouard reaction	$2\,CO \rightarrow C + CO_2$

Franz Fischer (1877-1947)

Profeſſor Dr. Franz Fiſcher, Geh. Reg.-Rat
(Direktor des Inſtituts von der Gründung bis heute)

Hans Tropsch (1889-1935)

Dr.-Ing. Hans Tropſch,
Abteilungsvorſteher von 1921—1928
(am Inſtitut tätig von 1916—1917 und 1921—1928)

01663

CHEMISCHE WERKE ESSENER STEINKOHLE A.G., Bergkamen

Staatsgeheimnis
...en, bei Post
...n".
...antwortung des
...herem Verschluß.

Patentanmeldung C 56 917 IV d/12 o vom 27. November 1941.

Verfahren zur Herstellung höherer Kohlenwasserstoffe durch katalytische Hydrierung von Oxyden des Kohlenstoffs.

- Basic F-T reaction

$$nCO + 2nH_2 \Rightarrow (-CH_2-)_n + nH_2O \quad (\Delta H_R = -39.4 \text{ kcal/gmol}) \text{ [1]}$$

- Stoichiometric H_2/CO ratio = 2
- Products predominantly normal paraffins, but may contain significant quantities of α-olefins and/or alcohols:

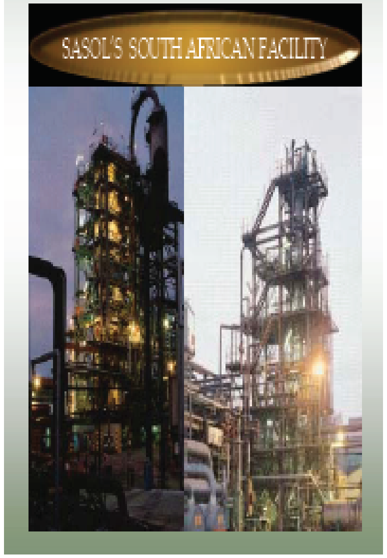
$$nCO + (2n+1)H_2 \Rightarrow C_nH_{2n+2} + nH_2O \quad \text{(n-paraffins)}$$
$$nCO + 2nH_2 \Rightarrow C_nH_{2n} + nH_2O \quad (\alpha\text{-olefins})$$
$$nCO + 2nH_2 \Rightarrow C_nH_{2n+1}OH + nH_2O \quad \text{(alcohols)}$$

Fischer-Tropsch

- Hans Fischer and Franz Tropsch discovered the chemistry in 1923
- Germany commercialized the technology in WWII
- Today the future is bright

SASOL

- 160,000 b/d+
- Feedstock - Coal

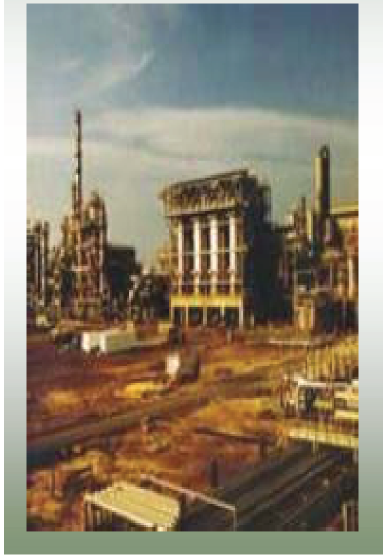


Petro SA

- 22,500 b/d+
- Feedstock - Natural Gas

Shell

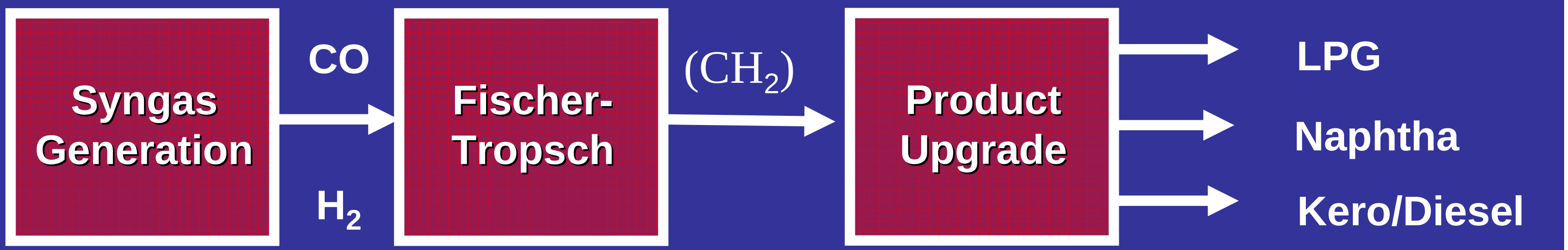
- 15,000 b/d+
- Feedstock - Natural Gas



Sasol Oryx Project

- 34,000 b/d
- Feedstock - Natural Gas
- Online 2006

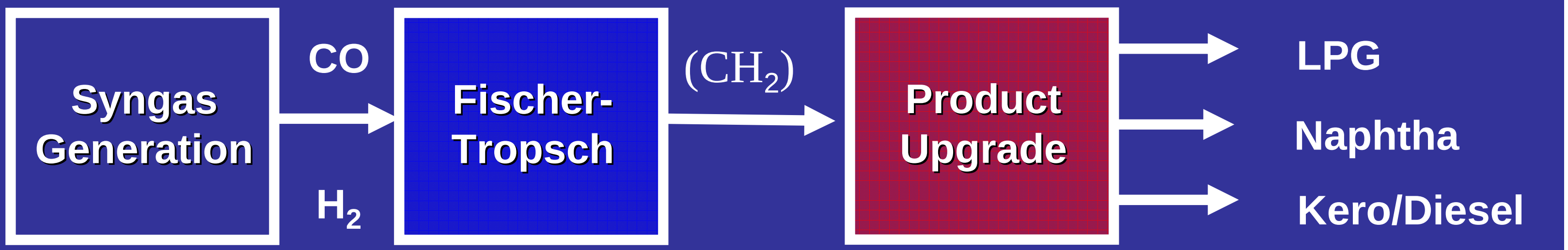
Gas-to-Liquids (FT) Process



Technology – *FT Process*

Technical challenges

- Catalyst
- Heat removal
- Reactor design
- Scale-up



The Sasol Slurry Bed Reactor

Technical challenges

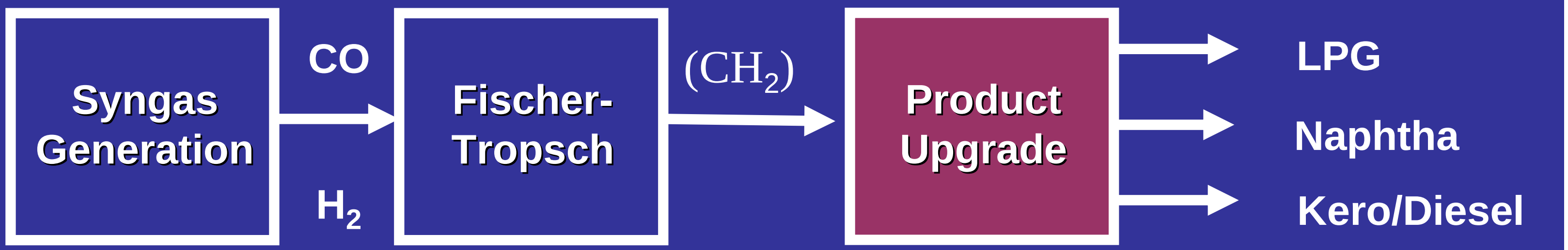
The largest commercial-sized FT reactor - SASOL

Pictures Courtesy of Sasol

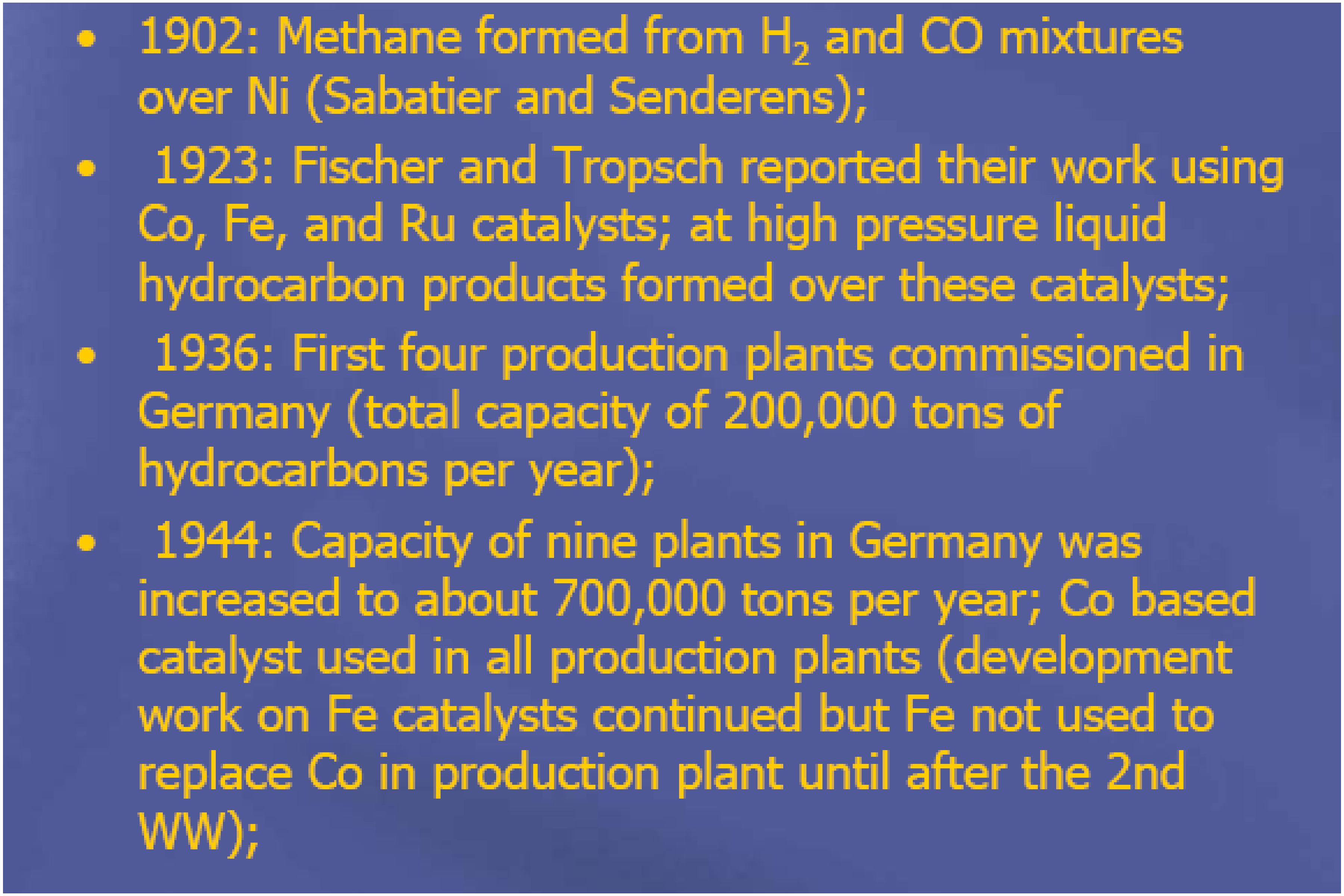
Technical challenges

Technology – *Product Upgrade*

- Catalyst
- Capacity

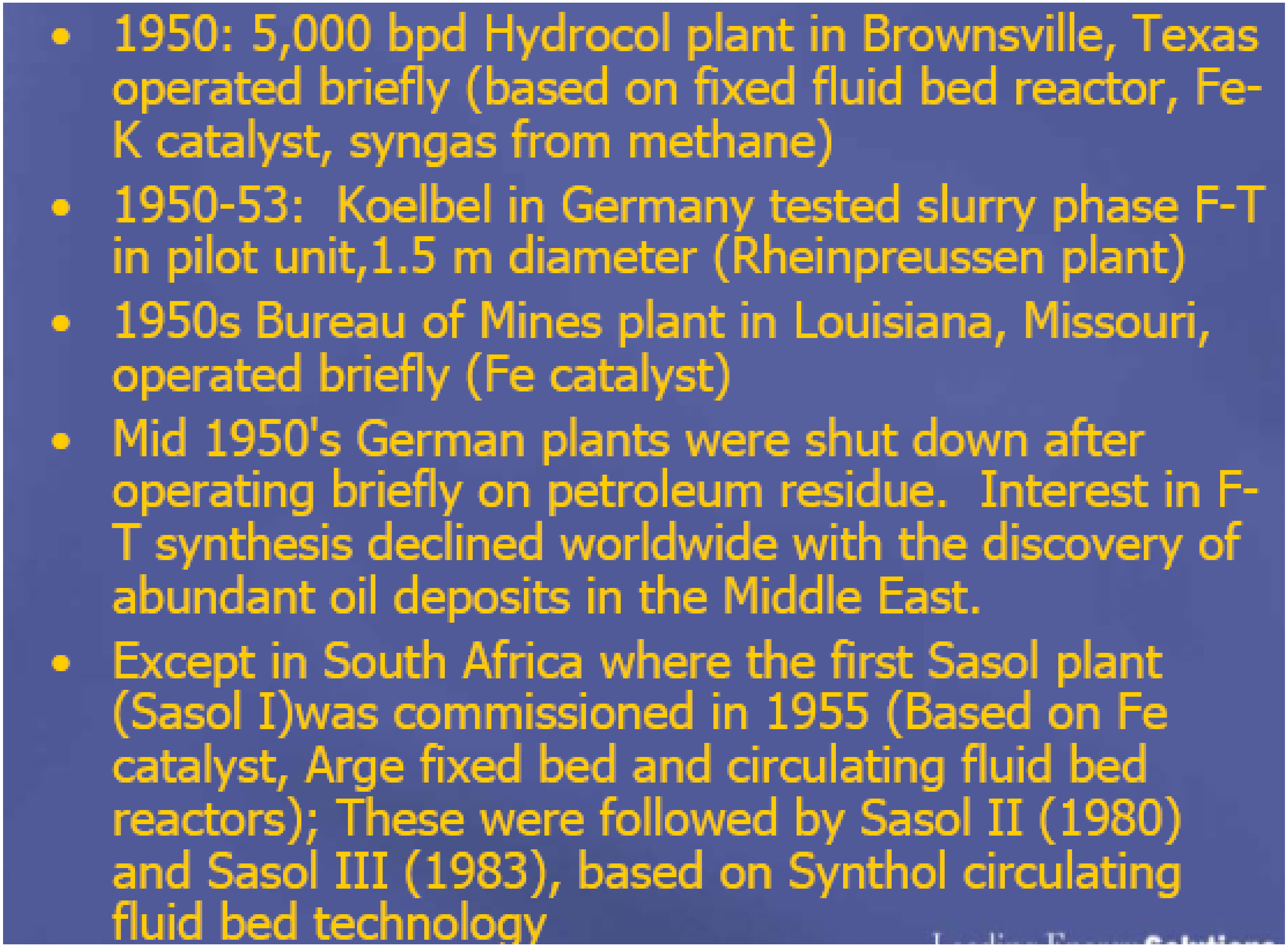


History



- 1902: Methane formed from H_2 and CO mixtures over Ni (Sabatier and Senderens);
- 1923: Fischer and Tropsch reported their work using Co, Fe, and Ru catalysts; at high pressure liquid hydrocarbon products formed over these catalysts;
- 1936: First four production plants commissioned in Germany (total capacity of 200,000 tons of hydrocarbons per year);
- 1944: Capacity of nine plants in Germany was increased to about 700,000 tons per year; Co based catalyst used in all production plants (development work on Fe catalysts continued but Fe not used to replace Co in production plant until after the 2nd WW);

History

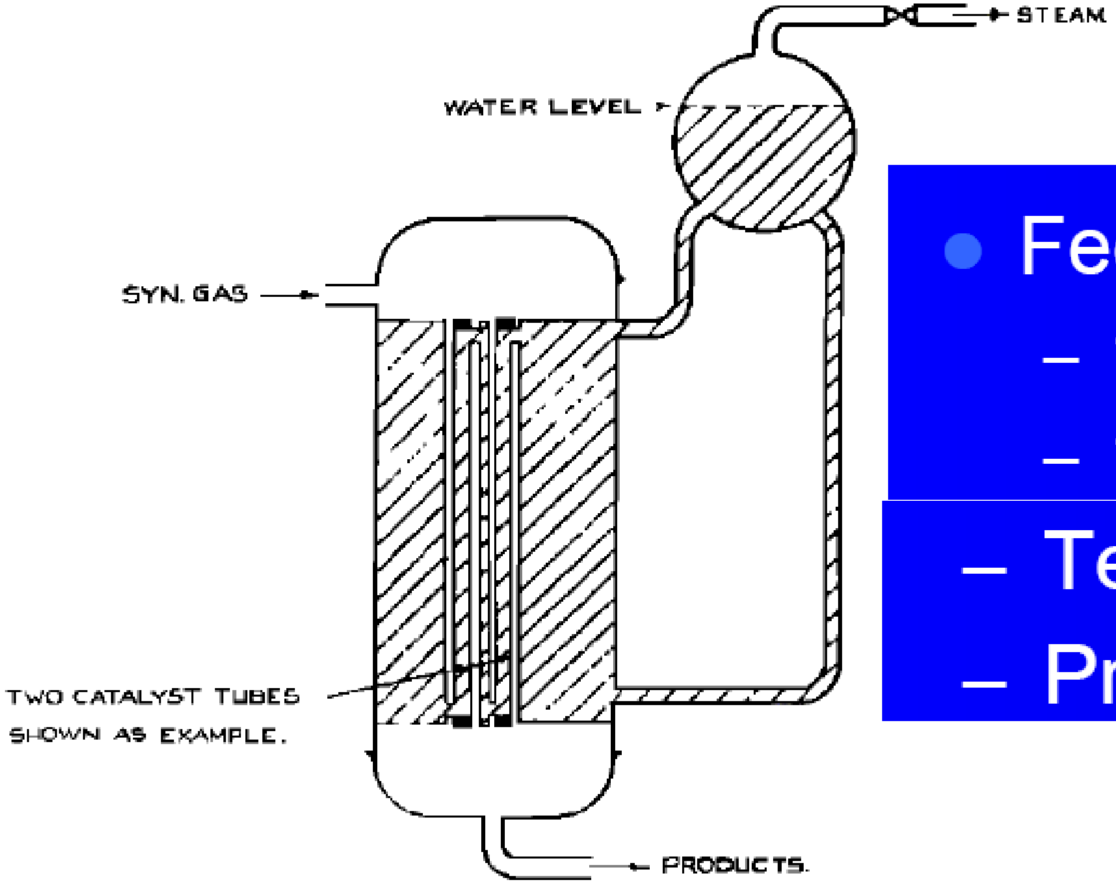


- 1950: 5,000 bpd Hydrocol plant in Brownsville, Texas operated briefly (based on fixed fluid bed reactor, Fe-K catalyst, syngas from methane)
- 1950-53: Koelbel in Germany tested slurry phase F-T in pilot unit,1.5 m diameter (Rheinpreussen plant)
- 1950s Bureau of Mines plant in Louisiana, Missouri, operated briefly (Fe catalyst)
- Mid 1950's German plants were shut down after operating briefly on petroleum residue. Interest in F-T synthesis declined worldwide with the discovery of abundant oil deposits in the Middle East.
- Except in South Africa where the first Sasol plant (Sasol I)was commissioned in 1955 (Based on Fe catalyst, Arge fixed bed and circulating fluid bed reactors); These were followed by Sasol II (1980) and Sasol III (1983), based on Synthol circulating fluid bed technology

NOVOCHERKASSK SYNTHETIC PRODUCTS PLANT 1954-1992

- Design FT Plant
  - Planned capacity 50,000 tpy
  - Primary commercial products
    - *n*-paraffins(C_5-C_{24} reference cetane)
    - solvents (C_5-C_6 and C_6-C_7 paraffin fractions)
    - Oxidation feedstocks (paraffin fractions 179-270, 260-290°C)
    - solid paraffins (ceresin)
- Disadvantages
  - Low process productivity
    - 4 t catalyst reactor load produces 2.5 t/day of C_{2+}
  - Uneconomical production
  - Co catalyst is no more than 9-12 months.

Novocherkassk



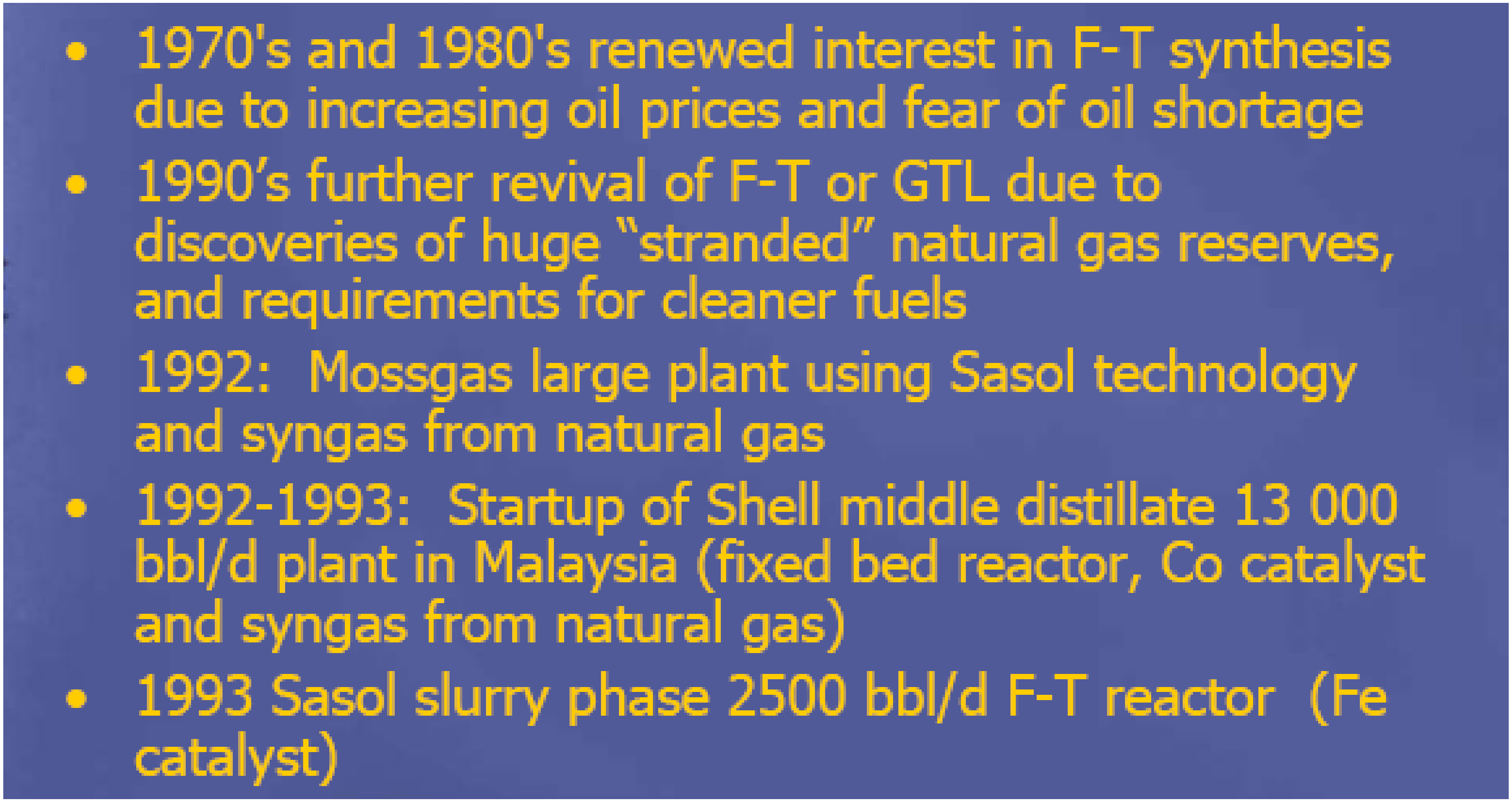
(B) REACTION VESSEL FOR MEDIUM PRESSURE SYNTHESIS.

- Feed
  - 1954 to 1978 anthracite
  - 1978 to 1992 natural gas
- Temp. 170 to 200° C
- Pressure 8-10 atm

Novocherkassk

- 1954- 1967 German Formulation
  - 100 Co, 8 MgO, 5 ThO_2, 200 kieselgur
- 1967 – 1977 Thoria Free Catalyst
  - 200 Co, 10 MgO, 260-280 kieselgur
- 1977 – 1981 Ceresin yield improvement
  - 100 Co, 10 ZrO_2, 200 kieselgur
- 1981-1992 Ceresin yield improvement
  - 100 Co, 10 MgO, 10 ZrO_2, 200 amorphous synthetic aluminosilicate

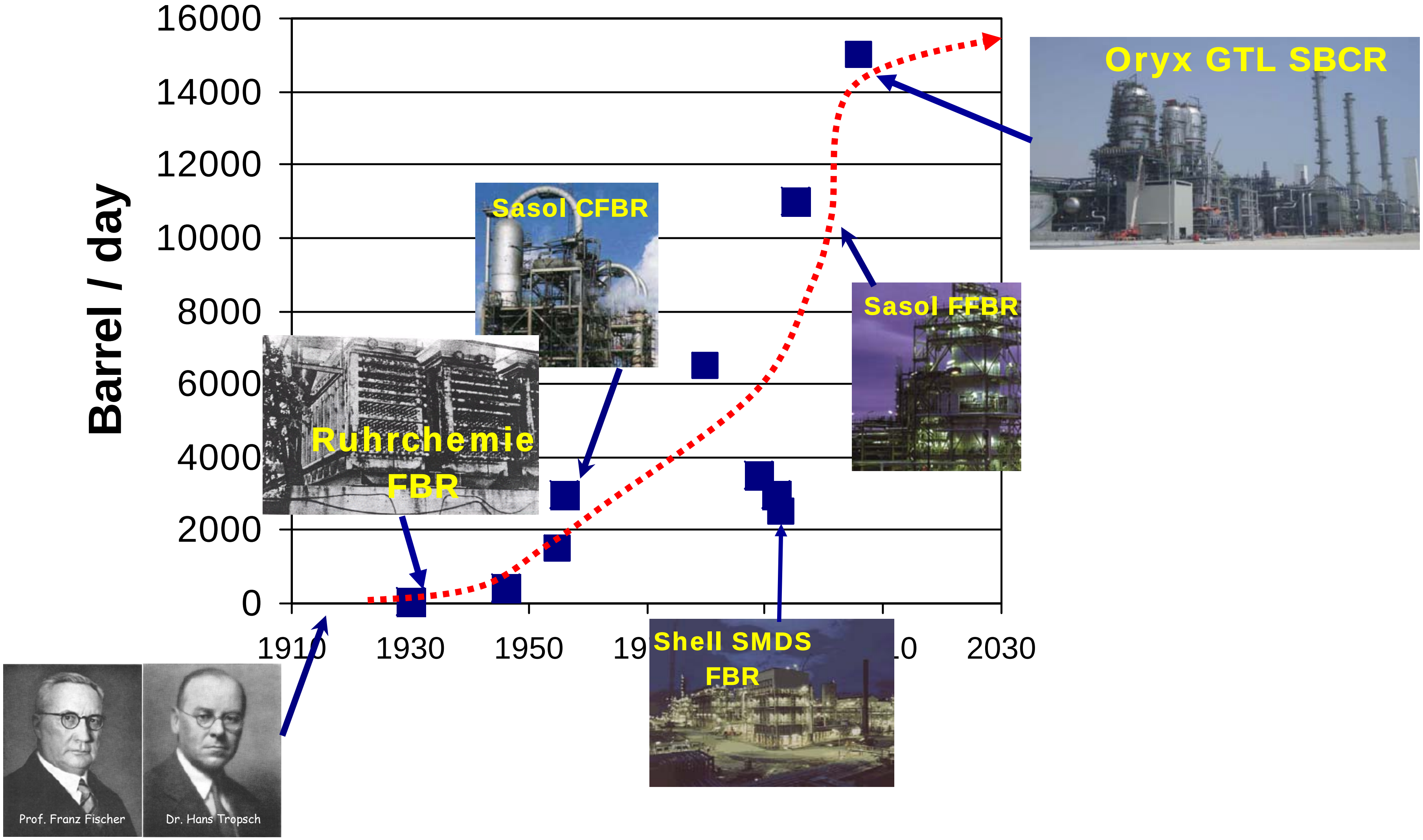
History



- 1970's and 1980's renewed interest in F-T synthesis due to increasing oil prices and fear of oil shortage
- 1990's further revival of F-T or GTL due to discoveries of huge "stranded" natural gas reserves, and requirements for cleaner fuels
- 1992: Mossgas large plant using Sasol technology and syngas from natural gas
- 1992-1993: Startup of Shell middle distillate 13 000 bbl/d plant in Malaysia (fixed bed reactor, Co catalyst and syngas from natural gas)
- 1993 Sasol slurry phase 2500 bbl/d F-T reactor (Fe catalyst)

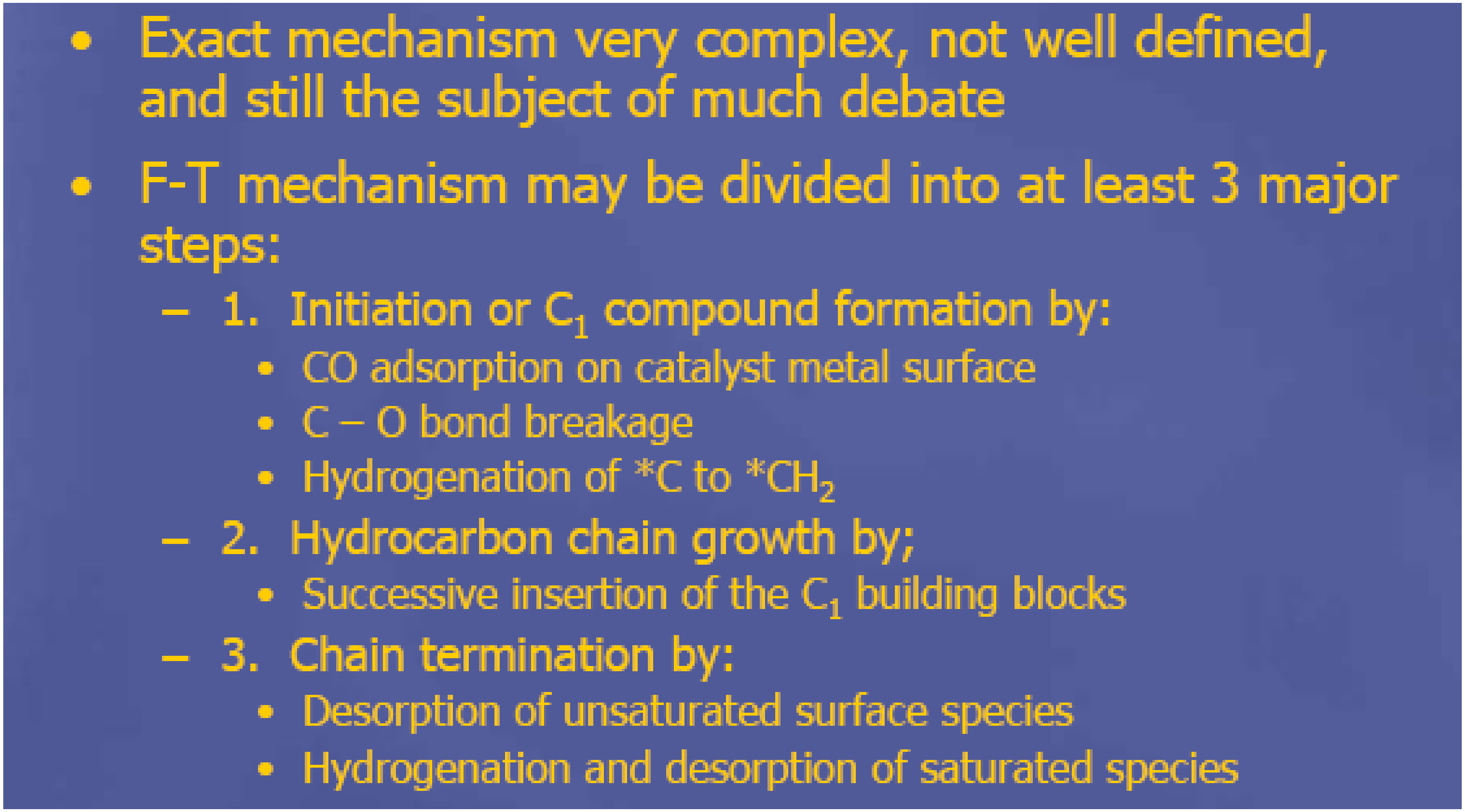
FT Reactor Capacities

Historical overview



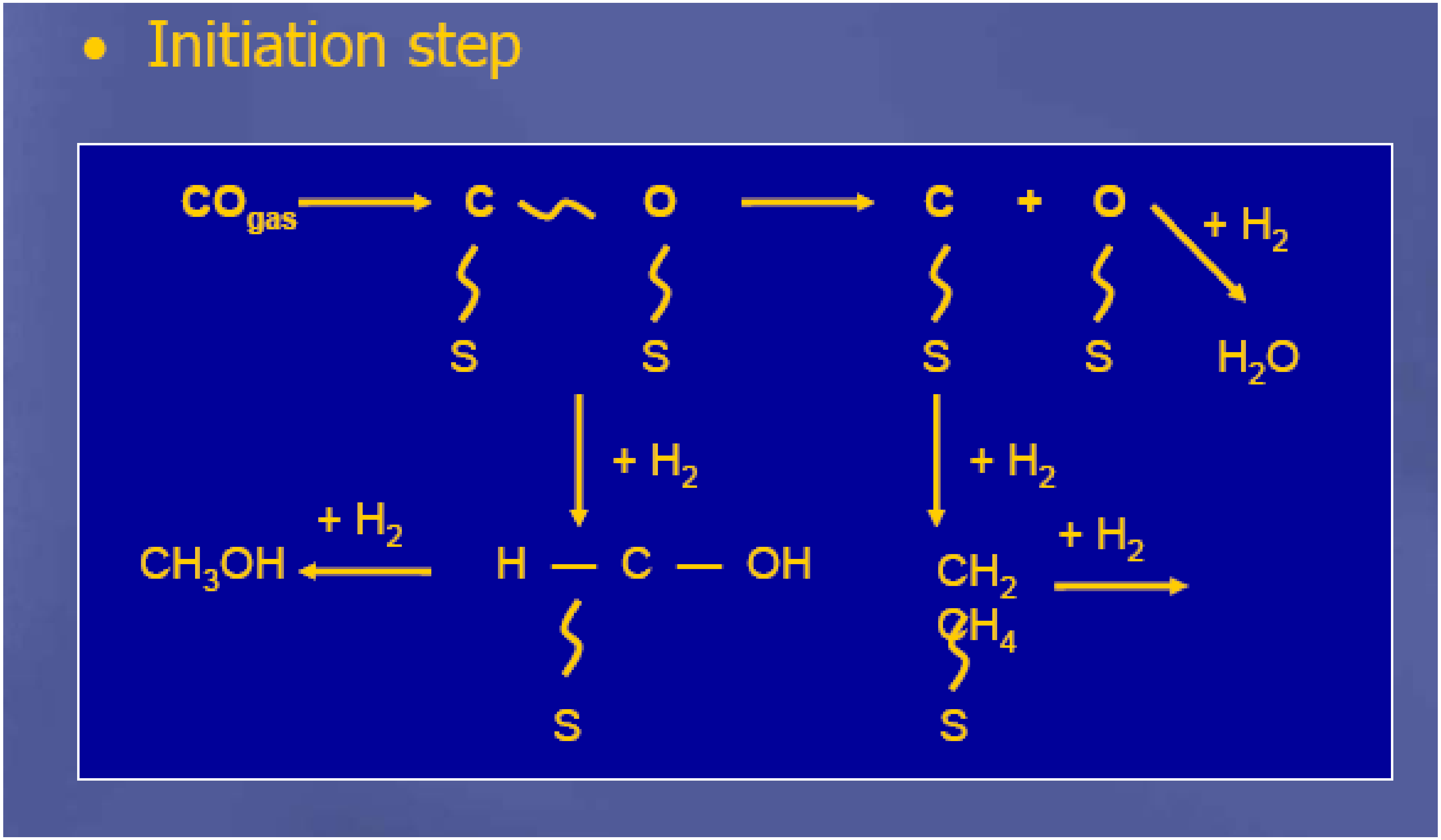
Sasol Plant, South Africa

Mechanism



- Exact mechanism very complex, not well defined, and still the subject of much debate
- F-T mechanism may be divided into at least 3 major steps:
  - 1. Initiation or C_1 compound formation by:
    - CO adsorption on catalyst metal surface
    - C – O bond breakage
    - Hydrogenation of *C to *CH_2
  - 2. Hydrocarbon chain growth by;
    - Successive insertion of the C_1 building blocks
  - 3. Chain termination by:
    - Desorption of unsaturated surface species
    - Hydrogenation and desorption of saturated species

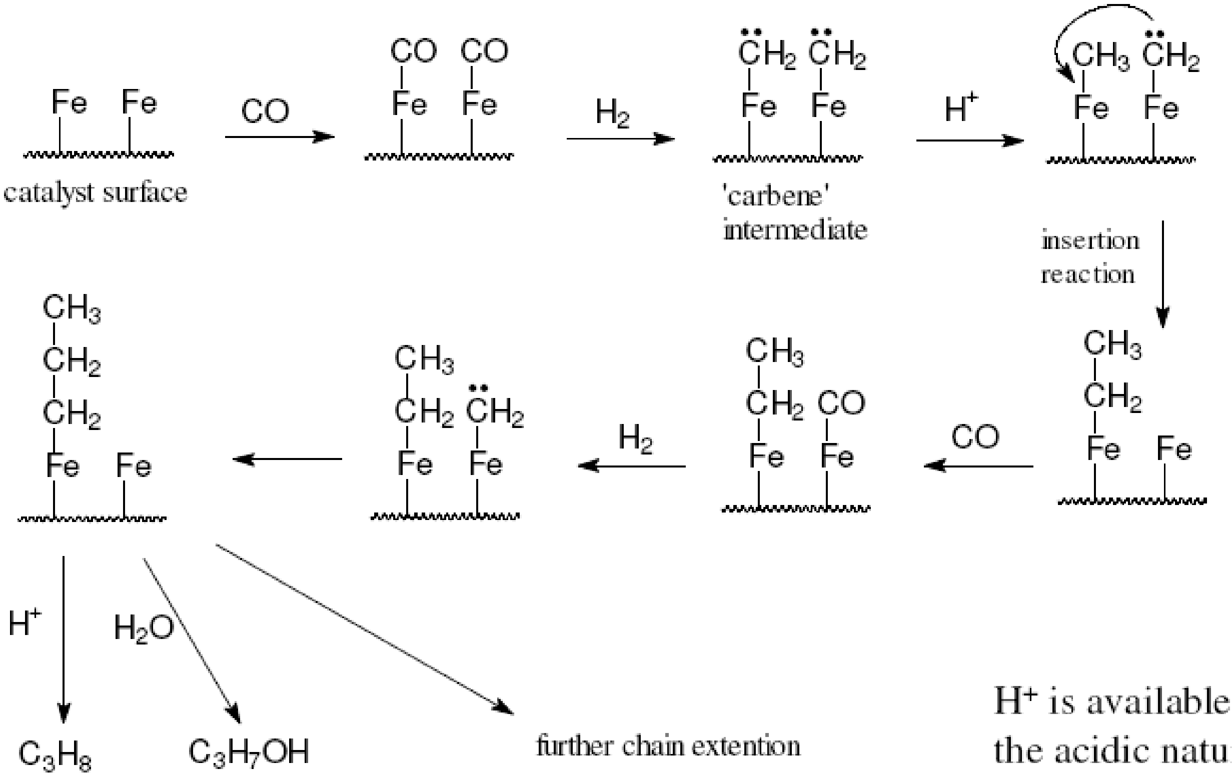
Mechanism



- Initiation step

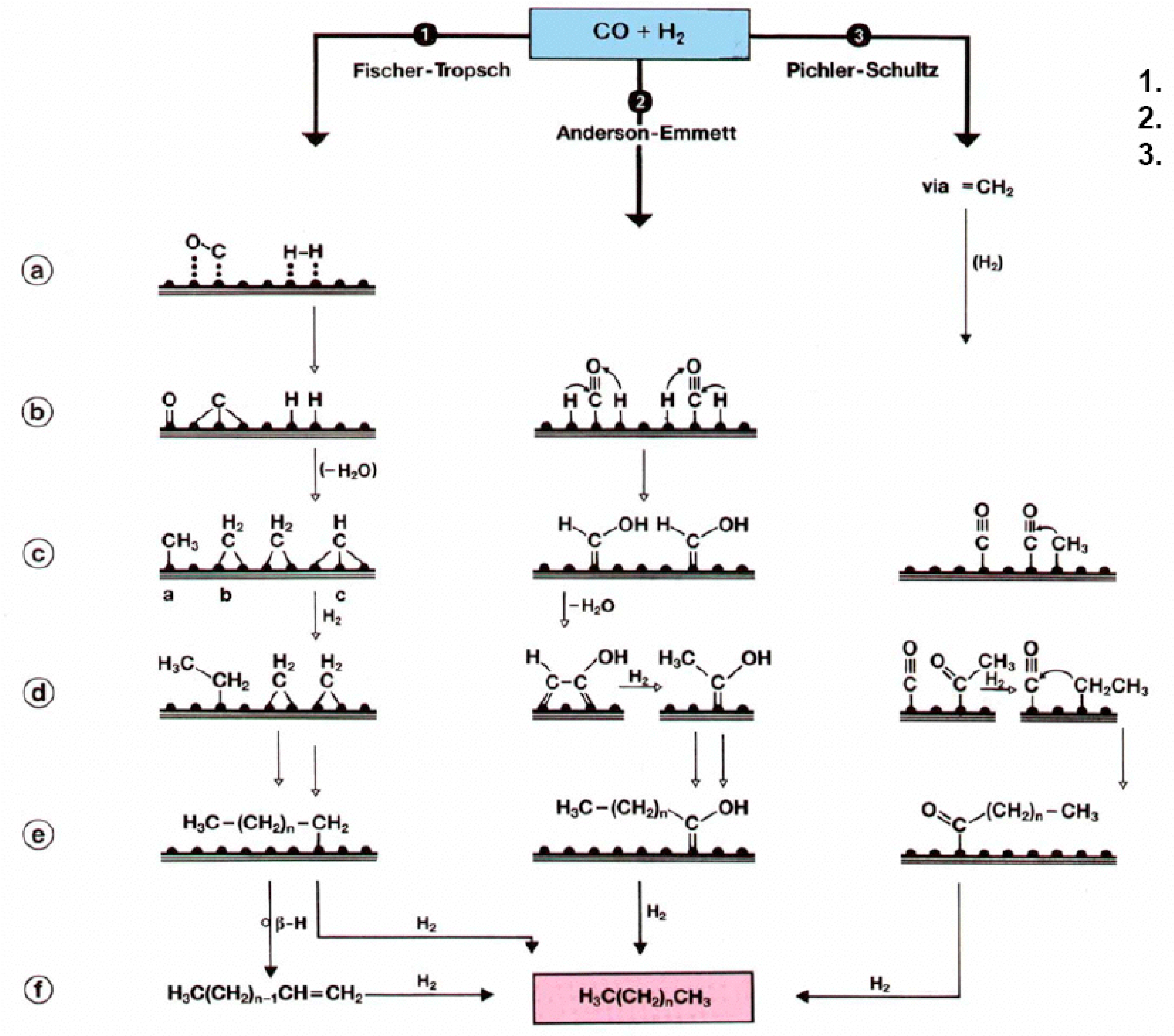
Mechanism: chain growth

The mechanism of the Fischer Tropsch process appears to involve **carbene** formation on the catalyst surface.



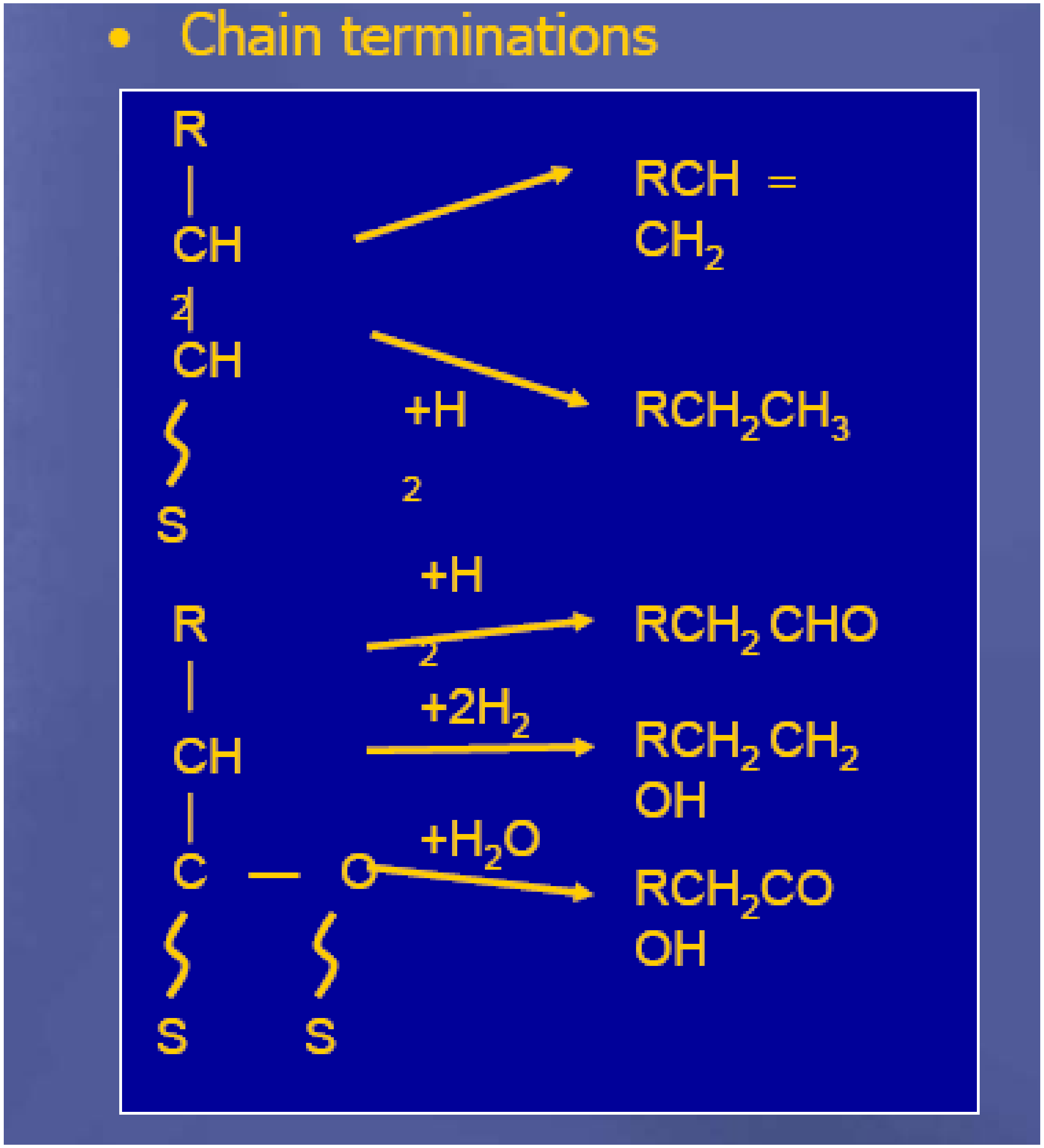
H^+ is available due to the acidic nature of the catalyst

Fischer Tropsch Chemistry: Mechanisms



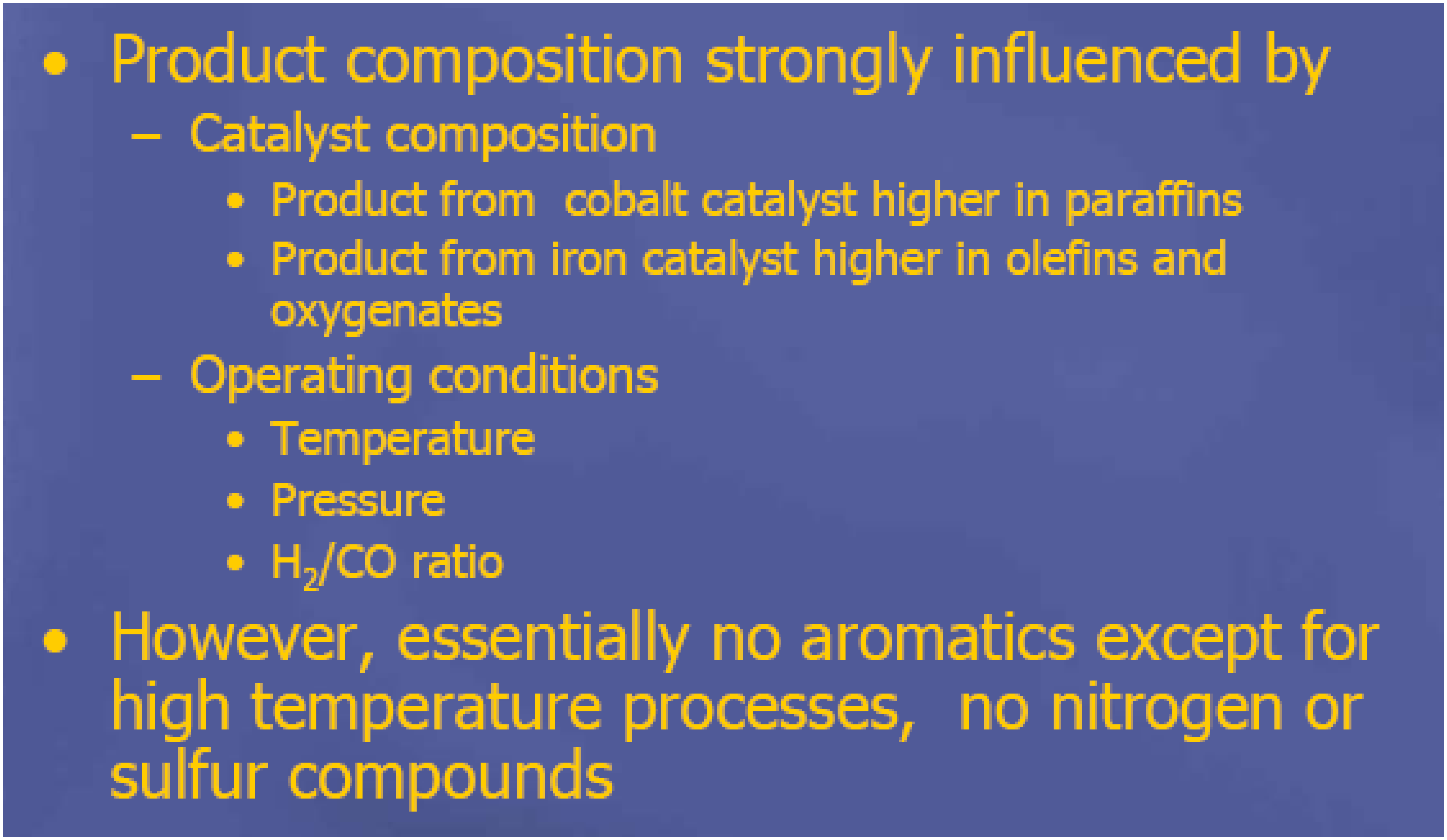
1. Carbide-methylene
2. Hydroxycarbene
3. CO insertion/M-Me

Mechanism

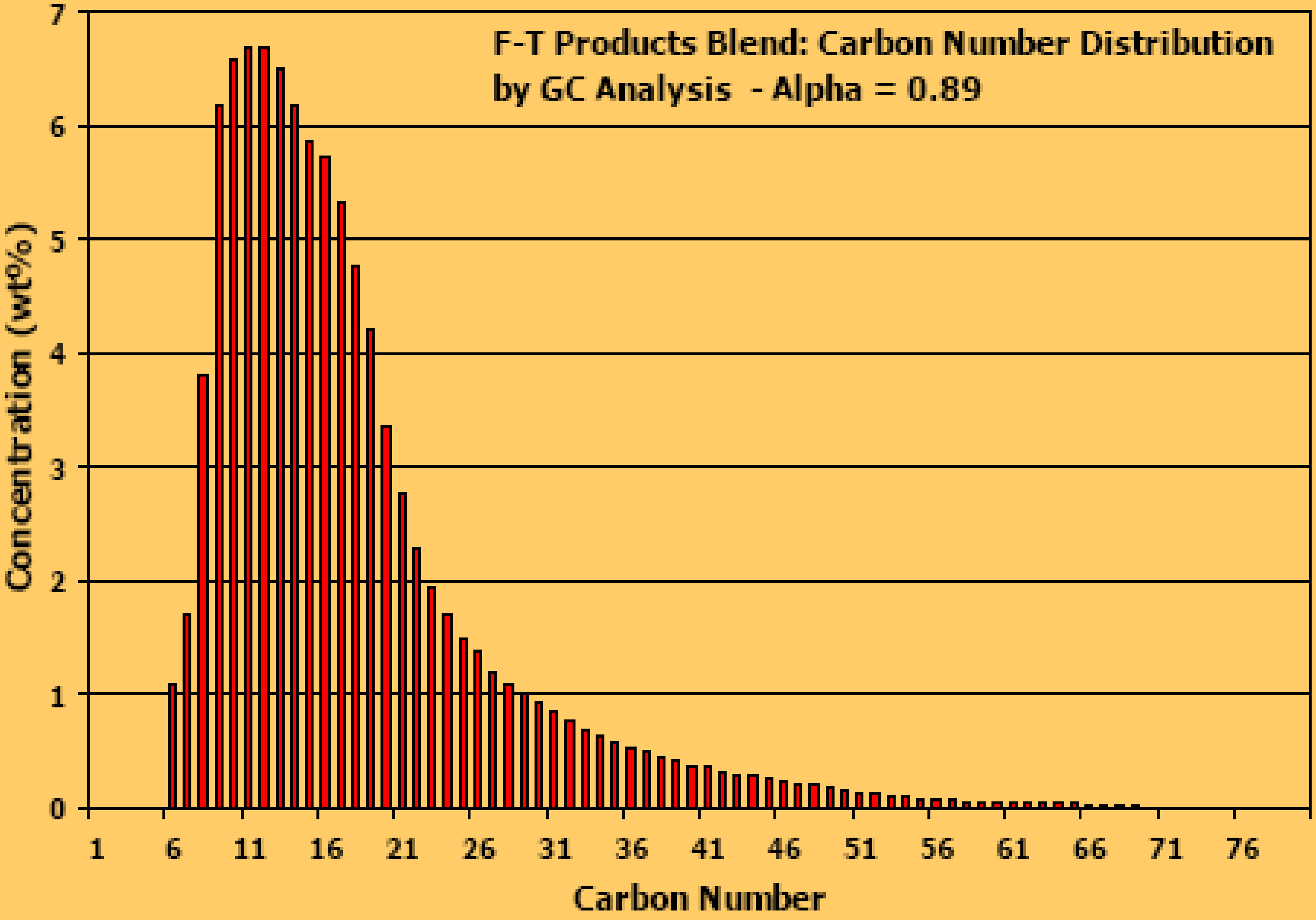


- Chain terminations

Products



- Product composition strongly influenced by
  - Catalyst composition
    - Product from cobalt catalyst higher in paraffins
    - Product from iron catalyst higher in olefins and oxygenates
  - Operating conditions
    - Temperature
    - Pressure
    - H_2/CO ratio
- However, essentially no aromatics except for high temperature processes, no nitrogen or sulfur compounds



F-T Products Blend: Carbon Number Distribution by GC Analysis - Alpha = 0.89
Concentration (wt%)
0
1
2
3
4
5
6
7
Carbon Number
1
6
11
16
21
26
31
36
41
46
51
56
61
66
71
76

- F-T chemistry can be viewed as a polymerization reaction
- Applying polymerization kinetics, a simple one-parameter equation can describe the entire product distribution, referred to as the Anderson-Shultz-Flory (A-S-F) distribution:

$$W_n = (1-\alpha)^2 \, n \, \alpha^{n-1}$$

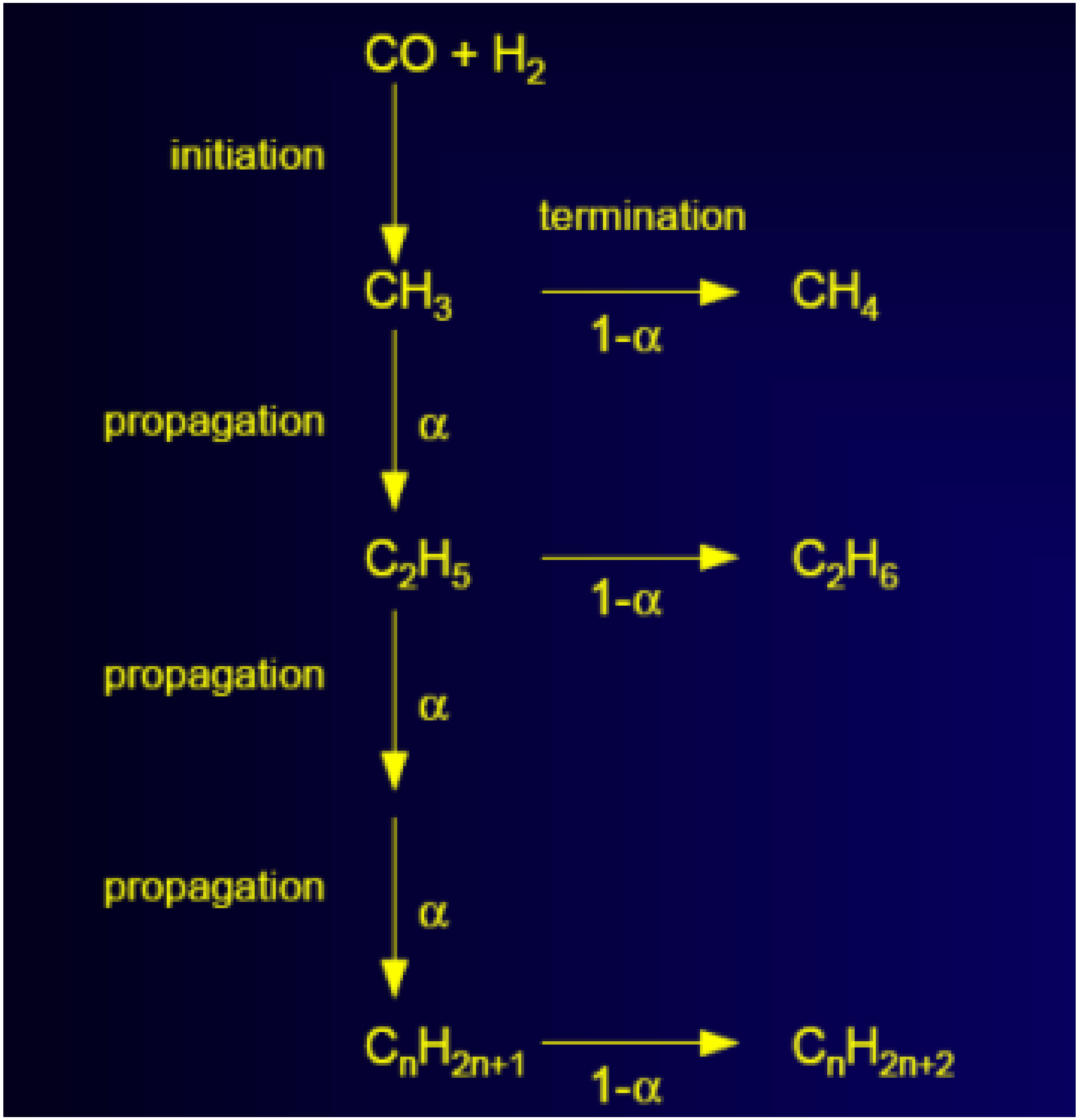
where:

n = carbon number

W_n = Weight fraction of product with carbon number n

α = Chain growth probability

- The higher the value of α the longer the average chain length



$CO + H_2$

initiation

CH_3

termination

CH_4

$1-\alpha$

propagation

α

C_2H_5

C_2H_6

$1-\alpha$

propagation

α

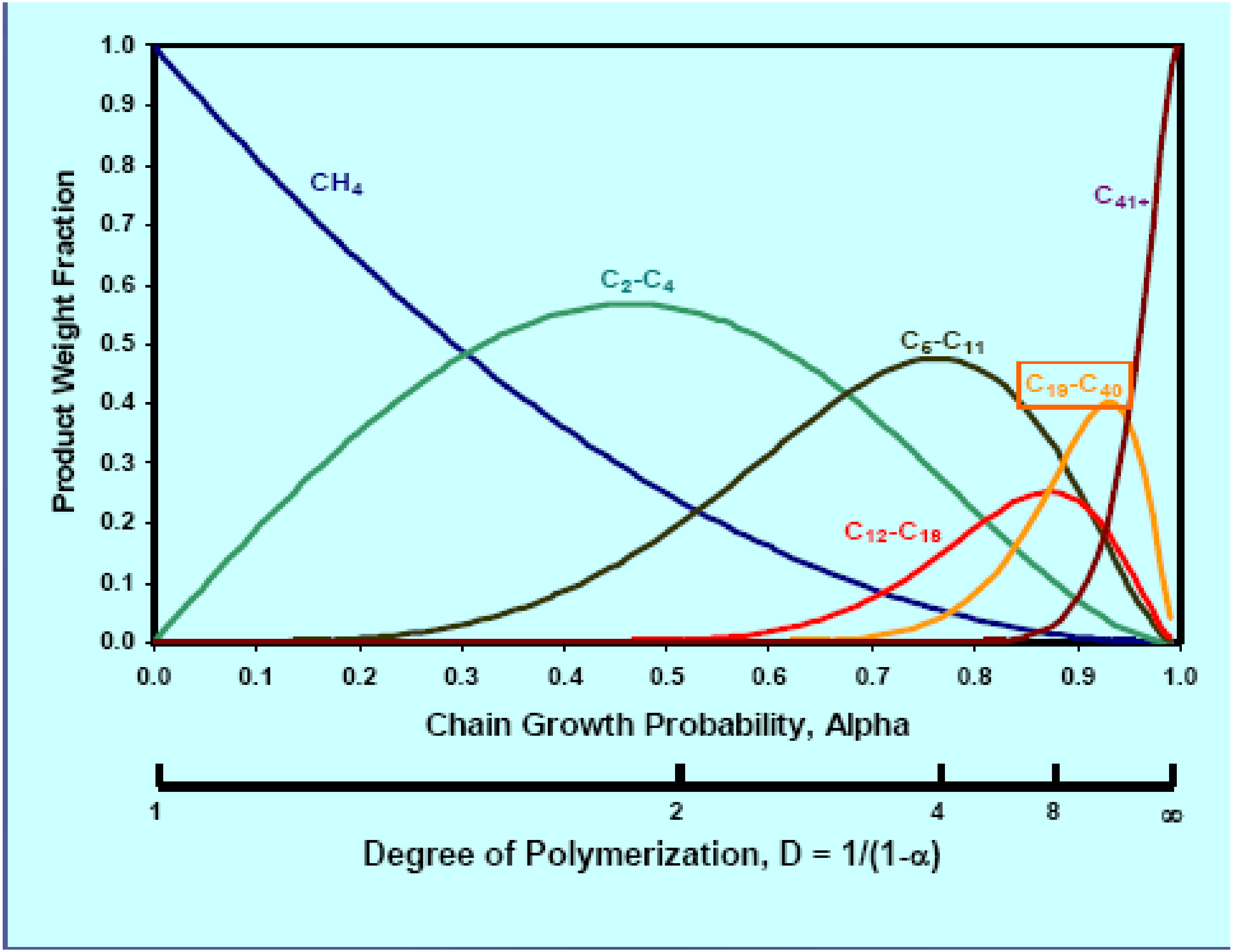
propagation

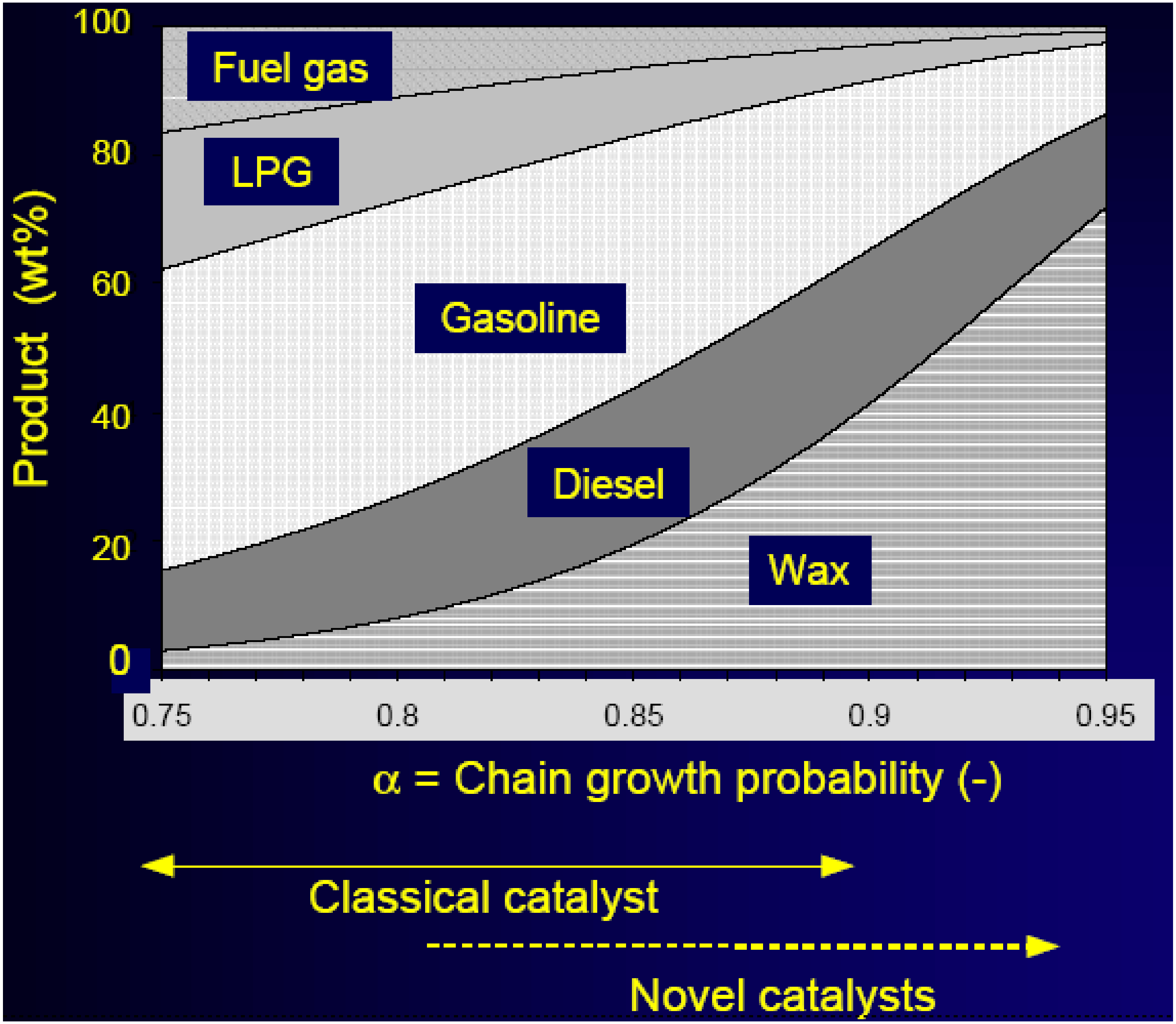
α

C_nH_{2n+1}

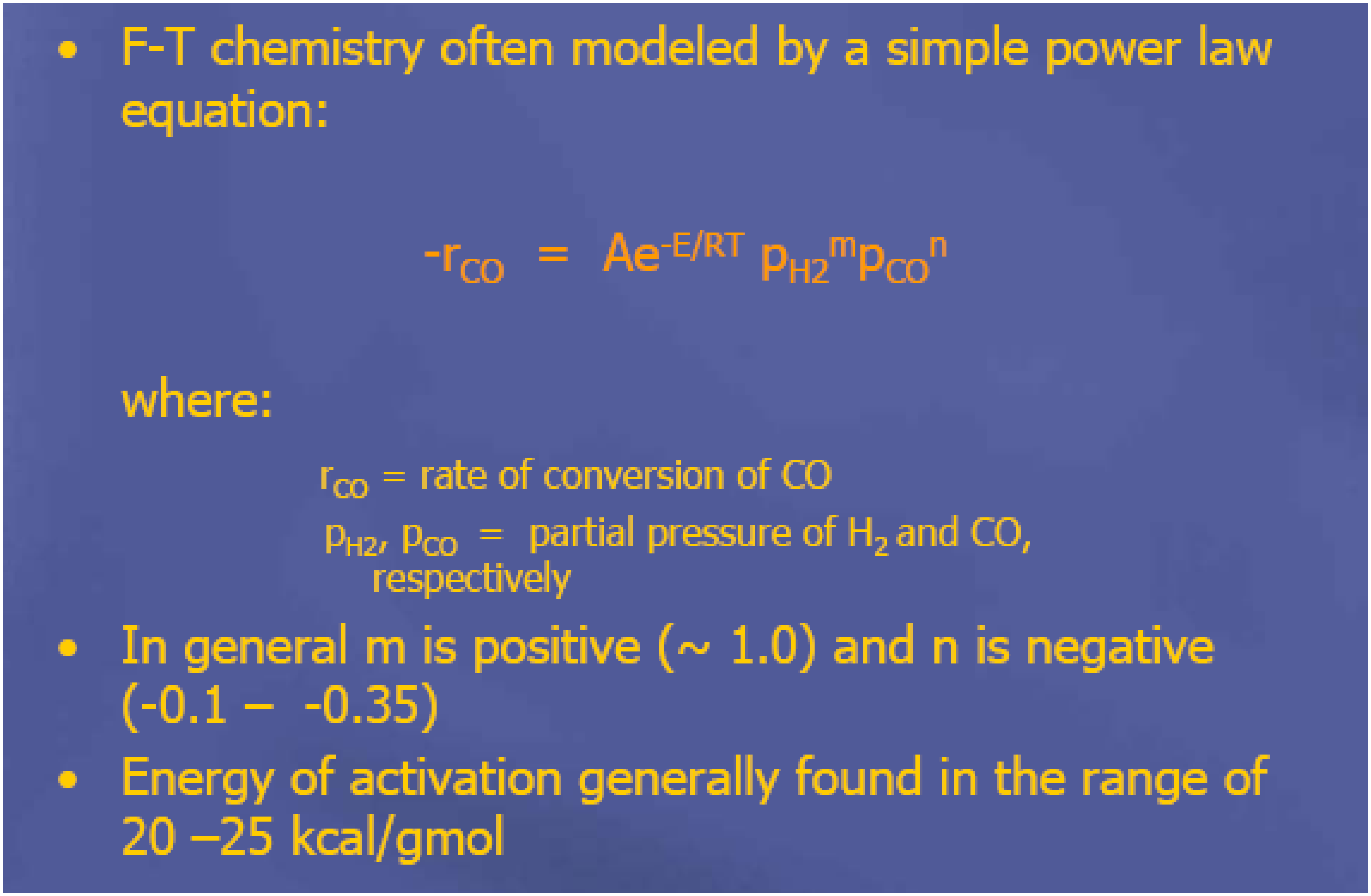
C_nH_{2n+2}

$1-\alpha$


Product Weight Fraction
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
CH_4
C_2-C_4
C_5-C_{11}
C_{19}-C_{40}
C_{41+}
C_{12}-C_{18}
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Chain Growth Probability, Alpha
1
2
4
8
∞
Degree of Polymerization, D = 1/(1-α)


Fuel gas
LPG
Gasoline
Diesel
Wax
Product (wt%)
100
80
60
40
20
0
0.75
0.8
0.85
0.9
0.95
α = Chain growth probability (-)
Classical catalyst
Novel catalysts

Kinetics



- F-T chemistry often modeled by a simple power law equation:

$$-r_{CO} = Ae^{-E/RT}\, p_{H2}{}^{m} p_{CO}{}^{n}$$

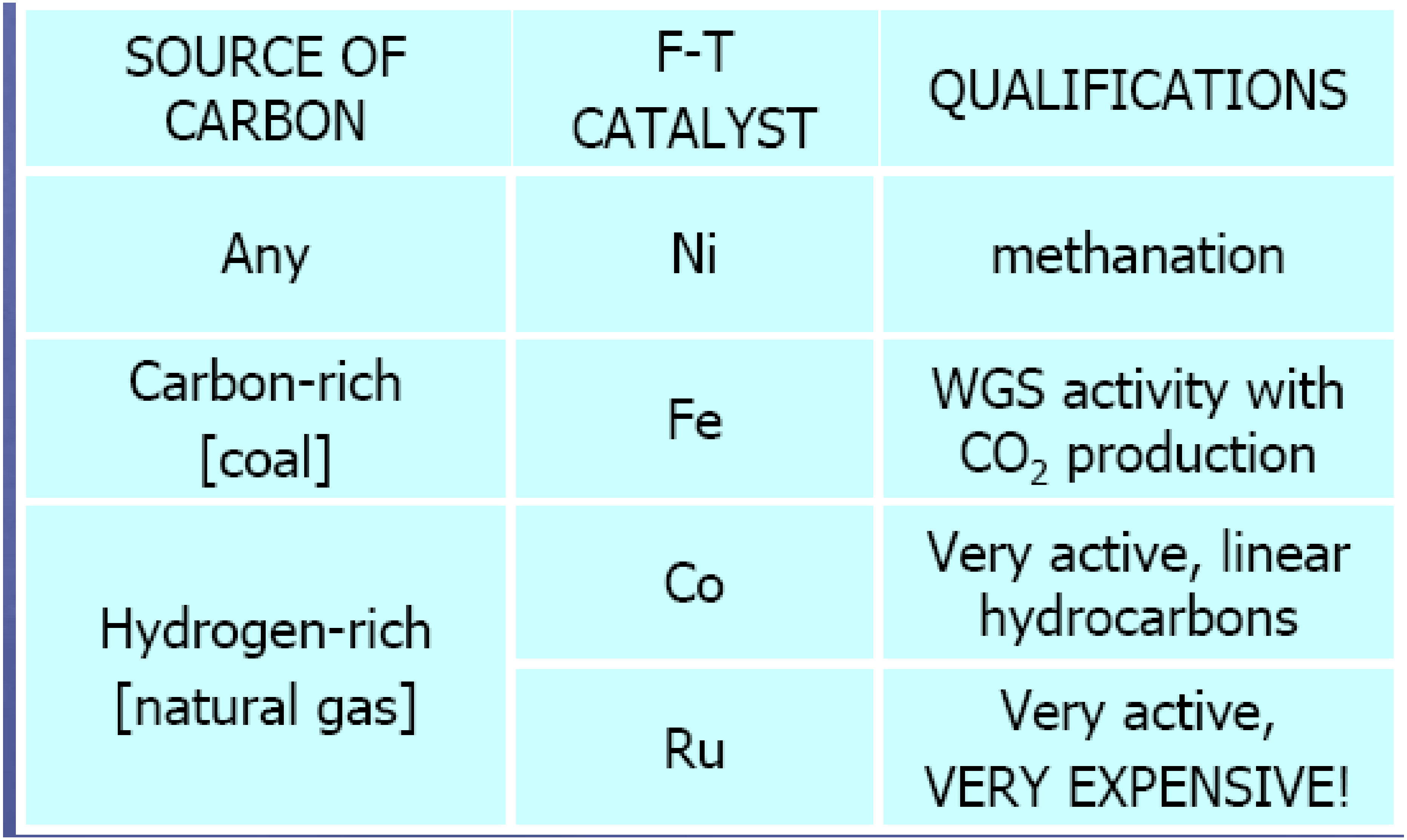
where:

r_{CO} = rate of conversion of CO

p_{H2}, p_{CO} = partial pressure of H_2 and CO, respectively

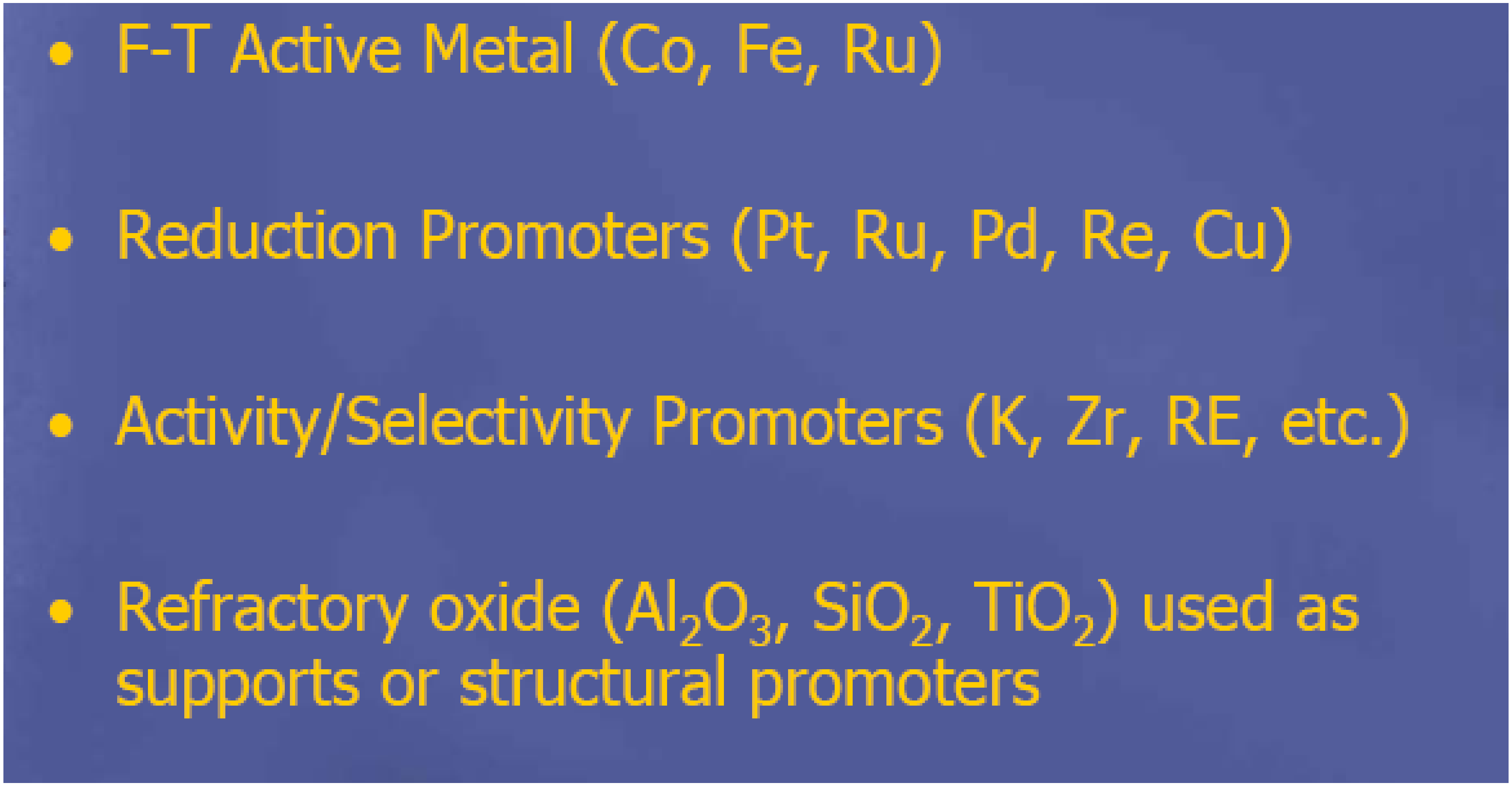
- In general m is positive (~ 1.0) and n is negative (-0.1 – -0.35)
- Energy of activation generally found in the range of 20 –25 kcal/gmol

Catalysts



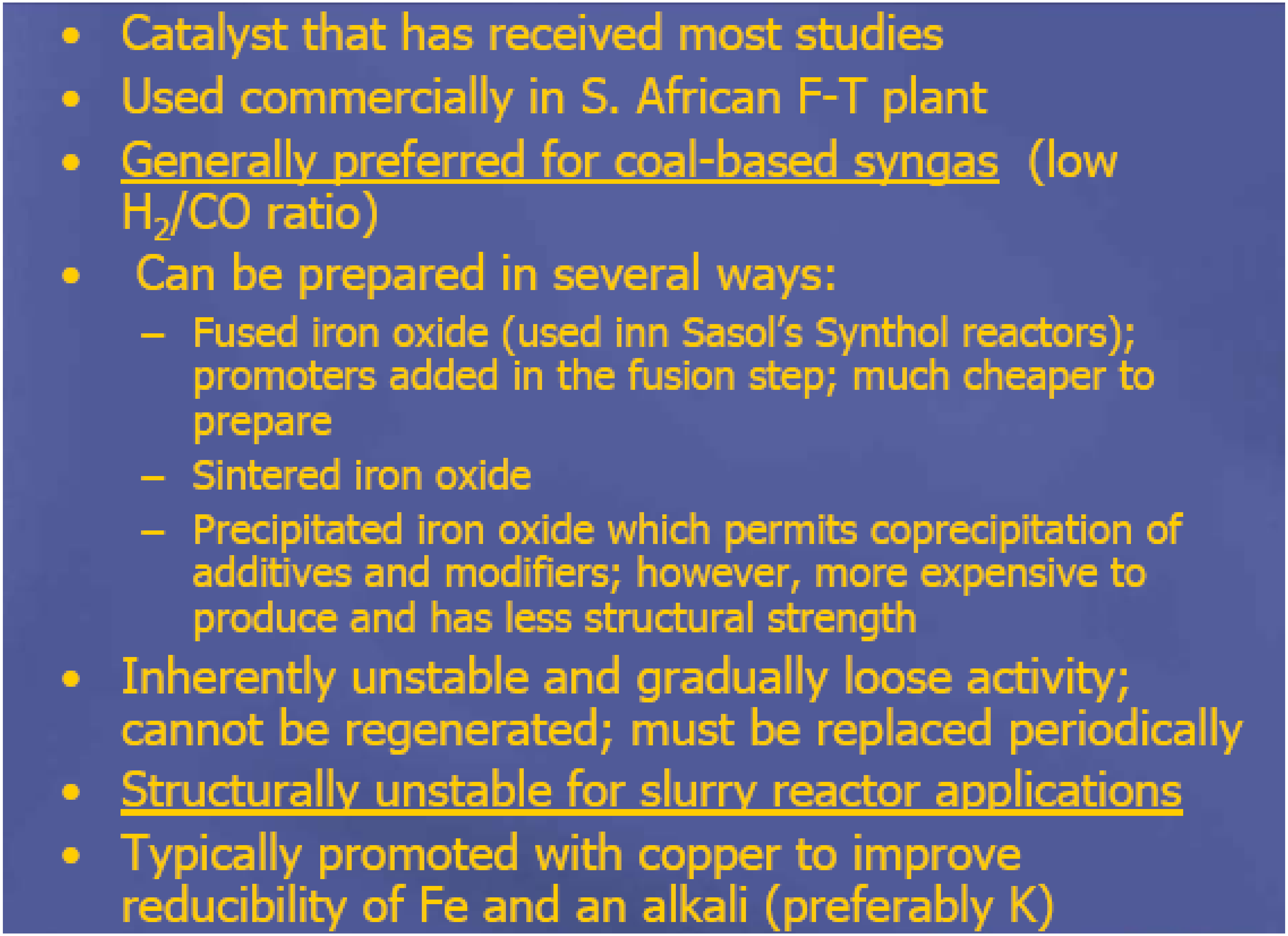
SOURCE OF CARBON	F-T CATALYST	QUALIFICATIONS
Any	Ni	methanation
Carbon-rich [coal]	Fe	WGS activity with CO_2 production
Hydrogen-rich [natural gas]	Co	Very active, linear hydrocarbons
	Ru	Very active, VERY EXPENSIVE!

Catalysts



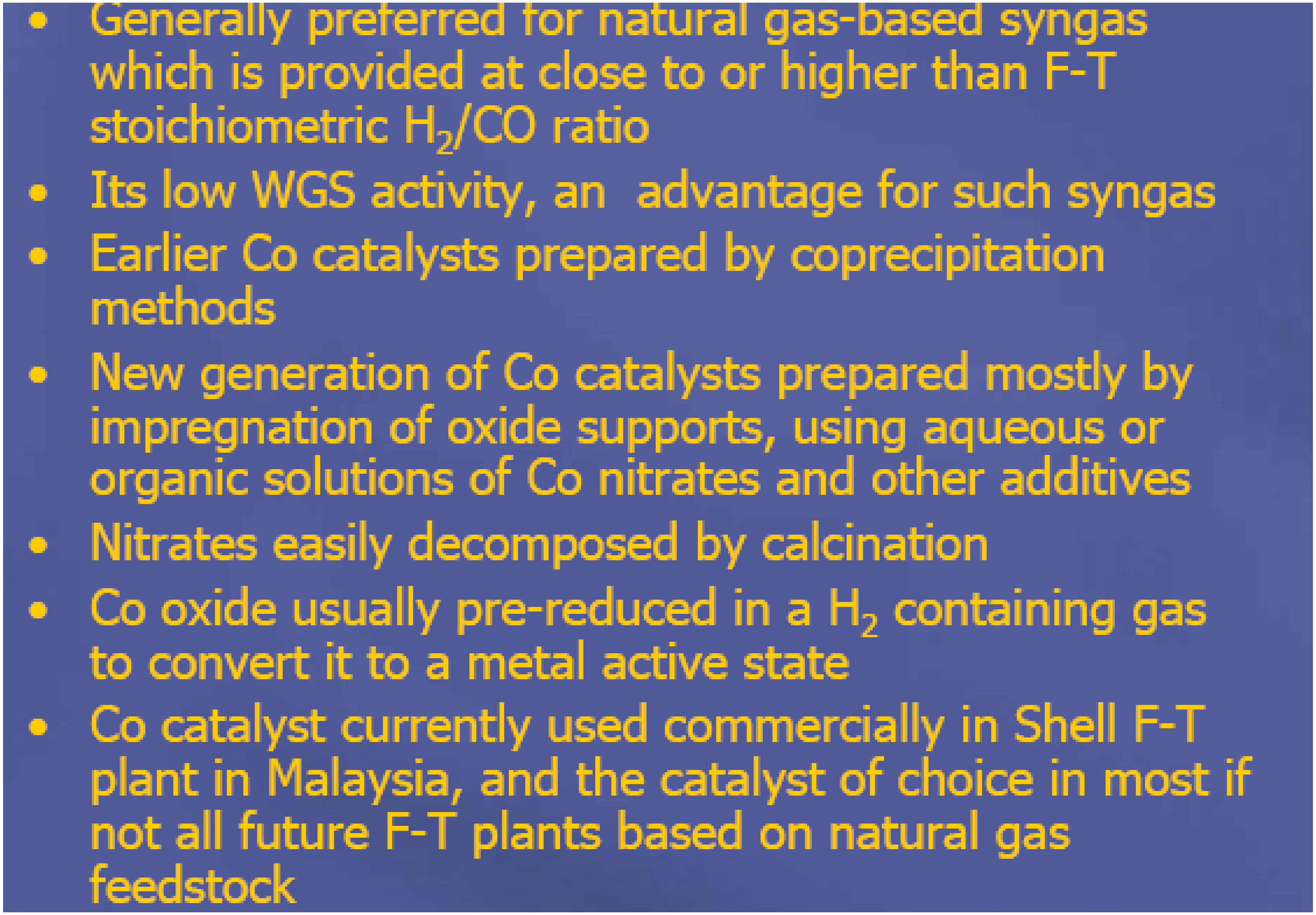
- F-T Active Metal (Co, Fe, Ru)
- Reduction Promoters (Pt, Ru, Pd, Re, Cu)
- Activity/Selectivity Promoters (K, Zr, RE, etc.)
- Refractory oxide (Al_2O_3, SiO_2, TiO_2) used as supports or structural promoters

Fe



- Catalyst that has received most studies
- Used commercially in S. African F-T plant
- Generally preferred for coal-based syngas (low H_2/CO ratio)
- Can be prepared in several ways:
  - Fused iron oxide (used inn Sasol's Synthol reactors); promoters added in the fusion step; much cheaper to prepare
  - Sintered iron oxide
  - Precipitated iron oxide which permits coprecipitation of additives and modifiers; however, more expensive to produce and has less structural strength
- Inherently unstable and gradually loose activity; cannot be regenerated; must be replaced periodically
- Structurally unstable for slurry reactor applications
- Typically promoted with copper to improve reducibility of Fe and an alkali (preferably K)

Co



- Generally preferred for natural gas-based syngas which is provided at close to or higher than F-T stoichiometric H_2/CO ratio
- Its low WGS activity, an advantage for such syngas
- Earlier Co catalysts prepared by coprecipitation methods
- New generation of Co catalysts prepared mostly by impregnation of oxide supports, using aqueous or organic solutions of Co nitrates and other additives
- Nitrates easily decomposed by calcination
- Co oxide usually pre-reduced in a H_2 containing gas to convert it to a metal active state
- Co catalyst currently used commercially in Shell F-T plant in Malaysia, and the catalyst of choice in most if not all future F-T plants based on natural gas feedstock

JACS
ARTICLES

Cobalt Particle Size Effects in the Fischer–Tropsch Reaction Studied with Carbon Nanofiber Supported Catalysts

G. Leendert Bezemer,† Johannes H. Bitter,† Herman P. C. E. Kuipers,‡
Heiko Oosterbeek,‡ Johannes E. Holewijn,‡ Xiaoding Xu,§ Freek Kapteijn,§
A. Jos van Dillen,† and Krijn P. de Jong*,†

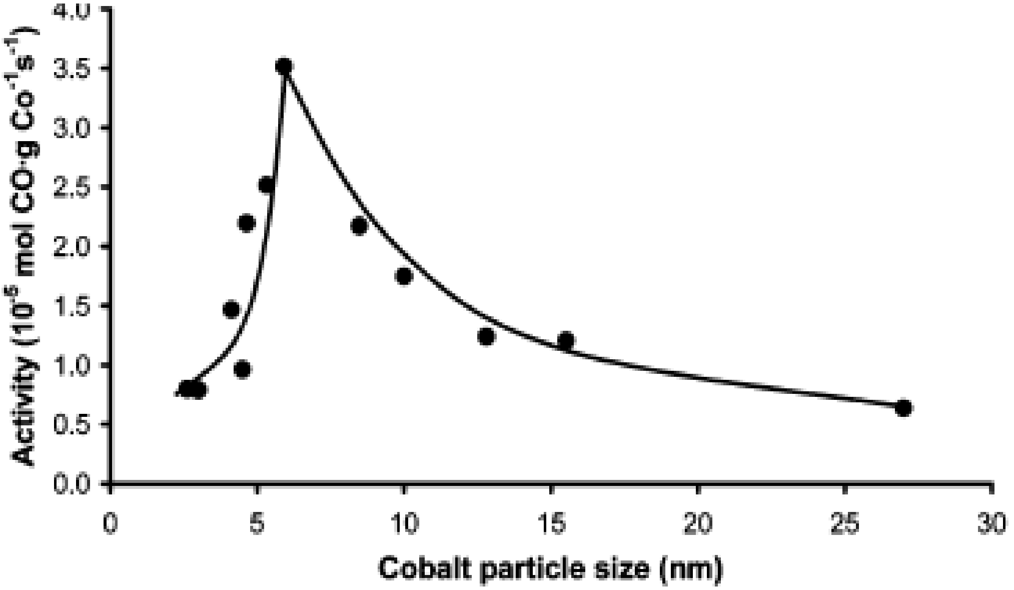
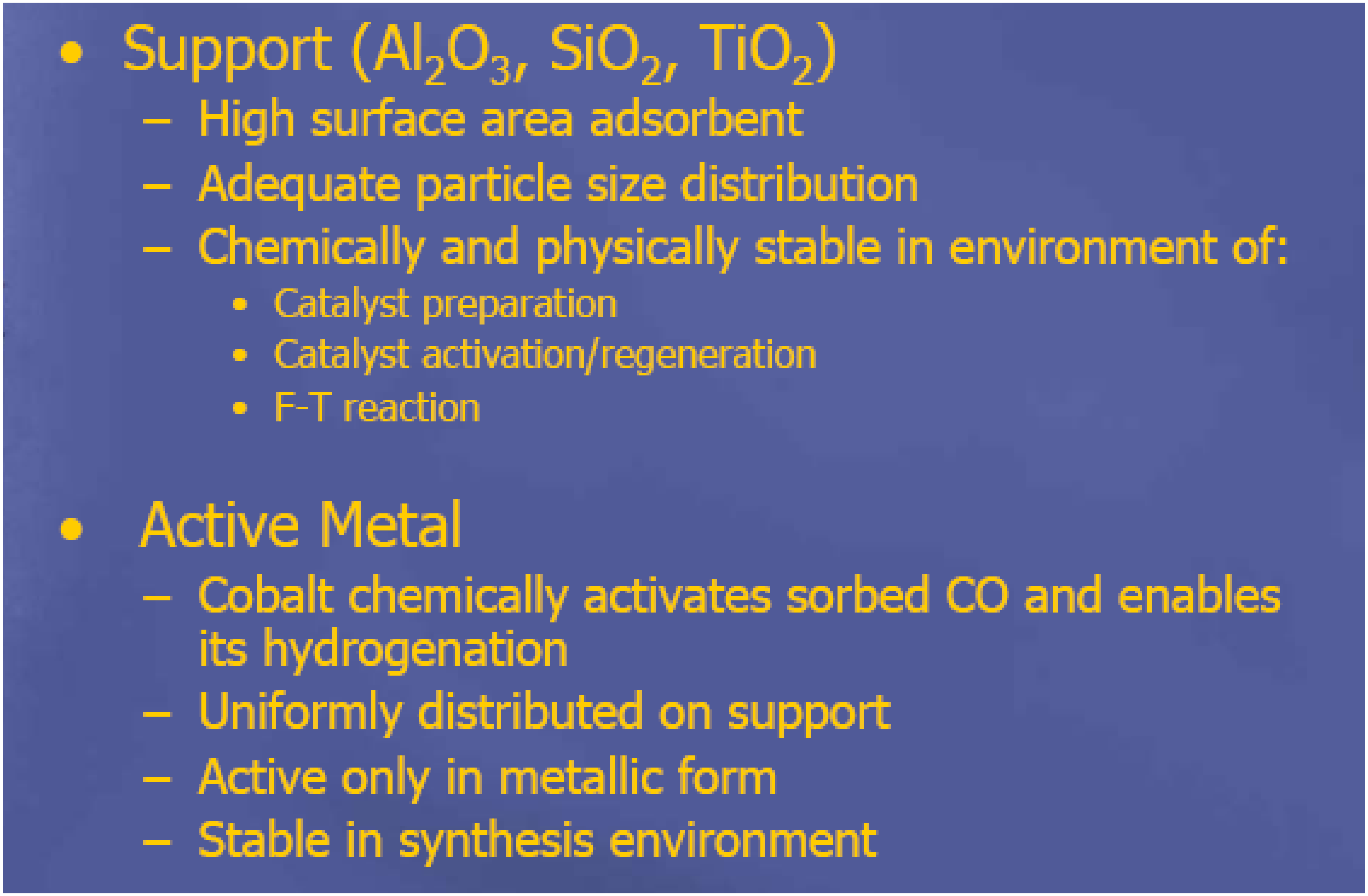


Figure 7. The influence of cobalt particle size on activity normalized to the cobalt loading (220 °C, H_2/CO = 2, 1 bar).

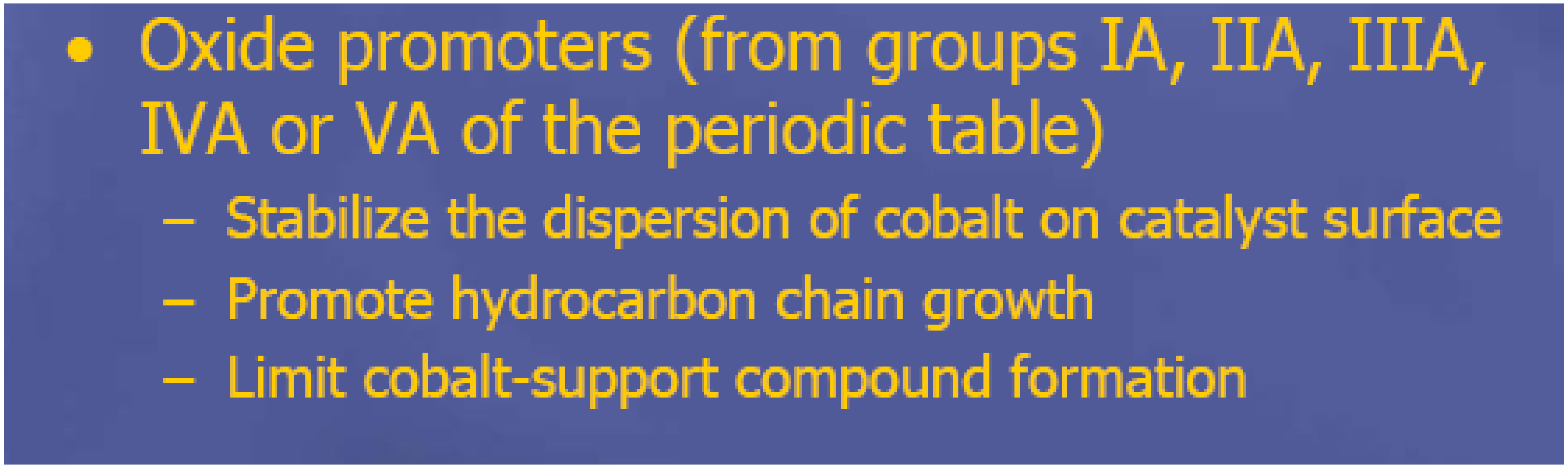
J. AM. CHEM. SOC. 2006, *128*, 3956

Co catalysts

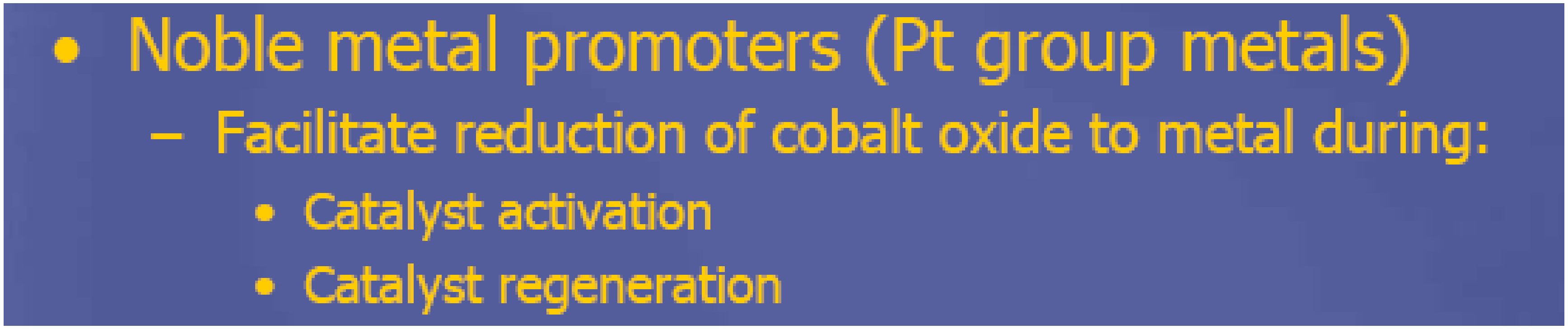


- Support (Al_2O_3, SiO_2, TiO_2)
  - High surface area adsorbent
  - Adequate particle size distribution
  - Chemically and physically stable in environment of:
    - Catalyst preparation
    - Catalyst activation/regeneration
    - F-T reaction
- Active Metal
  - Cobalt chemically activates sorbed CO and enables its hydrogenation
  - Uniformly distributed on support
  - Active only in metallic form
  - Stable in synthesis environment

Co catalysts



- Oxide promoters (from groups IA, IIA, IIIA, IVA or VA of the periodic table)
  - Stabilize the dispersion of cobalt on catalyst surface
  - Promote hydrocarbon chain growth
  - Limit cobalt-support compound formation



- Noble metal promoters (Pt group metals)
  - Facilitate reduction of cobalt oxide to metal during:
    - Catalyst activation
    - Catalyst regeneration

Summary: FT Catalyst

- Active Phase: Cobalt, Iron

Co based catalyst

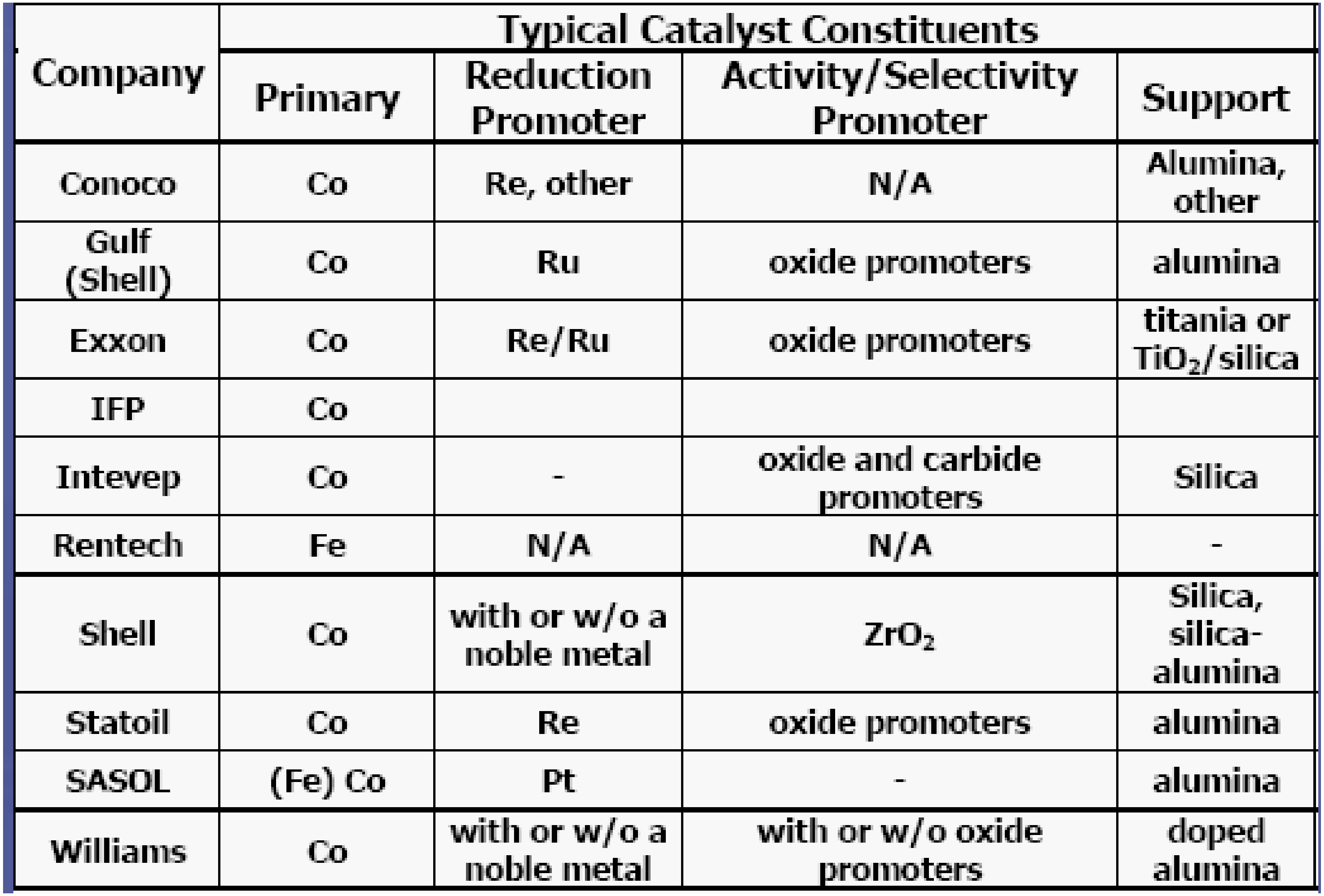
- Expensive
- High selectivity to long chain paraffins
- Low selectivity to olefins and oxygenates
- resistant to deactivation
- limited WGS activity

Fe based catalyst

- Economic
- Low selectivity to long chain paraffins
- High selectivity to olefins and oxygenates
- WGS catalyst
- Fast deactivation (coke)

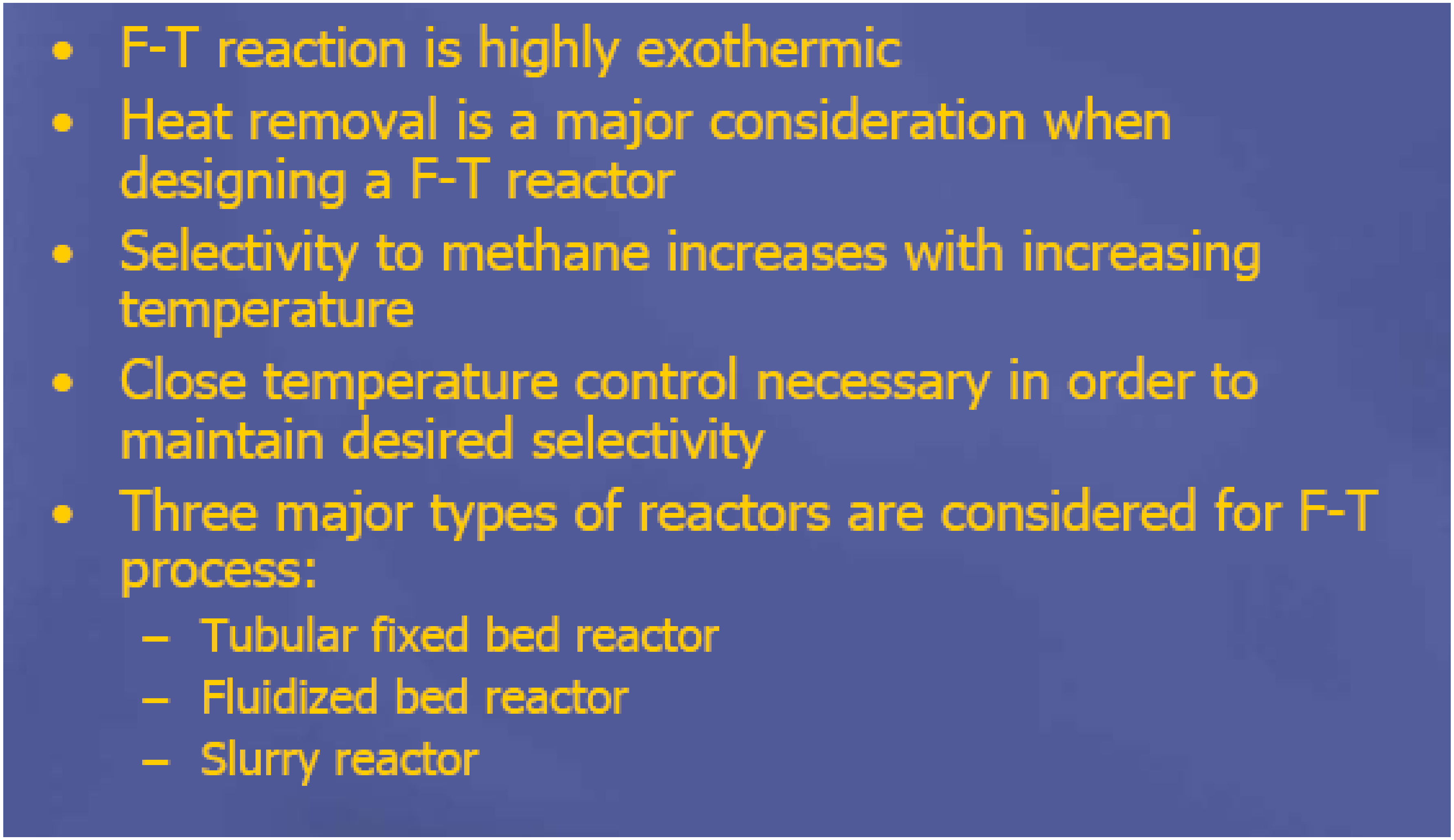
- Promoter
  - Structural: increase metal dispersion (Re, Zr, Hf, Ce)
  - Reduction: increase extent of reduction (Ru, Pd, Pt, Cu)
  - Activity: prevent coke deposition (Noble Metals)
  - Selectivity: alter the product distribution (Na, K, Cs)
- Carrier: SiO_2, Al_2O_3, TiO_2, mix
  - Structural promoter itself
  - Influence selectivity due to secondary reaction (i.e. acid sites)

Catalysts



Company	Typical Catalyst Constituents			
	Primary	Reduction Promoter	Activity/Selectivity Promoter	Support
Conoco	Co	Re, other	N/A	Alumina, other
Gulf (Shell)	Co	Ru	oxide promoters	alumina
Exxon	Co	Re/Ru	oxide promoters	titania or TiO_2/silica
IFP	Co			
Intevep	Co	-	oxide and carbide promoters	Silica
Rentech	Fe	N/A	N/A	-
Shell	Co	with or w/o a noble metal	ZrO_2	Silica, silica-alumina
Statoil	Co	Re	oxide promoters	alumina
SASOL	(Fe) Co	Pt	-	alumina
Williams	Co	with or w/o a noble metal	with or w/o oxide promoters	doped alumina

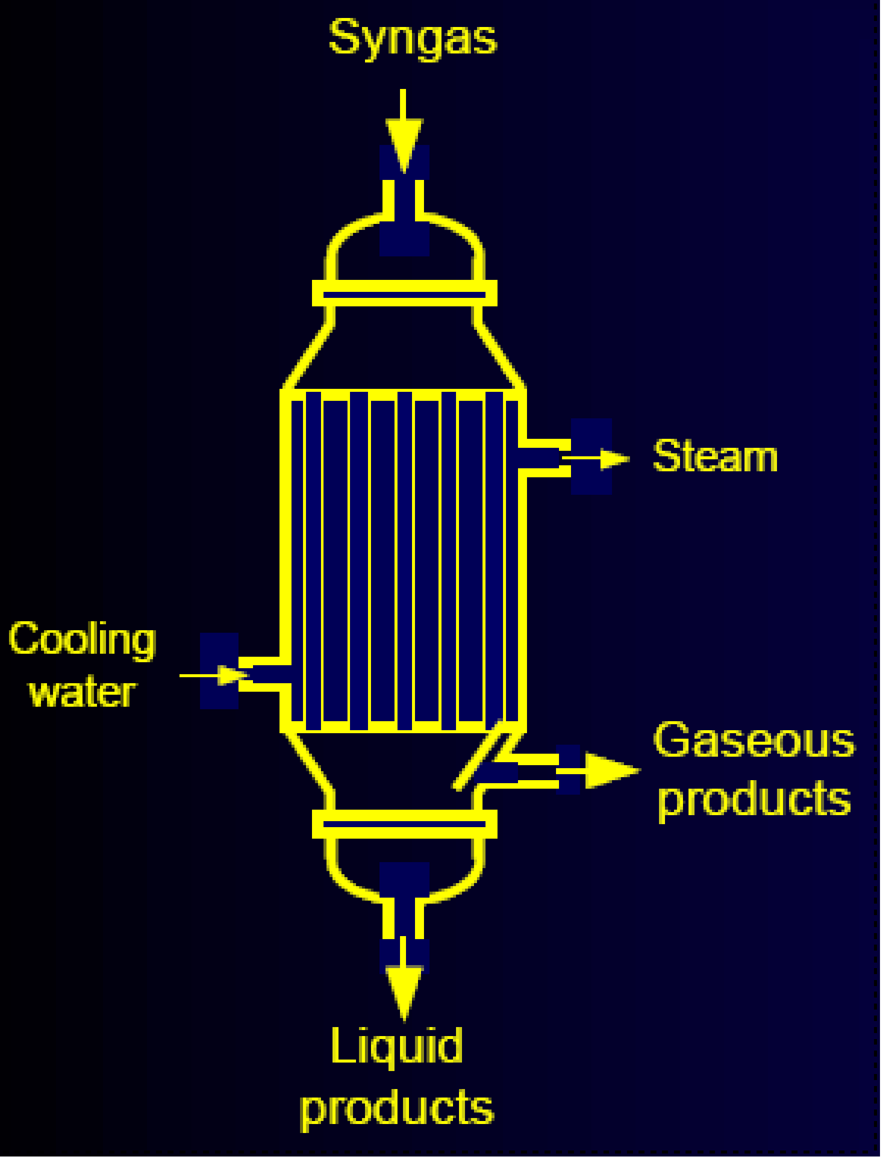
Reactors



- F-T reaction is highly exothermic
- Heat removal is a major consideration when designing a F-T reactor
- Selectivity to methane increases with increasing temperature
- Close temperature control necessary in order to maintain desired selectivity
- Three major types of reactors are considered for F-T process:
  - Tubular fixed bed reactor
  - Fluidized bed reactor
  - Slurry reactor

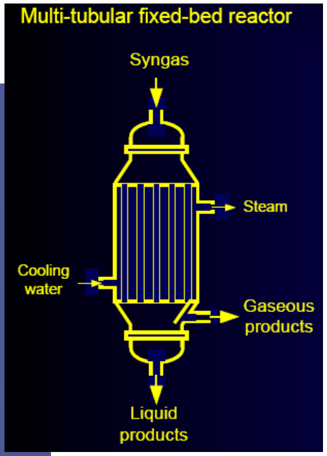
- First reactor type to be exploited commercially, e.g., Arge reactor
- TFB reactors used in Sasol I in South Africa and Shell plant in Malaysia
- Catalyst in pellet shape are placed in the tubes and the cooling medium flows around the outside of the tubes, similar to a shell and tube heat exchanger

Multi-tubular fixed-bed reactor



Fixed bed

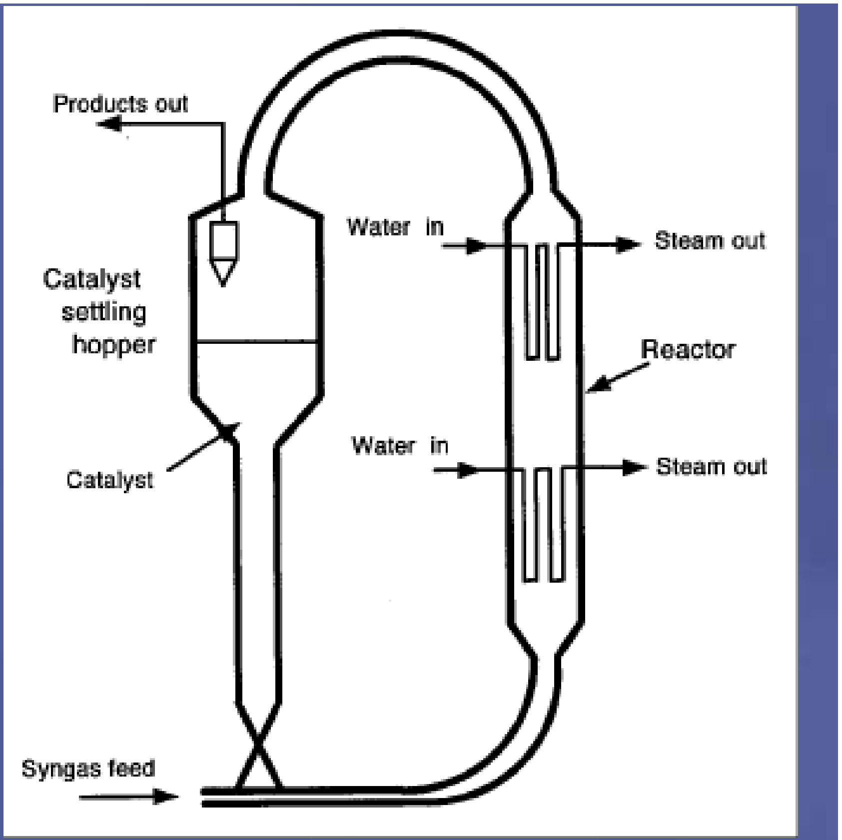
- Relatively simple design, but expensive construction with its large number of tubes required for a commercial scale plant
- Easy to scale-up from a single tube pilot plant
- Catalyst replacement is a major undertaking
- Iron catalysts inherently unstable have to be replaced periodically
- More stable cobalt catalysts can be regenerated and reactivated in-situ; may not have to be replaced for several year
- May experience temperature gradients in the tubes which can lead to catalyst sintering and deactivation
- Can also experience high pressure drop in tubes


Multi-tubular fixed-bed reactor

Catalyst d> 1mm; Effectiveness factor below unity

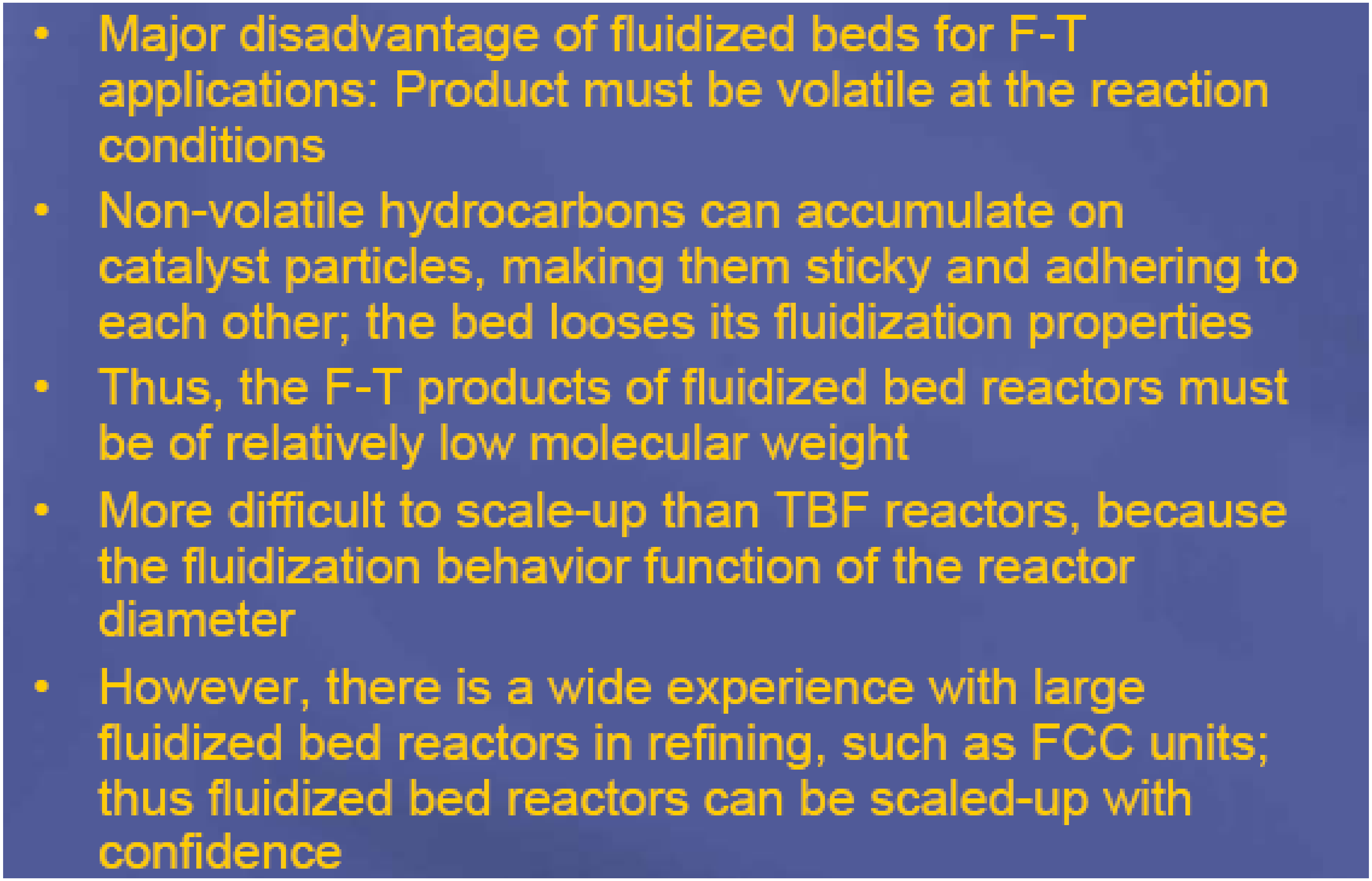
Reactors

- Two types of FB reactors:
  - Circulating fluidized bed (CFB) reactor such as the Sasol's Synthol reactor
  - Fixed fluidized bed reactor (Sasol Advanced Synthol, SAS reactor)
- CFB reactors used in Sasol I and II
- Better heat removal
- Better temperature control
- Less pressure drop problems
- Online catalyst removal and addition possible



Sasol's (Synthol) Circulating Fluidized Bed Reactor

Fluidized beds



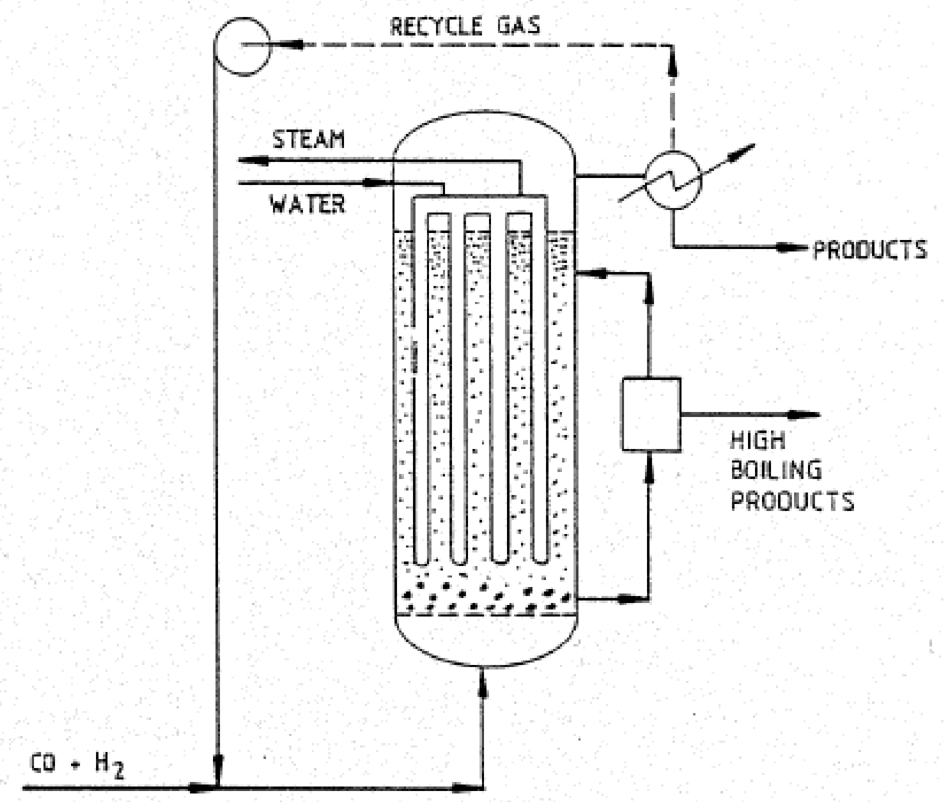
- Major disadvantage of fluidized beds for F-T applications: Product must be volatile at the reaction conditions
- Non-volatile hydrocarbons can accumulate on catalyst particles, making them sticky and adhering to each other; the bed looses its fluidization properties
- Thus, the F-T products of fluidized bed reactors must be of relatively low molecular weight
- More difficult to scale-up than TBF reactors, because the fluidization behavior function of the reactor diameter
- However, there is a wide experience with large fluidized bed reactors in refining, such as FCC units; thus fluidized bed reactors can be scaled-up with confidence

Slurry

The slurry-phase bubble column reactor (SBCR) considered the primary choice for the newer F-T processes using highly active cobalt catalysts

In a SBCR syngas is bubbled up through a slurry made up of hydrocarbon wax, liquid at the reaction conditions, and a catalyst suspended in it

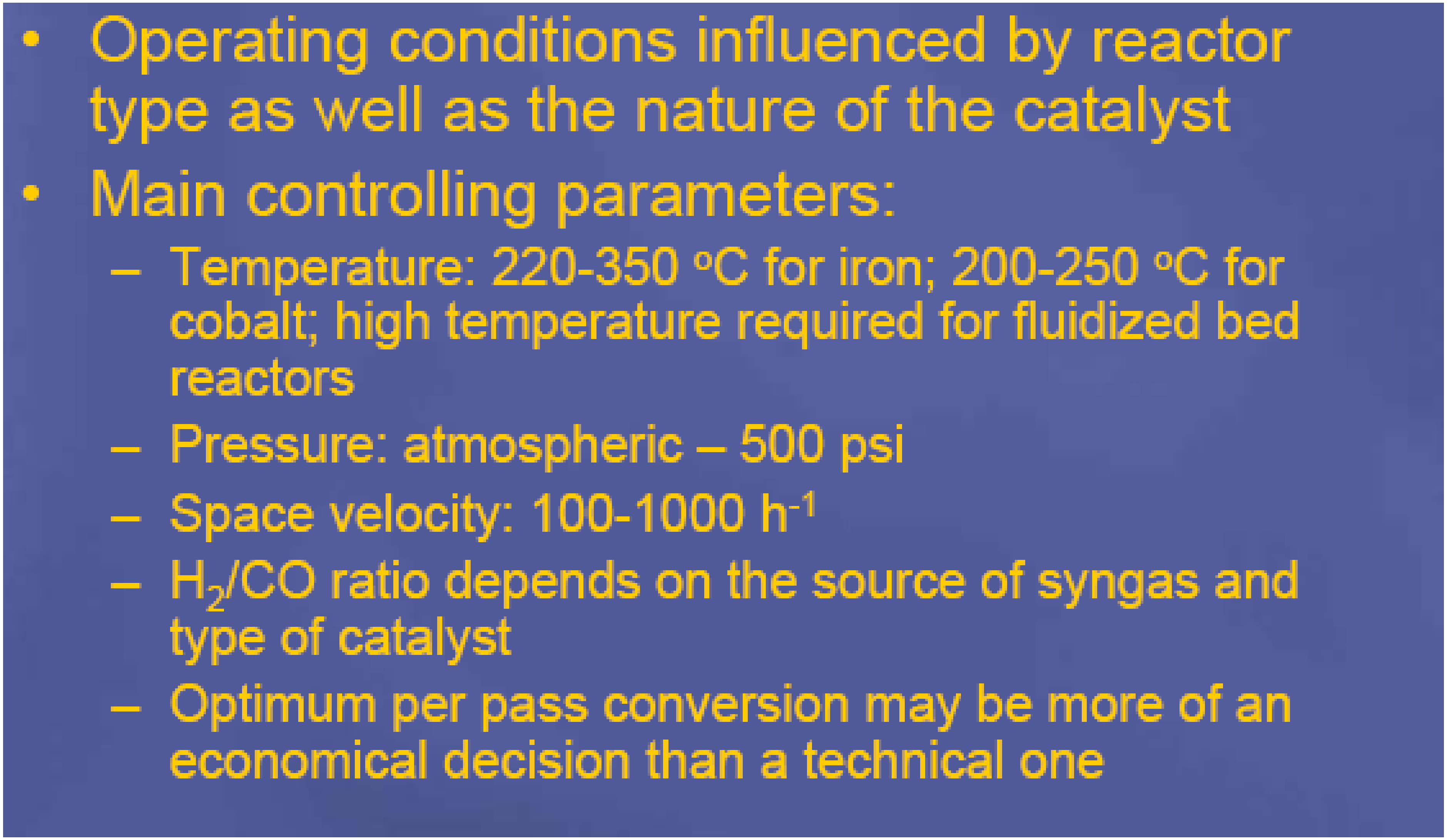
The catalyst is a finely divided powder with an average particle size of 50-80 μm



Slurry

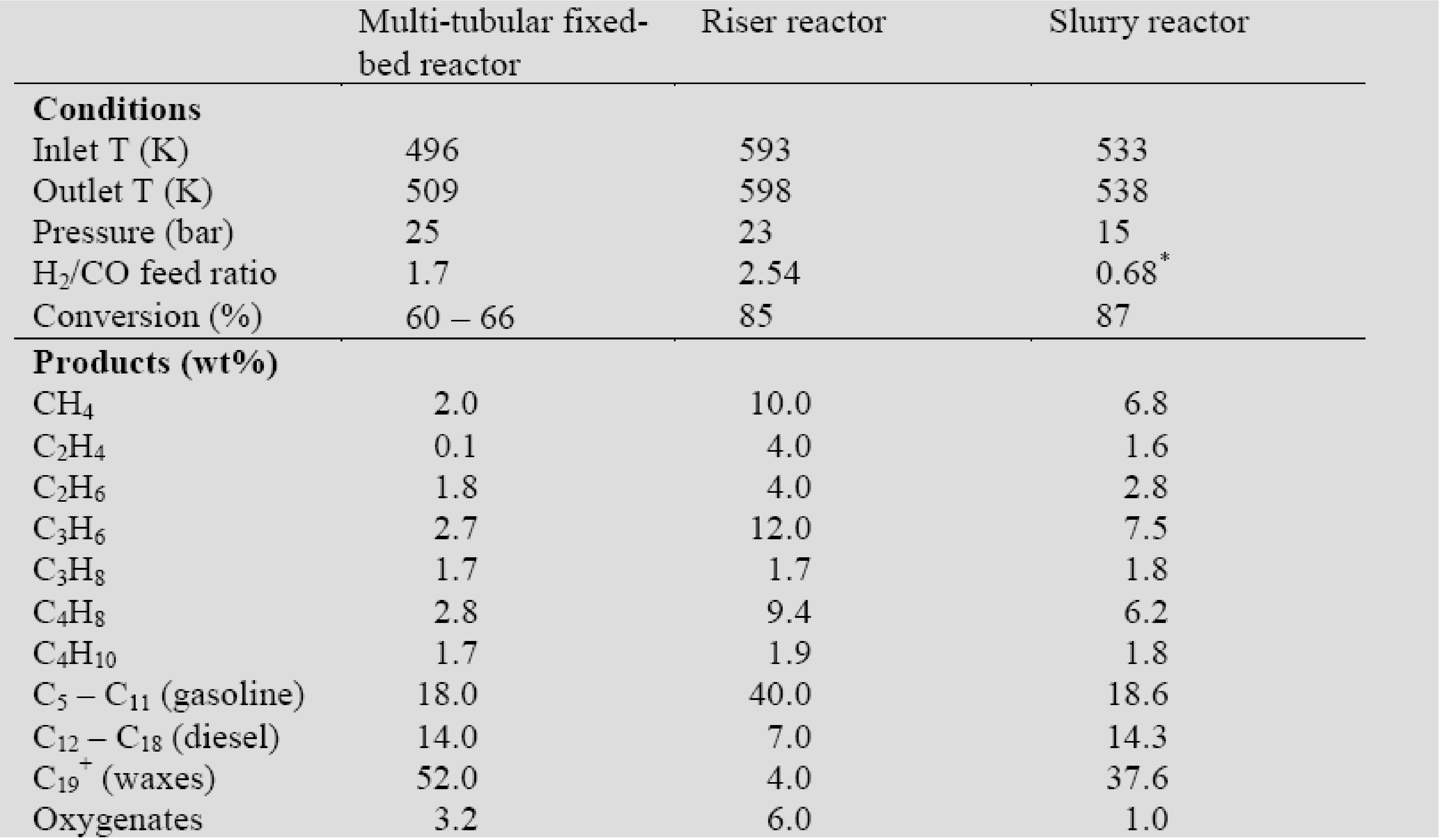
- Advantages provided by the use of SBCR:
  - Good heat transfer
  - Excellent temperature control
  - Better selectivity control
  - Ideal for higher boiling products
  - Low pressure drop
  - Ease of adding and removing catalyst
  - Simple design and construction
  - Potentially high capacity (10000-20000 bbl/d)
- The gaseous products are removed from the top of the reactor, while the heavy non-volatile wax must be separated from the catalyst which remains in the reactor
- Various proprietary internal or external filtration systems have been devised

Operation



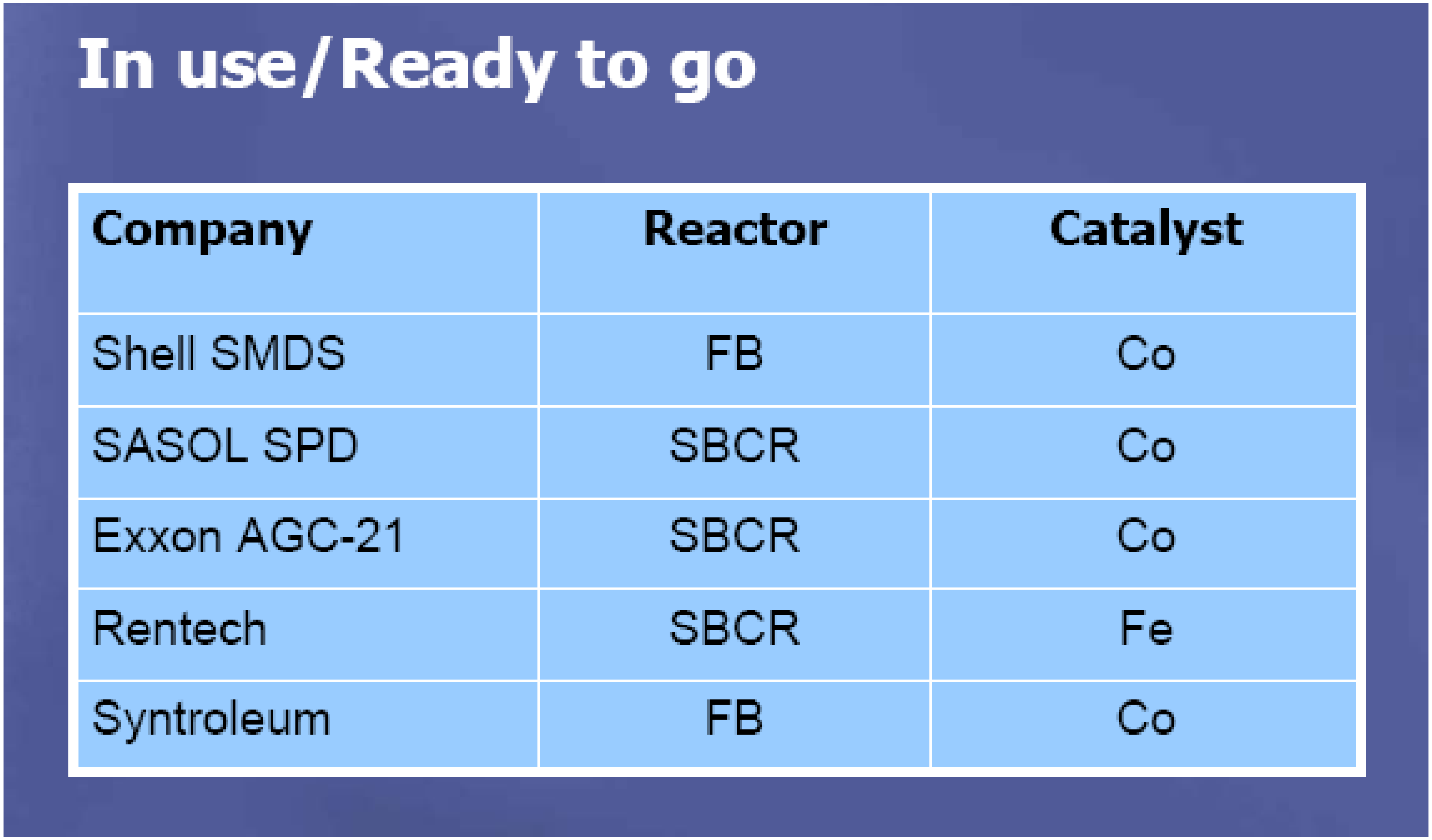
- Operating conditions influenced by reactor type as well as the nature of the catalyst
- Main controlling parameters:
  - Temperature: 220-350 °C for iron; 200-250 °C for cobalt; high temperature required for fluidized bed reactors
  - Pressure: atmospheric – 500 psi
  - Space velocity: 100-1000 h^{-1}
  - H_2/CO ratio depends on the source of syngas and type of catalyst
  - Optimum per pass conversion may be more of an economical decision than a technical one

Reactor comparison



	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_2H_4	0.1	4.0	1.6
C_2H_6	1.8	4.0	2.8
C_3H_6	2.7	12.0	7.5
C_3H_8	1.7	1.7	1.8
C_4H_8	2.8	9.4	6.2
C_4H_{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

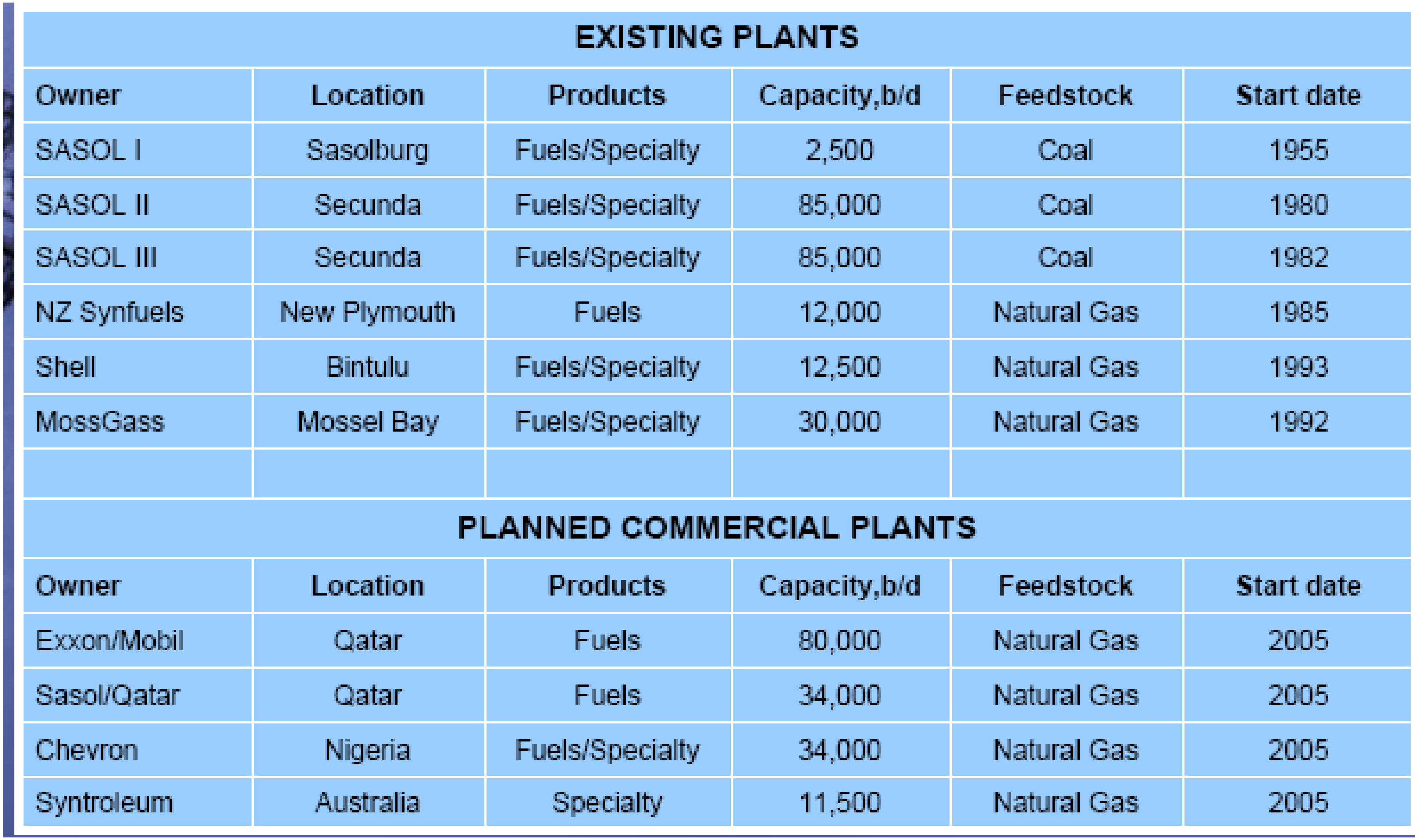
Technologies



In use/Ready to go

Company	Reactor	Catalyst
Shell SMDS	FB	Co
SASOL SPD	SBCR	Co
Exxon AGC-21	SBCR	Co
Rentech	SBCR	Fe
Syntroleum	FB	Co

Plants



EXISTING PLANTS

Owner	Location	Products	Capacity,b/d	Feedstock	Start date
SASOL I	Sasolburg	Fuels/Specialty	2,500	Coal	1955
SASOL II	Secunda	Fuels/Specialty	85,000	Coal	1980
SASOL III	Secunda	Fuels/Specialty	85,000	Coal	1982
NZ Synfuels	New Plymouth	Fuels	12,000	Natural Gas	1985
Shell	Bintulu	Fuels/Specialty	12,500	Natural Gas	1993
MossGass	Mossel Bay	Fuels/Specialty	30,000	Natural Gas	1992

PLANNED COMMERCIAL PLANTS

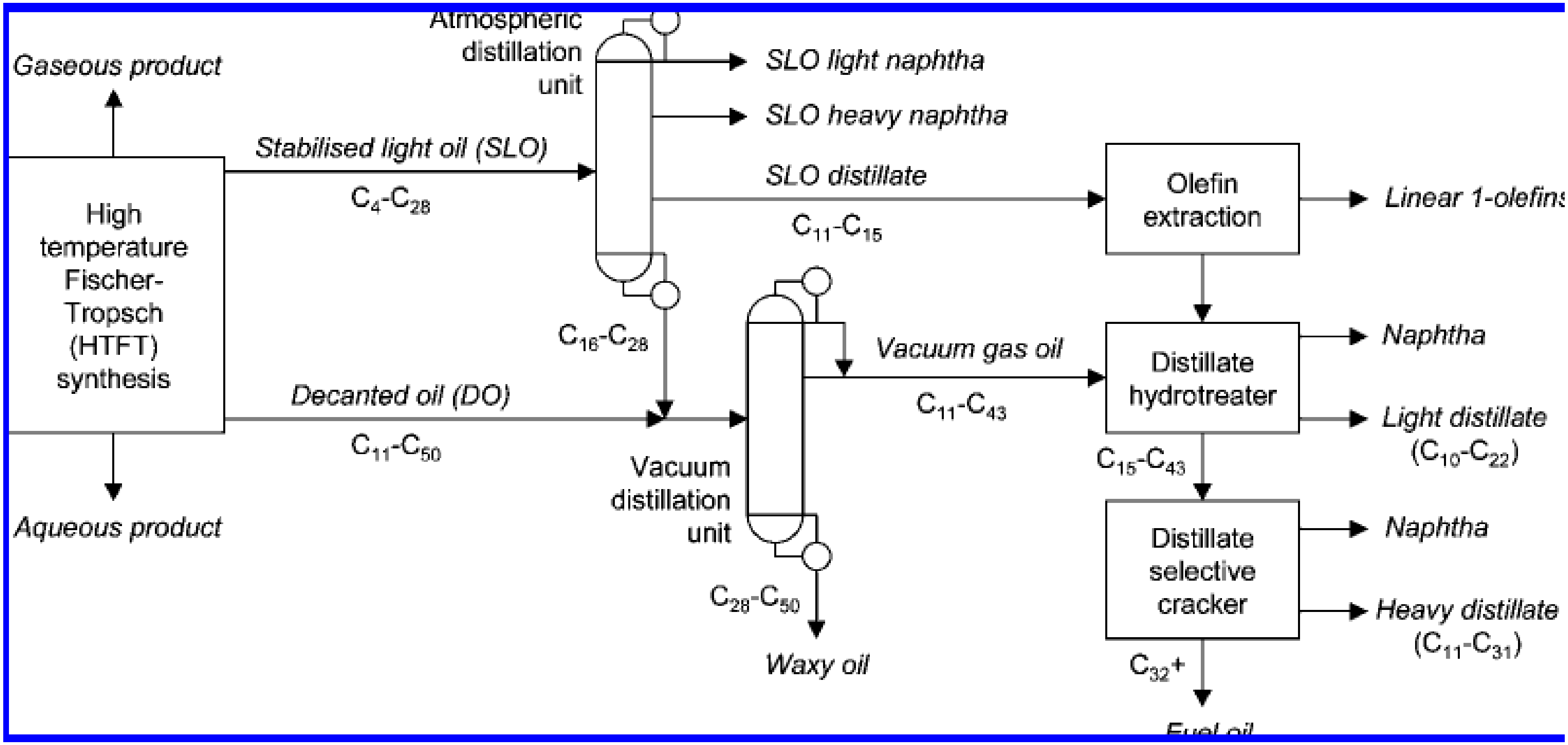
Owner	Location	Products	Capacity,b/d	Feedstock	Start date
Exxon/Mobil	Qatar	Fuels	80,000	Natural Gas	2005
Sasol/Qatar	Qatar	Fuels	34,000	Natural Gas	2005
Chevron	Nigeria	Fuels/Specialty	34,000	Natural Gas	2005
Syntroleum	Australia	Specialty	11,500	Natural Gas	2005

Table 1 Fischer–Tropsch processes currently in industrial operation

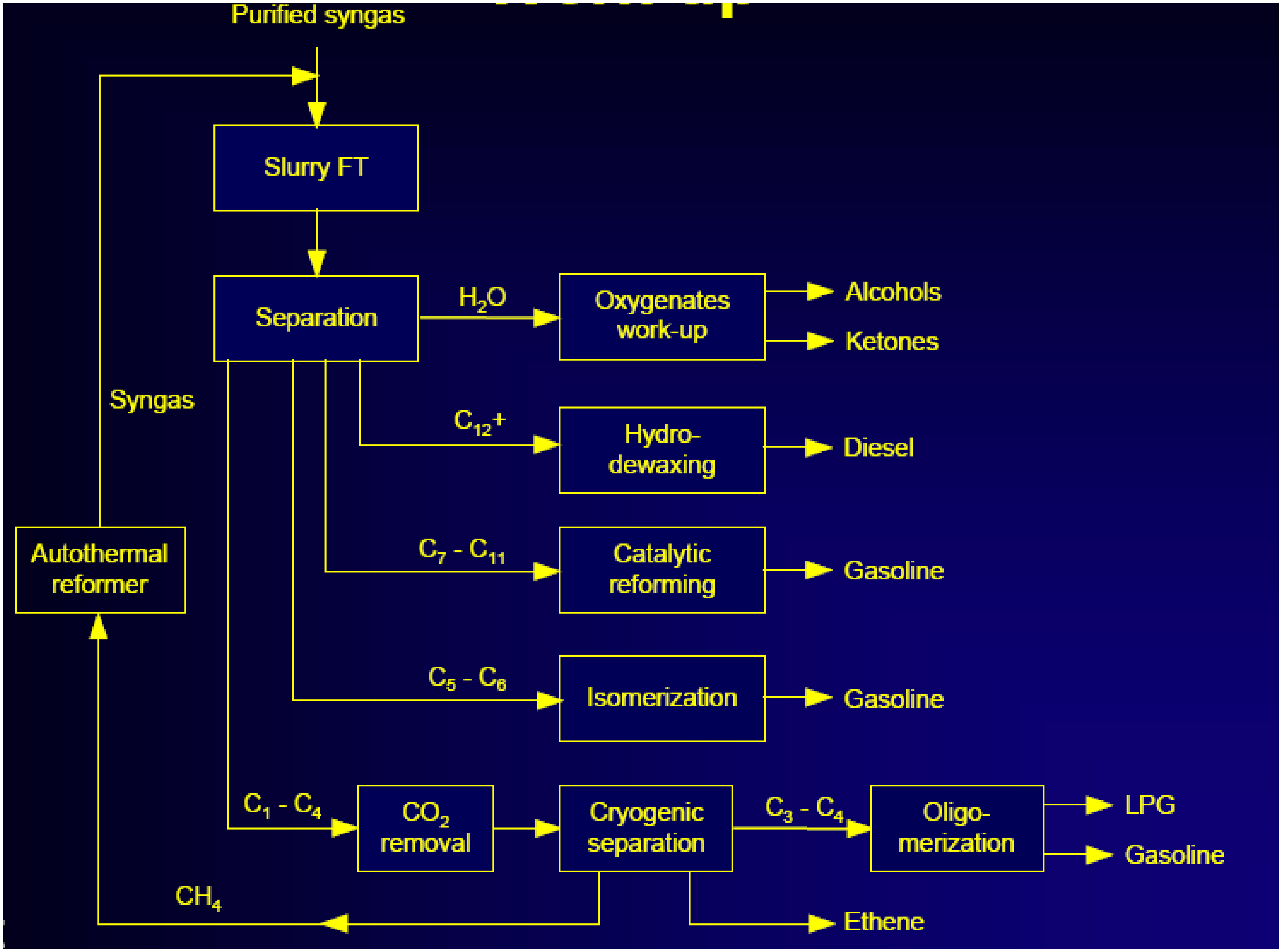
Type	FT catalyst	FT reactor type	FT technology	Operator	Commercial operation
HTFT	fused Fe	circulating fluidised bed	Sasol Synthol	PetroSA	Mossel Bay, South Africa
HTFT	fused Fe	fixed fluidised bed	Sasol Advanced Synthol (SAS)	Sasol	Secunda, South Africa
LTFT	precipitated Fe	fixed bed	ARGE[a]	Sasol	Sasolburg, South Africa
LTFT	precipitated Fe	slurry bubble column	Sasol Slurry Bed Process (SSBP)	Sasol	Sasolburg, South Africa
LTFT	Co-SiO_2	fixed bed	Shell Middle Distillate Synthesis (SMDS)	Shell	Bintulu, Malaysia
LTFT	Co-Al_2O_3	slurry bubble column	Sasol Slurry Bed Process (SSBP)	Sasol	Ras Laffan, Qatar

[a] ARGE = Arbeitsgemeinschaft Ruhrchemie-Lurgi.

Sasol Synfuels, Secunda, South Africa, (2008)



SASOL II



Purified syngas

Slurry FT

Separation

H_2O

Oxygenates work-up

Alcohols

Ketones

Syngas

C_{12}+

Hydro-dewaxing

Diesel

Autothermal reformer

C_7 - C_{11}

Catalytic reforming

Gasoline

C_5 - C_6

Isomerization

Gasoline

C_1 - C_4

CO_2 removal

Cryogenic separation

C_3 - C_4

Oligo-merization

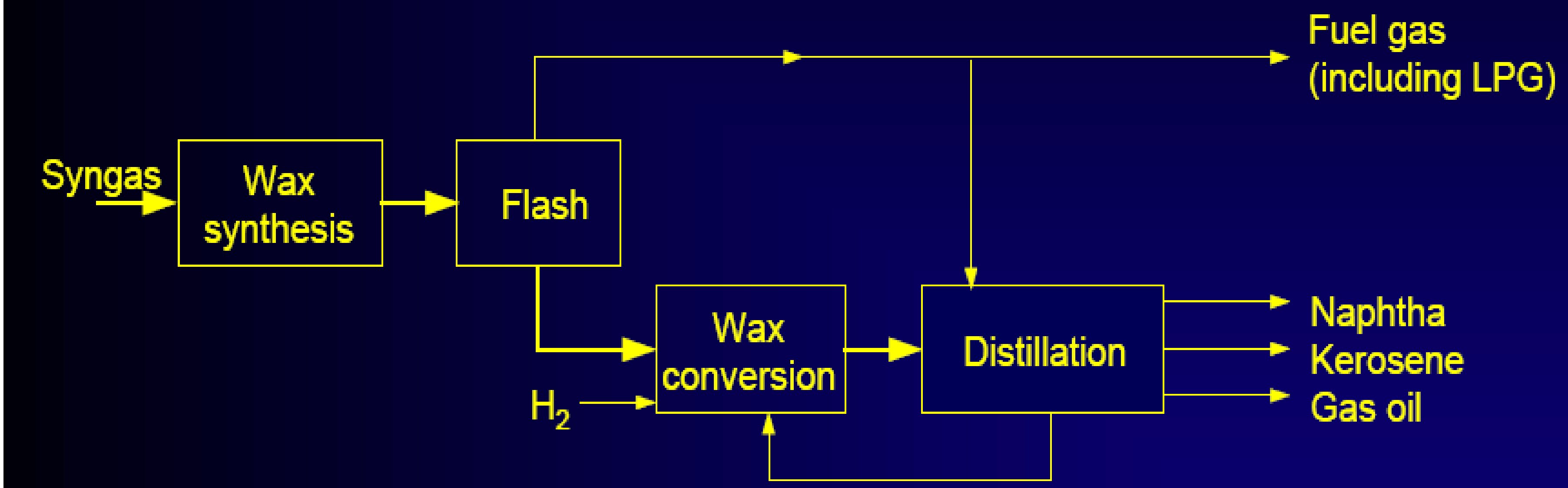
LPG

Gasoline

CH_4

Ethene

F-T Process - Shell Middle Distillate Synthesis (SMDS)



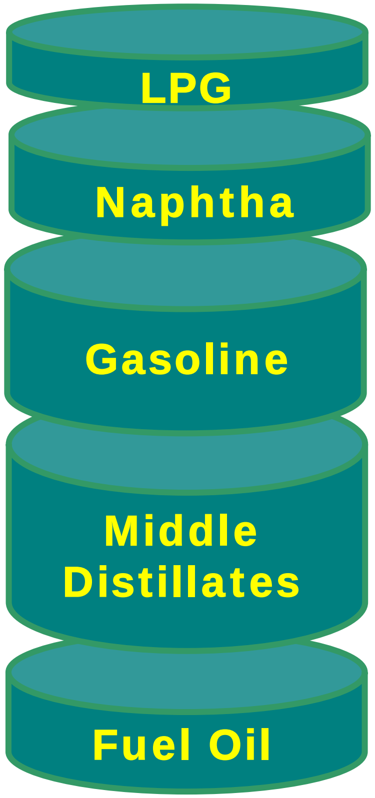
Products from GTL-FT process

Typical FT product composition after upgrading is:

25% Virgin Naphtha, 25% Jet Fuel and 50% Diesel

and minor amounts of LPG and bottom hydrocracking. The heavier fraction can be used for the production of lubricating bases or chemicals.

Refinery Barrel Yield (Brent, vol)



LPG	3%
Naphtha	10%
Gasoline	27%
Middle Distillates	40%
Fuel Oil	20%

GTL Barrel (vol)

LPG/Naphtha	20 - 35%
Middle Distillates	50 - 75%
Lubes/Waxes	0 - 30%

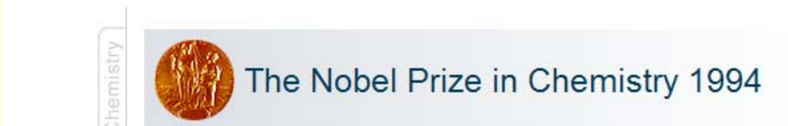
GtL Technology: Hydrocraking

Conventional vs. GtL Diesel

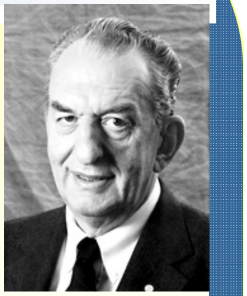
Quality	Conventional Diesel	SWCL1	Blu Diesel Agip	FT – Diesel #
Boiling range (°C)	180-360	180-275	180-360	150-360
Density @ 15°C (kg/m^3)	820 – 845	805	835	780
Sulfur (ppm vol)	50	6	4.5	< 1
Aromatics (% vol)	30	3	22	< 0.1
Cetane number (CN)	> 51	56	55	> 70
CFPP* (°C)	- 15	- 12	- 11	- 20
Cloud point (°C)	0	n.d.	-1	-15

* Cold Filter Plug Point;

Diesel from waxes produced on pilot runs

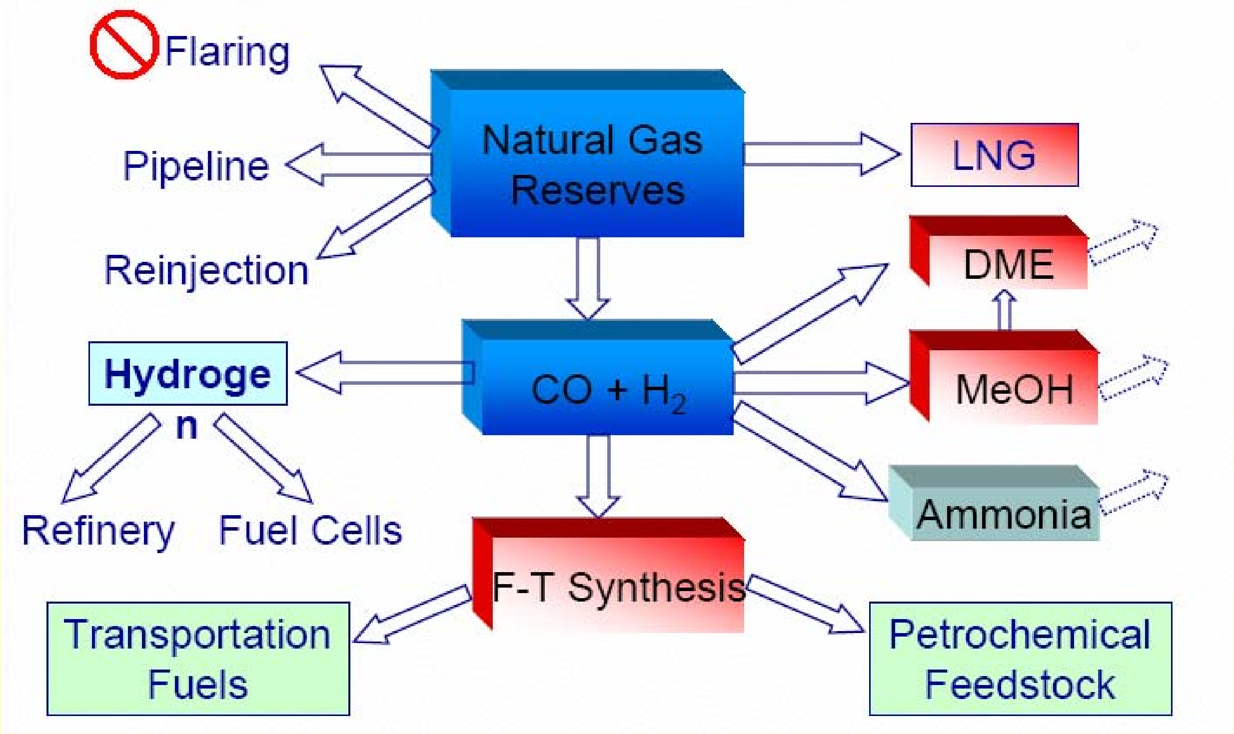


The Nobel Prize in Chemistry 1994



G.Olah : **Beyond Oil and Gas: The Methanol Economy**

- storing energy in the form of methanol
  - excellent fuel; easily stored, transported and used



Flaring

Pipeline

Reinjection

Natural Gas Reserves

LNG

$CO + H_2$

Hydrogen

Refinery

Fuel Cells

DME

MeOH

Ammonia

F-T Synthesis

Transportation Fuels

Petrochemical Feedstock

Methanol

$CO+2H_2 \rightleftharpoons CH_3OH,\quad \Delta H=-90.8\ kJ/mol$

$CO_2+3H_2 \rightleftharpoons CH_3OH+H_2O,\quad \Delta H=-49.6\ kJ/mol$

$CO+H_2O \rightleftharpoons CO_2+H_2,\quad \Delta H=-41\ kJ/mol$

T low
By-products: higher alcohols and hydrocarbons from CO
Phase: gas
Catalyst: selective $CuZn/Al_2O_3$

Methanol

Catalyst: sintering possible, thus t< 200-270°C
deactivation by S, C$\Rightarrow$(purification)

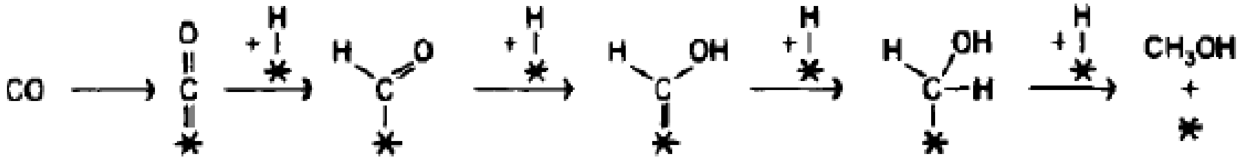
Operation policy : pressure increase with deactivation (not T)

Gas composition: 74% H_2, 15% CO, 8% CO_2, 3% CH_4
p=50-100 bar, conversion 15-30% in adiabatic reactor

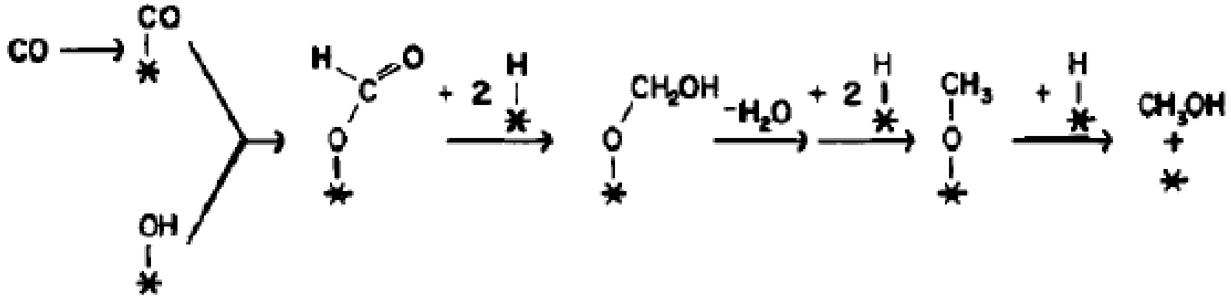
Recycle of gases : recycle/make-up = 3-7 (range to avoid build up of CH_4 and Ar)
Products : distillation
Improvements: 1) remove heat to keep reaction T as low as possible
2)removal of methanol to shift equilibrium
3) more active catalyst

Mechanism of methanol formation

MECHANISM A



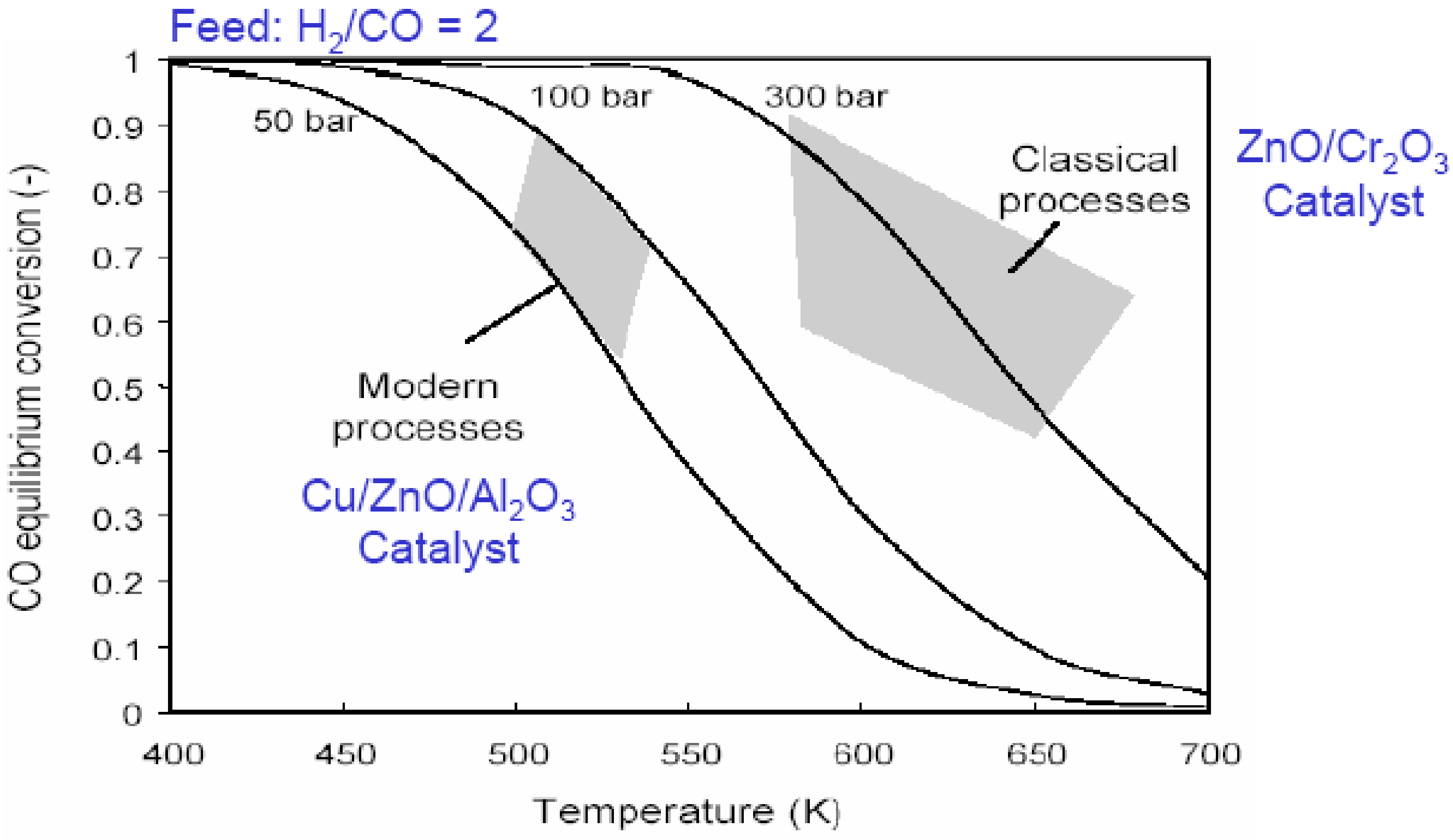
MECHANISM B



Methanol synthesis mechanism

$$
\begin{aligned}
H_2O(g) + * &\rightleftarrows H_2O* \\
H_2O* + * &\rightleftarrows OH* + H* \\
2OH* &\rightleftarrows H_2O* + O* \\
OH* + * &\rightleftarrows O* + H* \\
2H* &\rightleftarrows H_2(g) + 2* \\
CO(g) + * &\rightleftarrows CO* \\
CO* + O* &\rightleftarrows CO_2* + * \\
CO_2* &\rightleftarrows CO_2(g) + * \\
CO_2* + H* &\rightleftarrows HCOO* + * \\
HCOO* + H* &\rightleftarrows H_2COO* + * \\
H_2COO* + H* &\rightleftarrows H_3CO* + O* \\
H_3CO* + H* &\rightleftarrows CH_3OH* + * \\
CH_3OH* &\rightleftarrows CH_3OH(g) + *,
\end{aligned}
$$

Rate determining step


Feed: $H_2/CO = 2$
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
CO equilibrium conversion (-)
400
450
500
550
600
650
700
Temperature (K)
50 bar
100 bar
300 bar
Classical processes
Modern processes
ZnO/Cr_2O_3 Catalyst
$Cu/ZnO/Al_2O_3$ Catalyst

Methanol

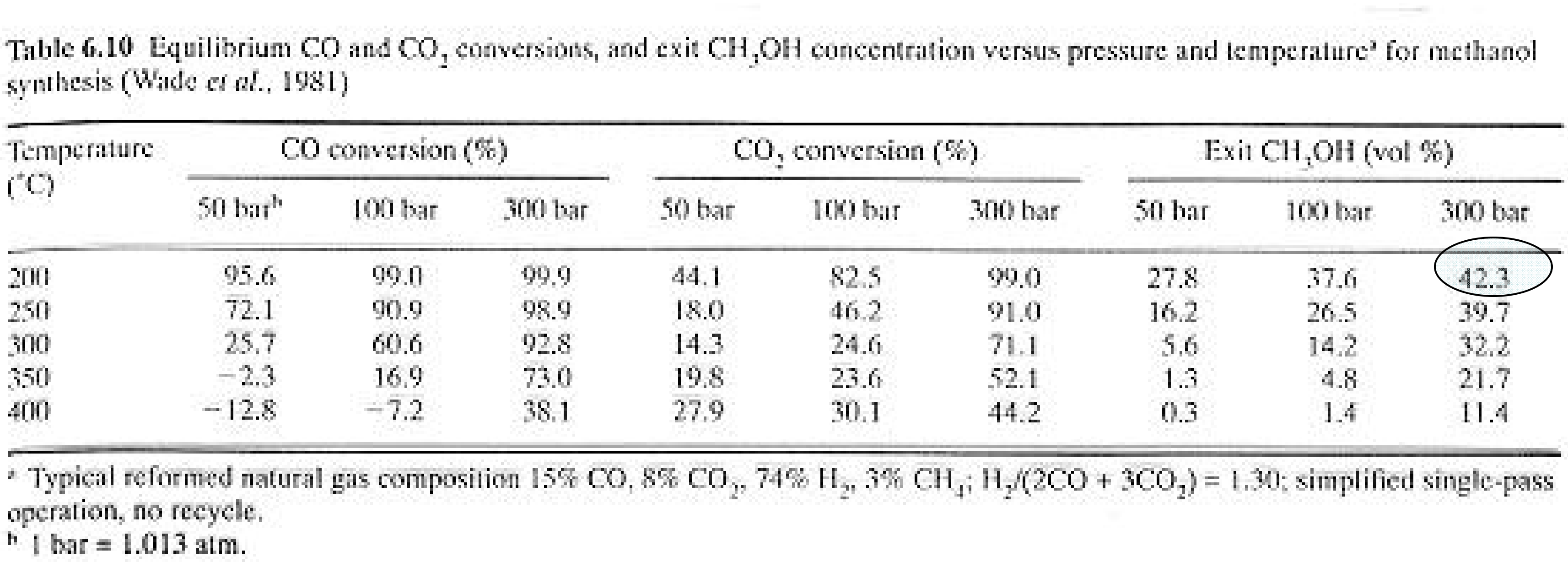


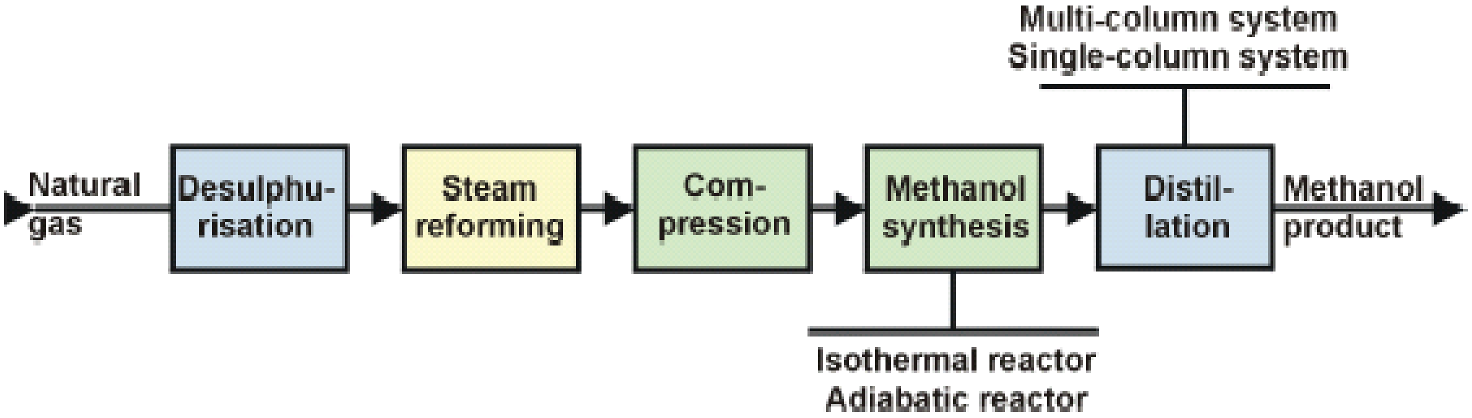
Table 6.10 Equilibrium CO and CO_2 conversions, and exit CH_3OH concentration versus pressure and temperature[a] for methanol synthesis (Wade *et al.*, 1981)

Temperature (°C)	CO conversion (%)			CO_2 conversion (%)			Exit CH_3OH (vol %)		
	50 bar[b]	100 bar	300 bar	50 bar	100 bar	300 bar	50 bar	100 bar	300 bar
200	95.6	99.0	99.9	44.1	82.5	99.0	27.8	37.6	42.3
250	72.1	90.9	98.9	18.0	46.2	91.0	16.2	26.5	39.7
300	25.7	60.6	92.8	14.3	24.6	71.1	5.6	14.2	32.2
350	−2.3	16.9	73.0	19.8	23.6	52.1	1.3	4.8	21.7
400	−12.8	−7.2	38.1	27.9	30.1	44.2	0.3	1.4	11.4

[a] Typical reformed natural gas composition 15% CO, 8% CO_2, 74% H_2, 3% CH_4; $H_2/(2CO + 3CO_2) = 1.30$; simplified single-pass operation, no recycle.

[b] 1 bar = 1.013 atm.

Methanol synthesis



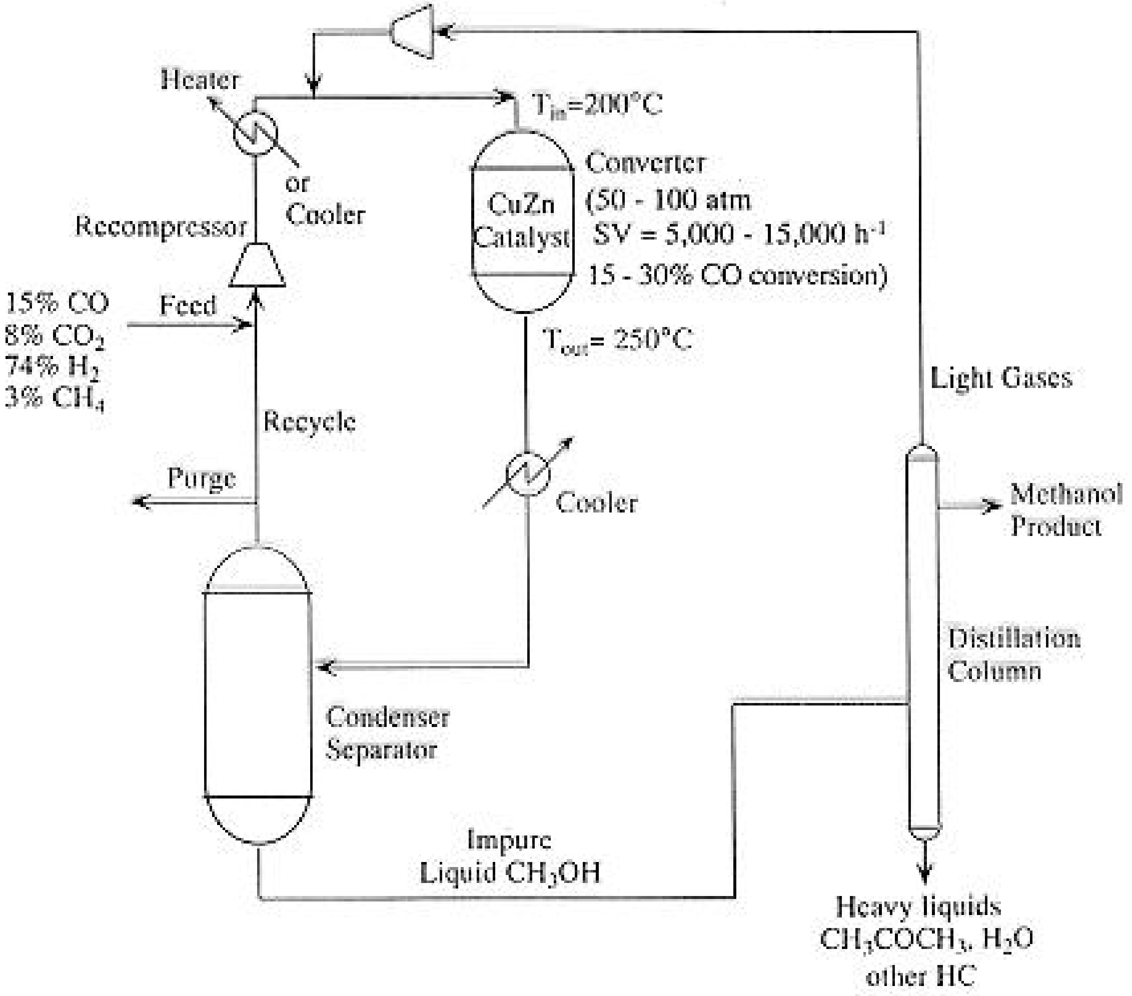
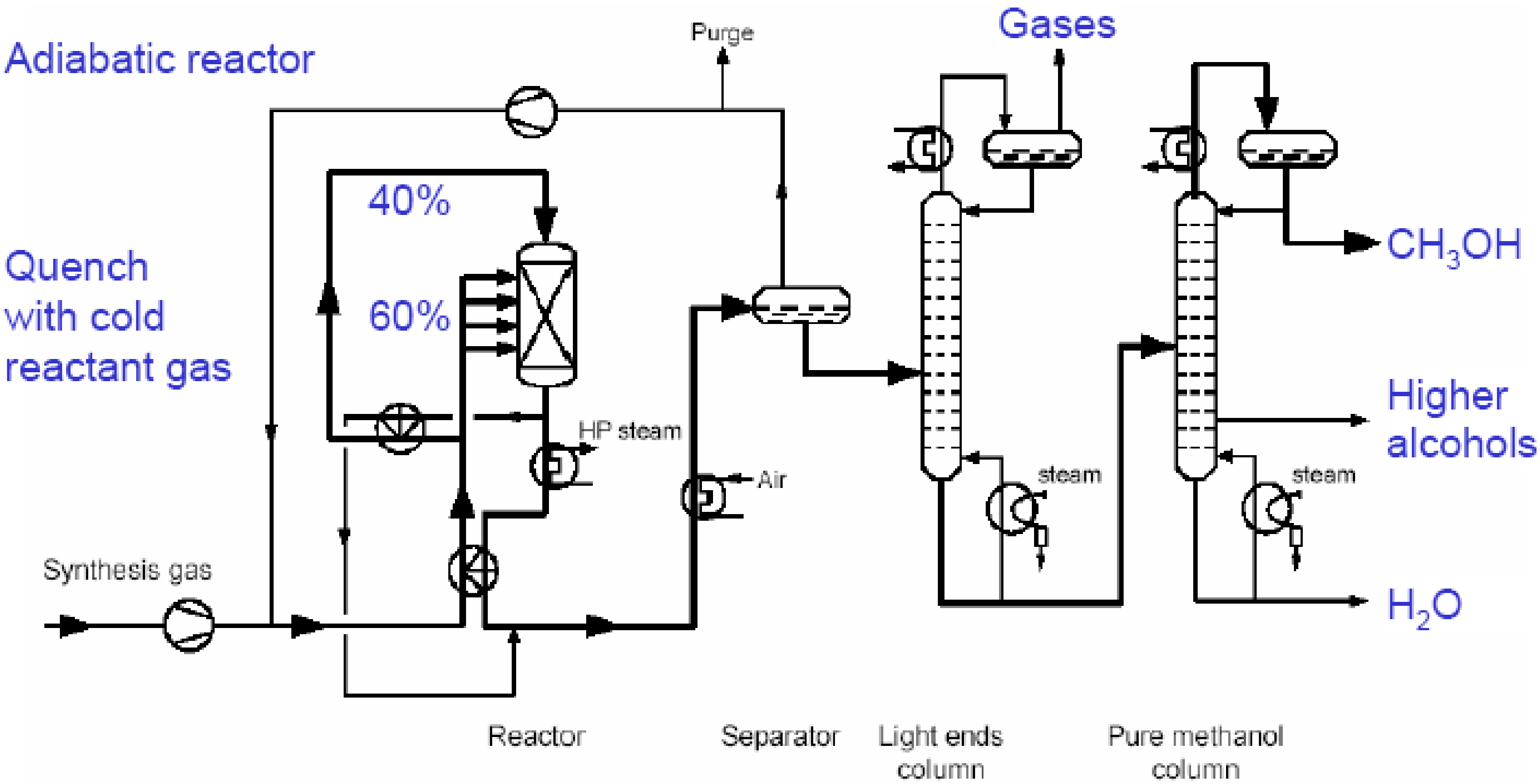


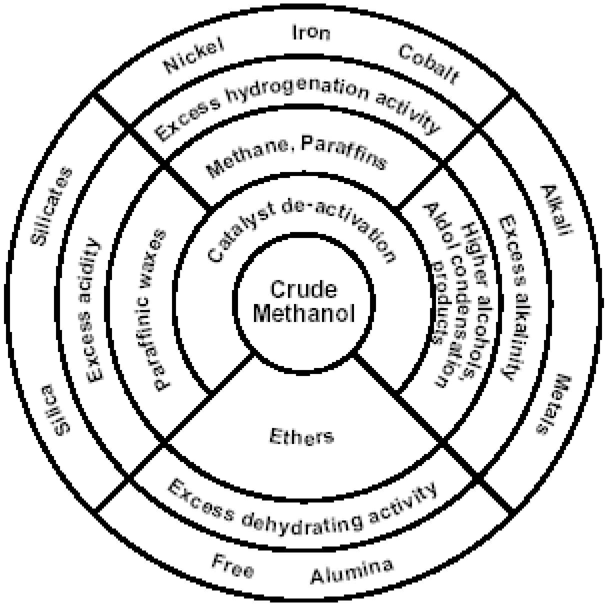
Figure 6.15 Flow sheet of typical low pressure methanol plant based on the steam reforming of natural gas.

ICI-low pressure methanol process

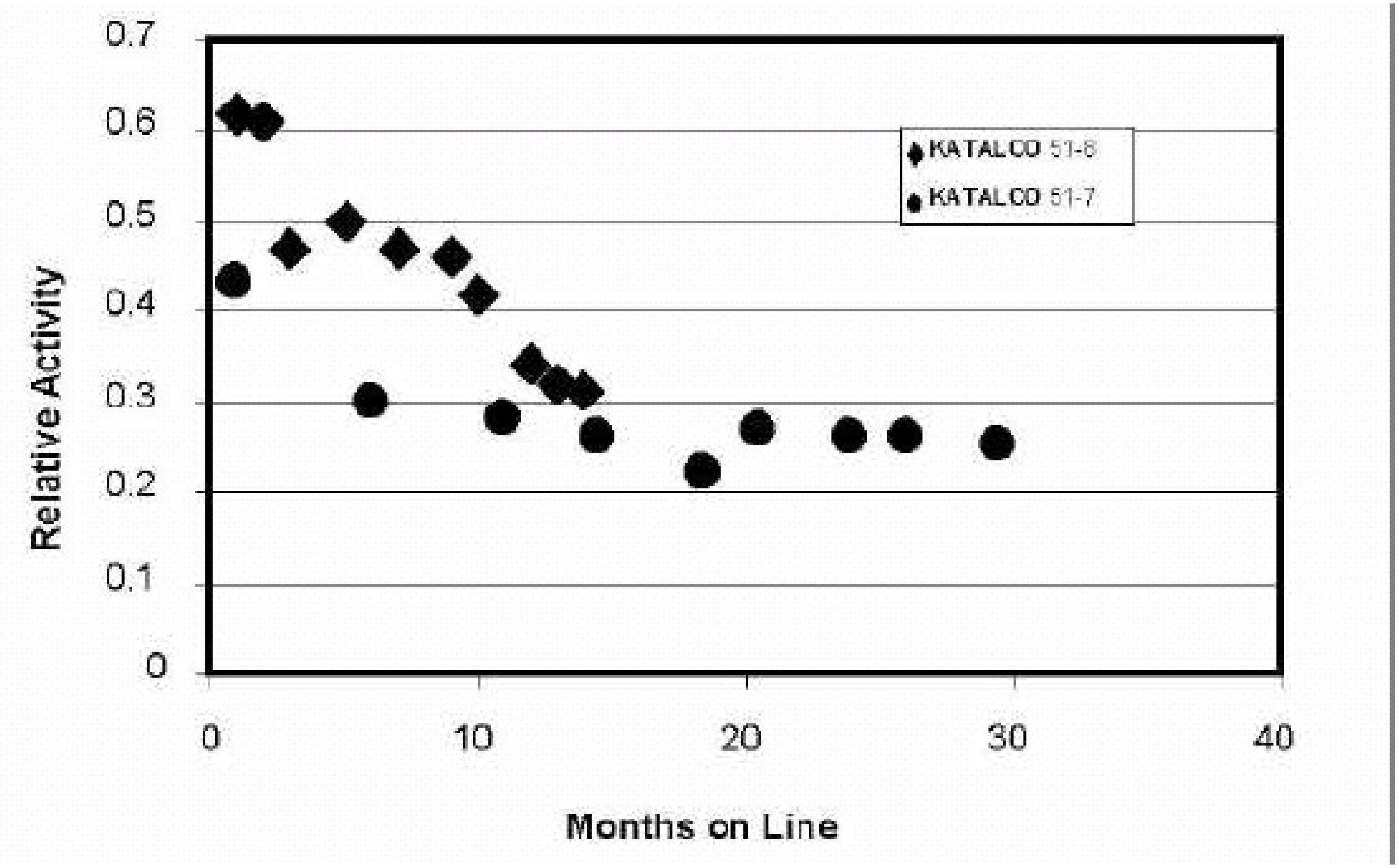


Catalysts

	Physical Properties (Typical)	Chemical Composition (Typical)	
	KATALCO 51-8		
Form	Cylindrical pellet	**CuO:**	64 wt%
Diameter	5.4 mm	**Al_2O_3:**	10 wt%
Length	5.2 mm	**ZnO:**	24 wt%
Bulk Density	1250 kg/m^3	**MgO:**	2 wt%
Crush Strength (axial)	80 kg$_f$		

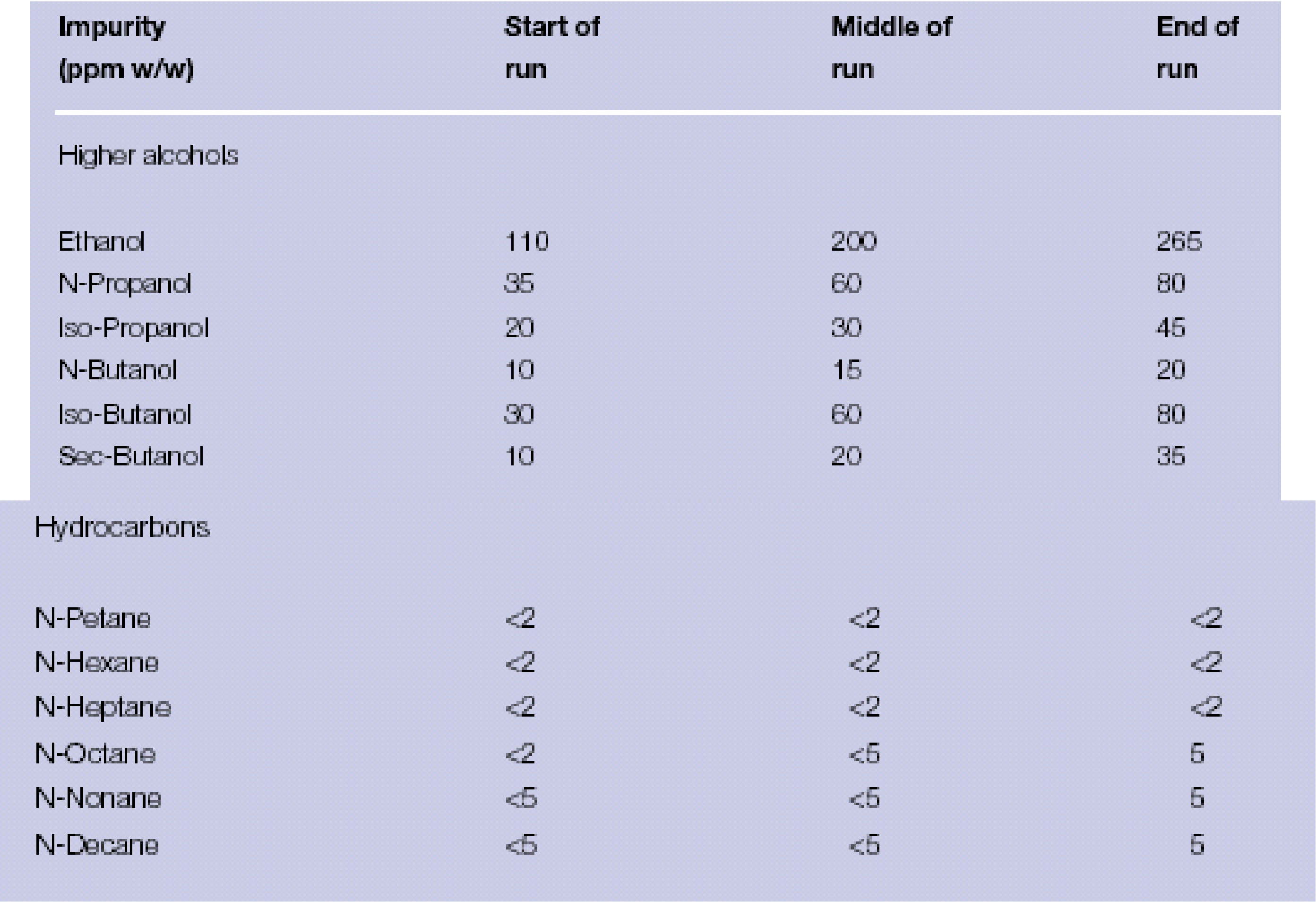


Catalyst Activity



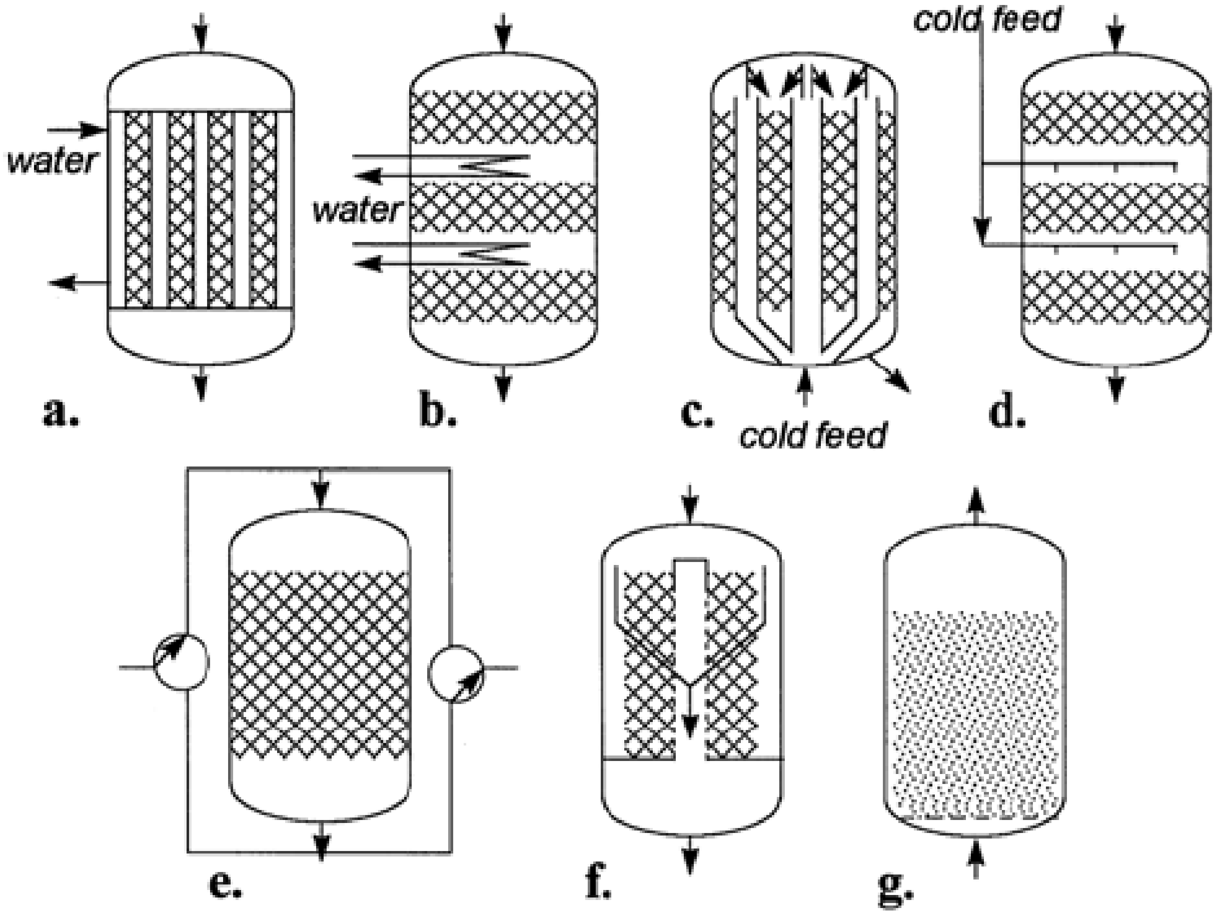
Operation policy: increase pressure, not T

Crude methanol analysis from a modern converter



Impurity (ppm w/w)	Start of run	Middle of run	End of run
Higher alcohols			
Ethanol	110	200	265
N-Propanol	35	60	80
Iso-Propanol	20	30	45
N-Butanol	10	15	20
Iso-Butanol	30	60	80
Sec-Butanol	10	20	35
Hydrocarbons			
N-Petane	<2	<2	<2
N-Hexane	<2	<2	<2
N-Heptane	<2	<2	<2
N-Octane	<2	<5	5
N-Nonane	<5	<5	5
N-Decane	<5	<5	5

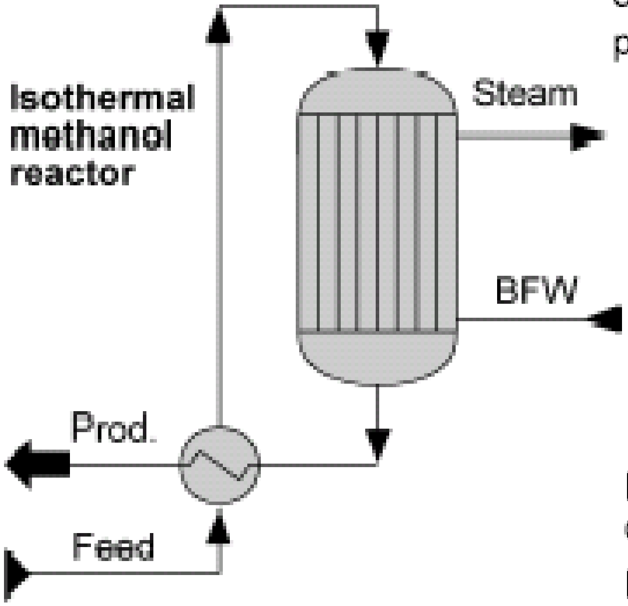
Types of reactors used for efficient cooling



(a) Cooling with water bath; (b)cooling with water coils; (c) cooling with cold feed; (d) feed gas quench; (e) feed–effluent heat exchange by periodic flow reversal; (f) lateral flow; (g) fluidised bed.

Reactor: isothermal

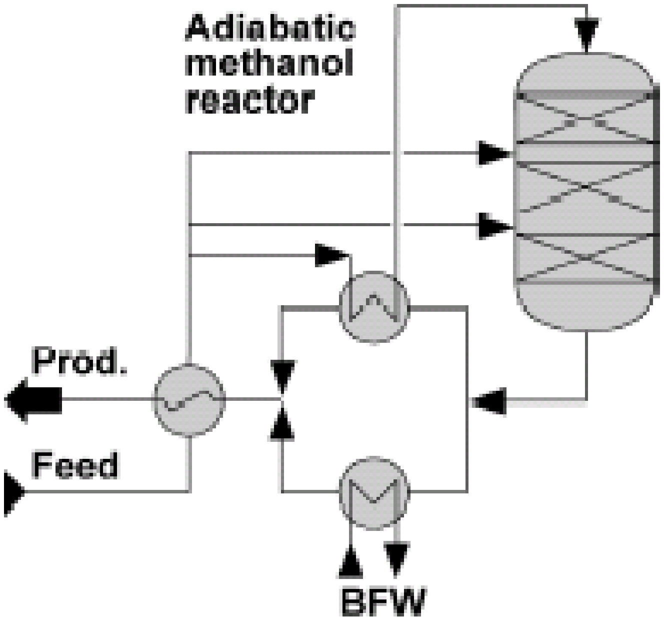
Uhde's isothermal reactor is a tubular reactor with a copper catalyst contained in vertical tubes and boiling water on the shell side. The methanol reaction heat is removed by partial evaporation of the boiler feed water, thus generating 1 metric ton of medium-pressure steam per 1.4 metric tons of methanol.



The advantages of this reactor type are: low by-product formation due to almost isothermal reaction conditions, high reaction heat recovery, and easy temperature control by regulating steam pressure.

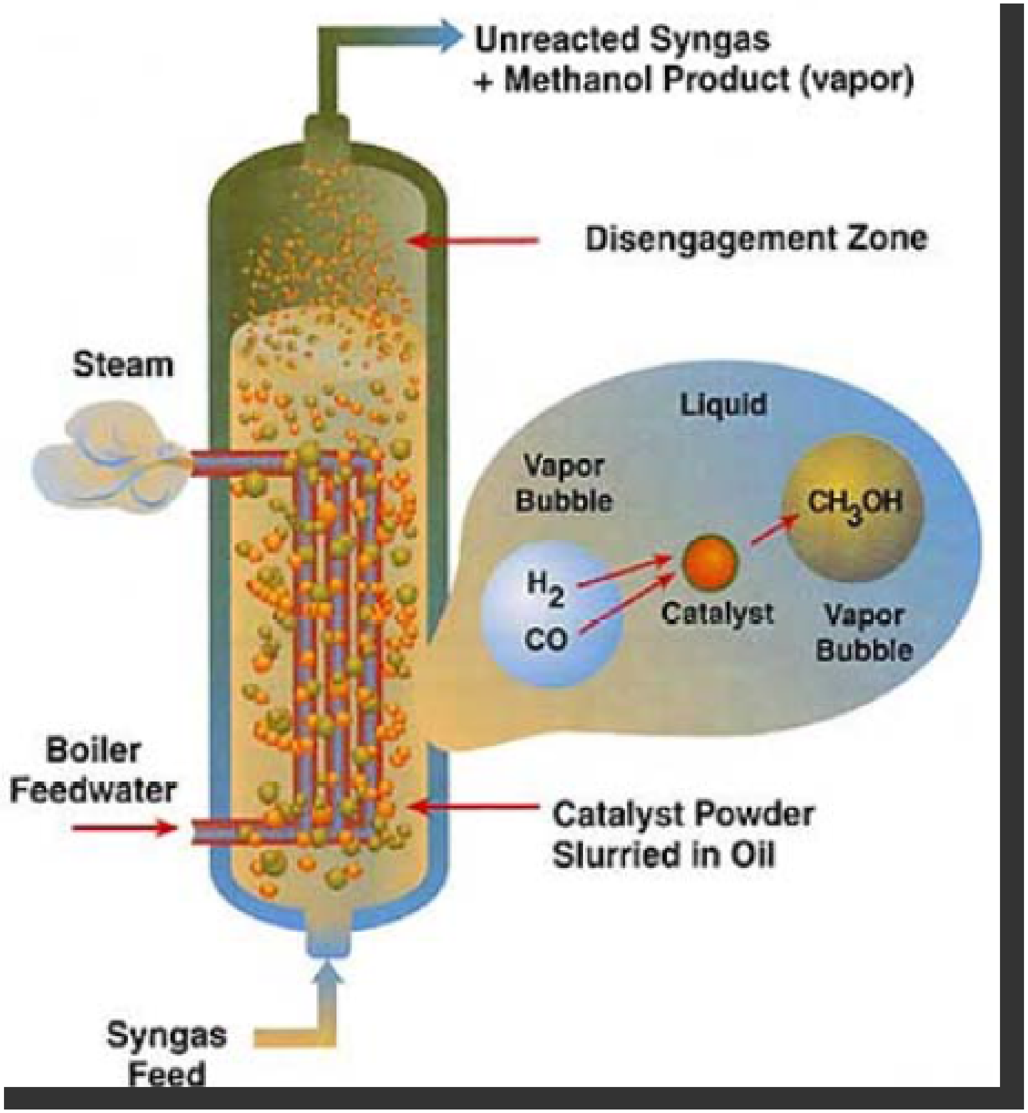
To avoid the build-up of inert components in the loop, a purge is withdrawn from the recycle gas and used as fuel for the reformer.

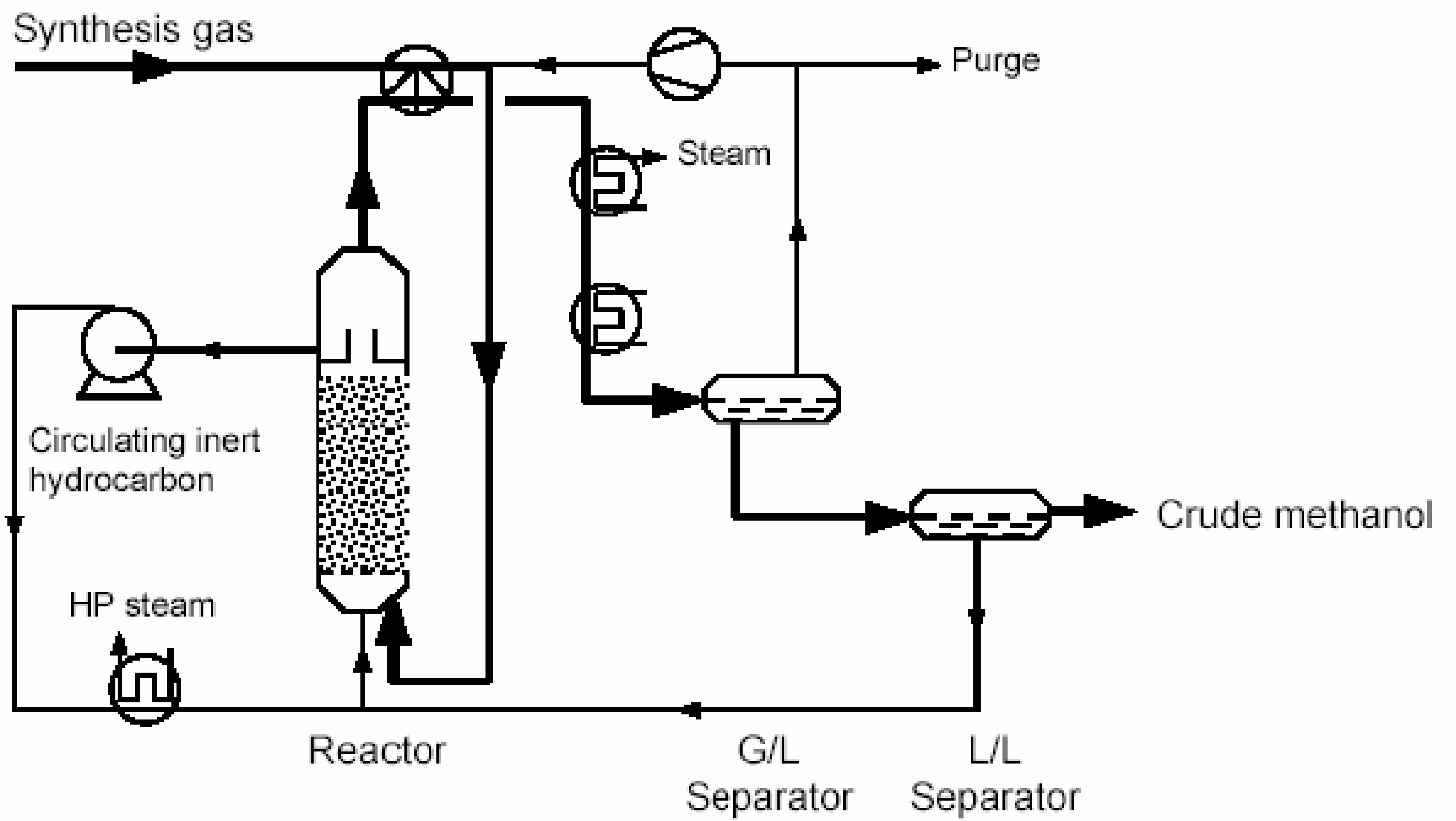
Reactor: adiabatic

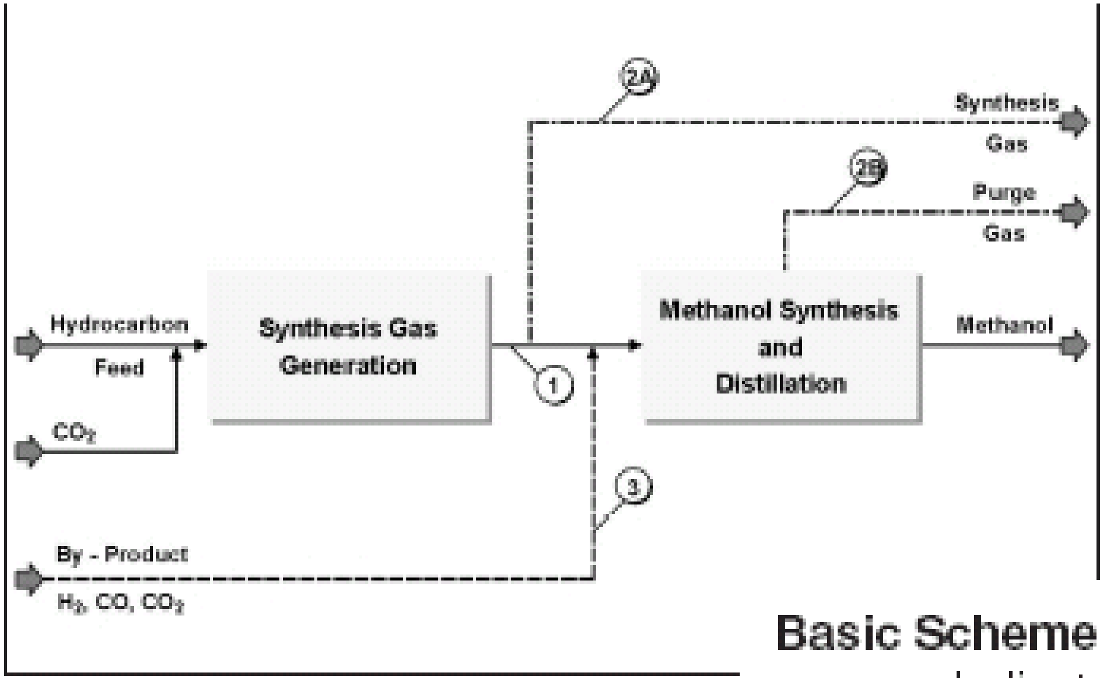


The axial radial multi-bed adiabatic quench is a low cost reactor concept. It is normally used for plants which require no steam in synthesis units, due to the fact, that surplus steam is produced during syngas generation (for instance steam reforming). Uhde can offer the ARC (Axial Radial Concept) technology licensed by Methanol Casale, Switzerland.

Methanol synthesis slurry process




Synthesis gas
Purge
Steam
Circulating inert hydrocarbon
HP steam
Crude methanol
Reactor
G/L Separator
L/L Separator

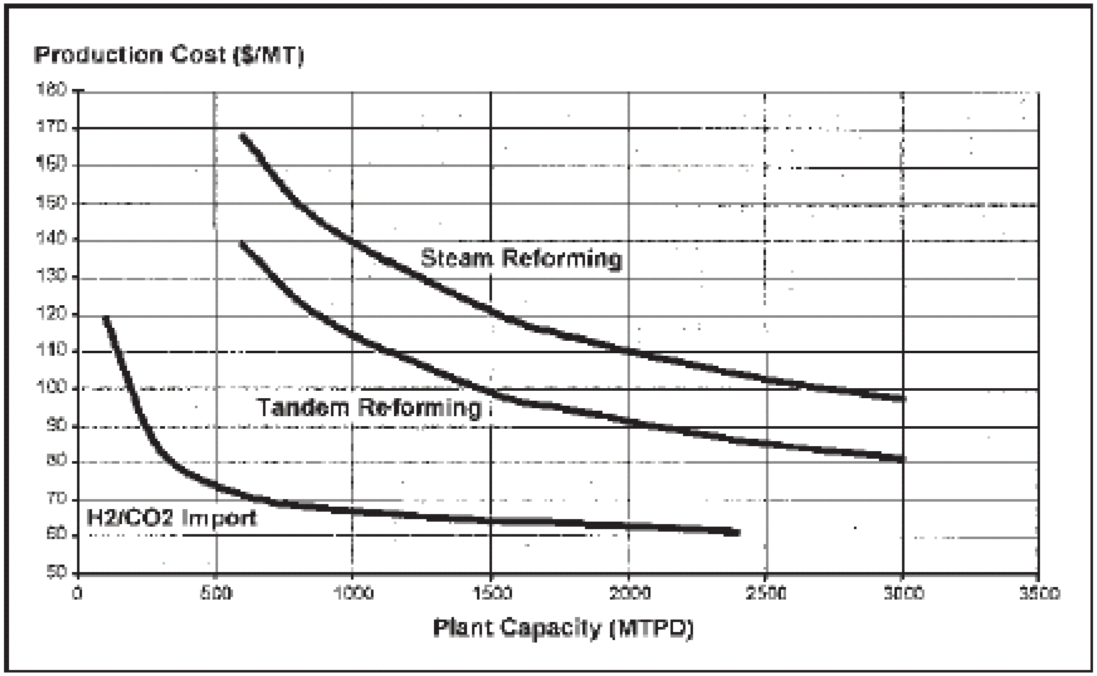


Basic Scheme 1: Routes producing syngas dedicated solely to methanol production

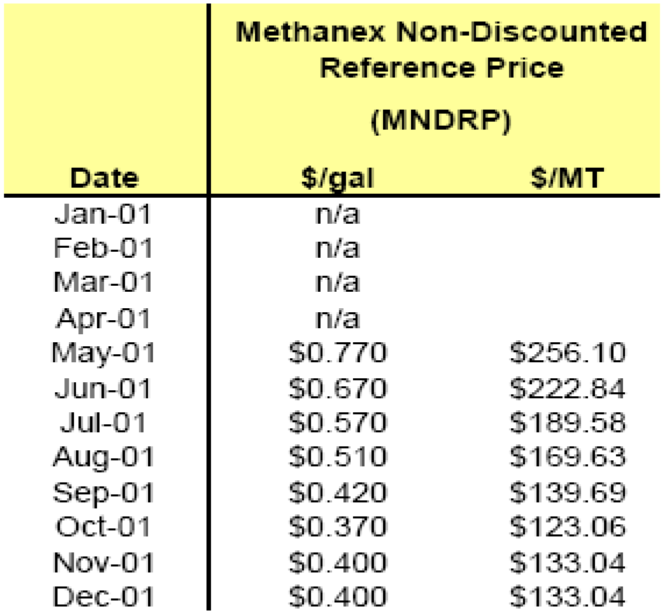
Basic Scheme 2: Routes producing syngas for methanol production as well as syngas and/or other by-products for other consumers in one train

Basic Scheme 3: Routes importing methanol syngas from by-product gases available from already existing sources

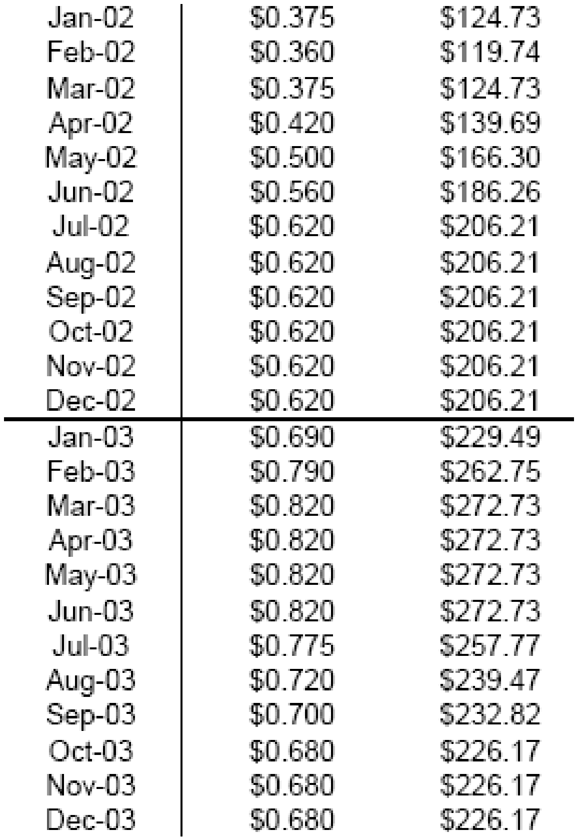
Tandem


Production Cost ($/MT)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
0
500
1000
1500
2000
2500
3000
3500
Plant Capacity (MTPD)
Steam Reforming
Tandem Reforming
H2/CO2 Import

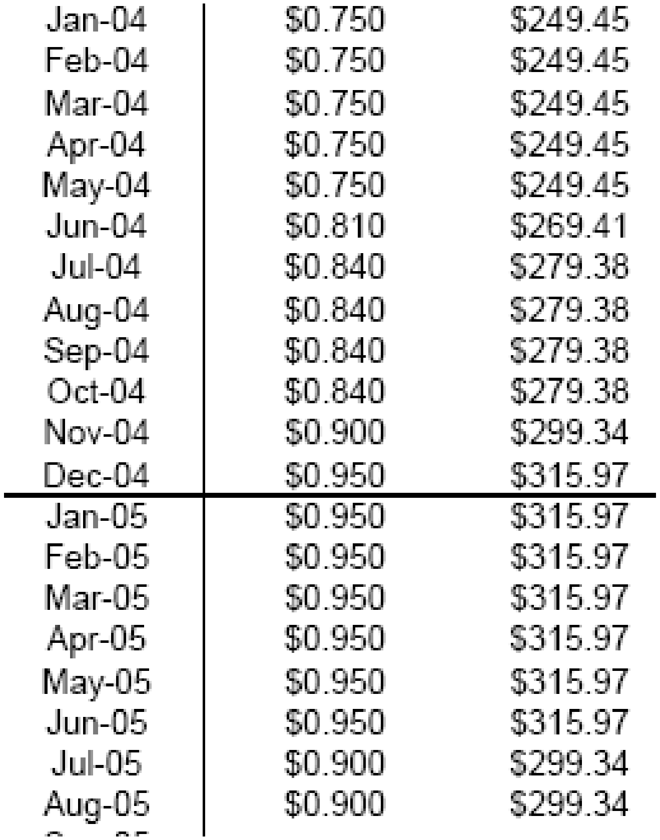
Prices



Date	Methanex Non-Discounted Reference Price (MNDRP) $/gal	$/MT
Jan-01	n/a	
Feb-01	n/a	
Mar-01	n/a	
Apr-01	n/a	
May-01	$0.770	$256.10
Jun-01	$0.670	$222.84
Jul-01	$0.570	$189.58
Aug-01	$0.510	$169.63
Sep-01	$0.420	$139.69
Oct-01	$0.370	$123.06
Nov-01	$0.400	$133.04
Dec-01	$0.400	$133.04

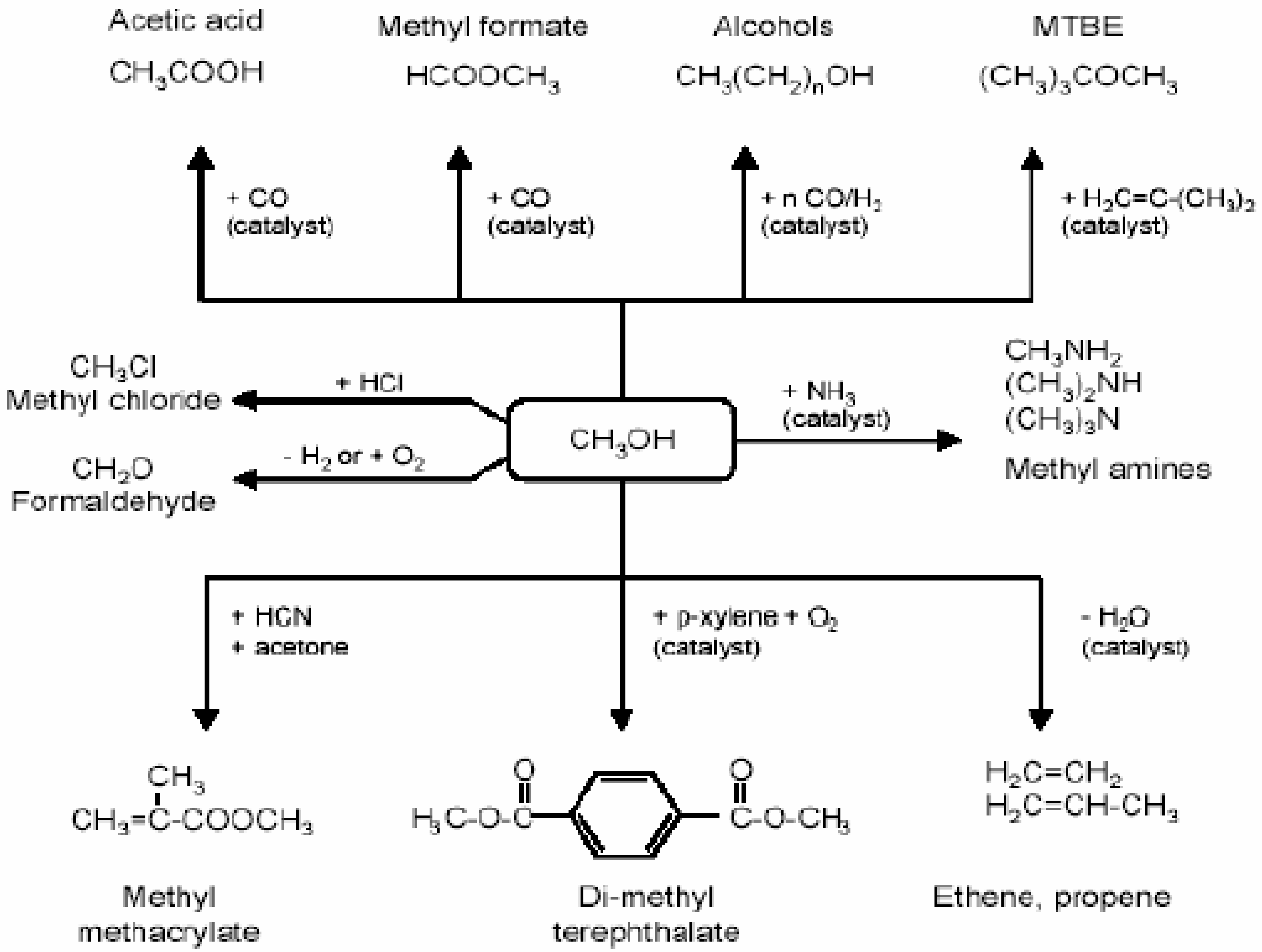


Jan-02	$0.375	$124.73
Feb-02	$0.360	$119.74
Mar-02	$0.375	$124.73
Apr-02	$0.420	$139.69
May-02	$0.500	$166.30
Jun-02	$0.560	$186.26
Jul-02	$0.620	$206.21
Aug-02	$0.620	$206.21
Sep-02	$0.620	$206.21
Oct-02	$0.620	$206.21
Nov-02	$0.620	$206.21
Dec-02	$0.620	$206.21
Jan-03	$0.690	$229.49
Feb-03	$0.790	$262.75
Mar-03	$0.820	$272.73
Apr-03	$0.820	$272.73
May-03	$0.820	$272.73
Jun-03	$0.820	$272.73
Jul-03	$0.775	$257.77
Aug-03	$0.720	$239.47
Sep-03	$0.700	$232.82
Oct-03	$0.680	$226.17
Nov-03	$0.680	$226.17
Dec-03	$0.680	$226.17



Jan-04	$0.750	$249.45
Feb-04	$0.750	$249.45
Mar-04	$0.750	$249.45
Apr-04	$0.750	$249.45
May-04	$0.750	$249.45
Jun-04	$0.810	$269.41
Jul-04	$0.840	$279.38
Aug-04	$0.840	$279.38
Sep-04	$0.840	$279.38
Oct-04	$0.840	$279.38
Nov-04	$0.900	$299.34
Dec-04	$0.950	$315.97
Jan-05	$0.950	$315.97
Feb-05	$0.950	$315.97
Mar-05	$0.950	$315.97
Apr-05	$0.950	$315.97
May-05	$0.950	$315.97
Jun-05	$0.950	$315.97
Jul-05	$0.900	$299.34
Aug-05	$0.900	$299.34

Methanol as base chemical



Acetic acid
CH_3COOH
+ CO
(catalyst)

Methyl formate
$HCOOCH_3$
+ CO
(catalyst)

Alcohols
$CH_3(CH_2)_nOH$
+ n CO/H_2
(catalyst)

MTBE
$(CH_3)_3COCH_3$
+ $H_2C{=}C\text{-}(CH_3)_2$
(catalyst)

CH_3Cl
Methyl chloride
+ HCl

CH_2O
Formaldehyde
- H_2 or + O_2

CH_3OH

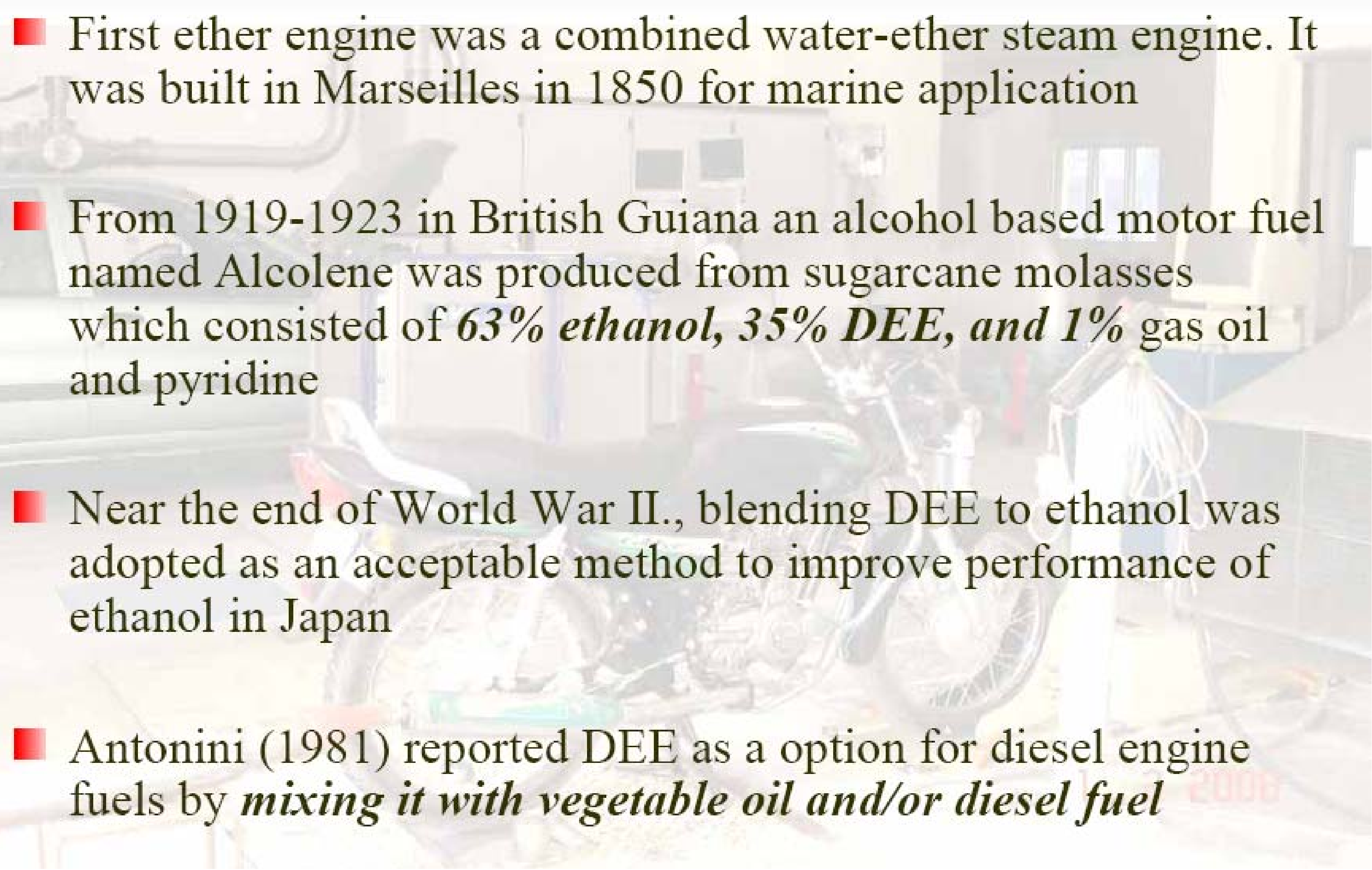
+ NH_3
(catalyst)
CH_3NH_2
$(CH_3)_2NH$
$(CH_3)_3N$
Methyl amines

+ HCN
+ acetone
$CH_2{=}C(CH_3)\text{-}COOCH_3$
Methyl methacrylate

+ p-xylene + O_2
(catalyst)
Di-methyl terephthalate

- H_2O
(catalyst)
$H_2C{=}CH_2$
$H_2C{=}CH\text{-}CH_3$
Ethene, propene

Background



- First ether engine was a combined water-ether steam engine. It was built in Marseilles in 1850 for marine application
- From 1919-1923 in British Guiana an alcohol based motor fuel named Alcolene was produced from sugarcane molasses which consisted of ***63% ethanol, 35% DEE, and 1%*** gas oil and pyridine
- Near the end of World War II., blending DEE to ethanol was adopted as an acceptable method to improve performance of ethanol in Japan
- Antonini (1981) reported DEE as a option for diesel engine fuels by ***mixing it with vegetable oil and/or diesel fuel***

Benefits of DEE

- Very High Cetane Number
- Reasonable Energy Density
- Liquid at room temperature

Challenges with DEE

- Stability in Storage
- Lower Lubricity
- Seal Compatibility