Supercritical Water Biomass Gasification:

Fuel Gas from Waste

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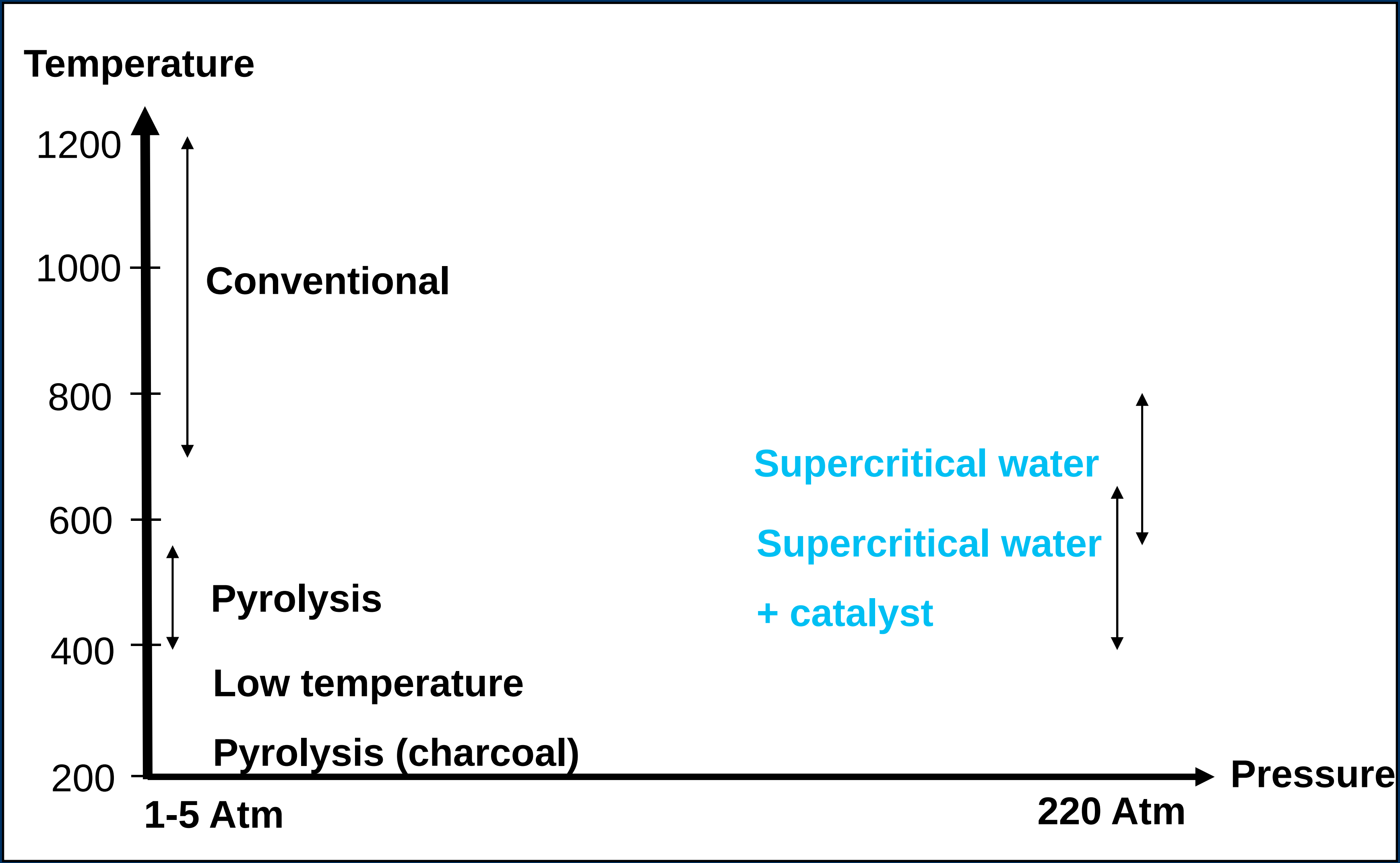
Menu

- Waste Sources
- Gasification Technologies
- Properties of Supercritical Water (SCW)
- SCW Gasification – Process and Potential

Waste Sources

- Animal waste
- Animal carcasses
- Domestic / Municipal
- Forestry
- Packaged food
- Vegetable

Gasification Technologies



Pyrolysis

- 400-550^{o}C, 1-5 bar
- Anerobic
- Slow – charcoal
- Fast – dark brown mobile liquid

Conventional Gasification

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- 700 – 1200C

- Need to drive off water before gasification
- Water content can be ca. 90% by mass
- Inefficient for high water content materials

- Suited to dry materials (e.g. sawdust)

- Problems:
- Char (always at 1 bar), tar

Tar Avoidance Options

- $>1000^oC$
- Dolomite
- Alkali metal oxides
- Catalyst
- Secondary air injection

Char

- Result of polymerisation of fragments broken down by hydrolysis

- Builds up at low temperatures

- Can be burnt off at high T

Avoidance strategies

- Rapid heating zone
- Catalyst
- SCW

Properties of Water

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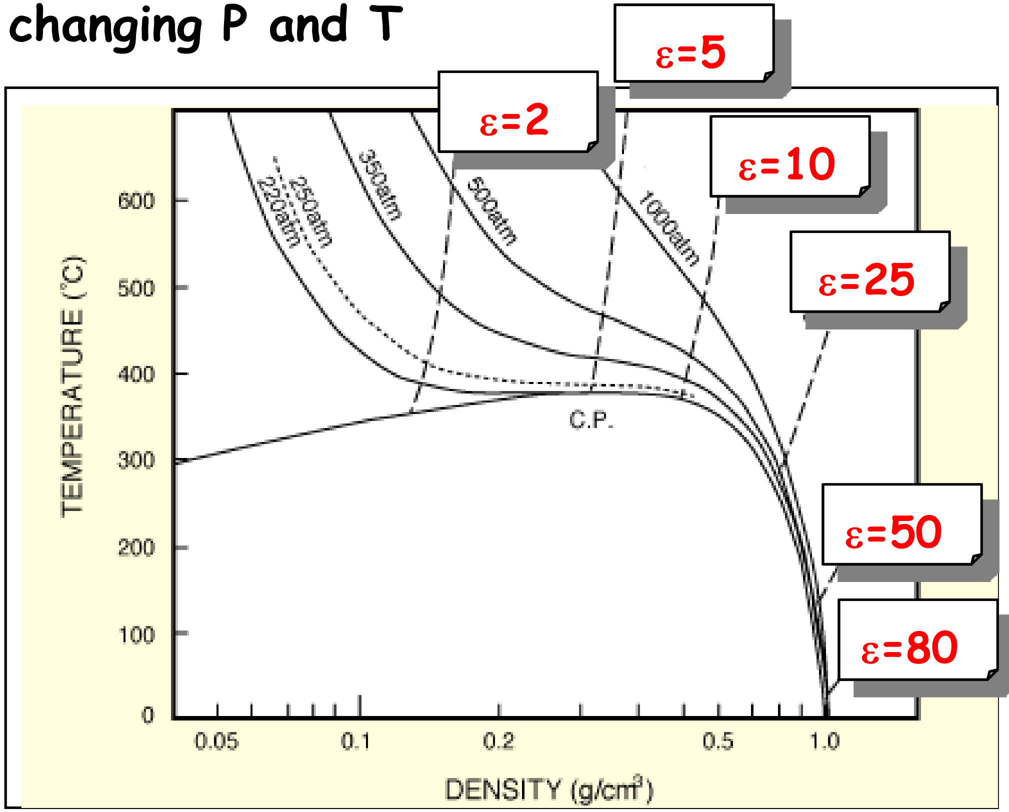
- Covalent molecule
- Extensive hydrogen bonding
- Dissociation: Acid/Base
- Dielectric constant
- Unusual properties of ice

Dielectric constant

A significant change of the dielectric constant can be obtained by changing P and T



Relative dielectric constant (ε) of different solvents

Solvent	ε
Propane	1.6
Hexane	1.8
Carbon tetrachloride	2.2
Acetone	20.7
Ethanol	24.5
Methanol	32.6

Change of ε with P and T increase the dissolving power. *At 300°C, the H_2O is similar to acetone*: dissolving organic compounds and precipitating inorganic salts.

Supercritical Water

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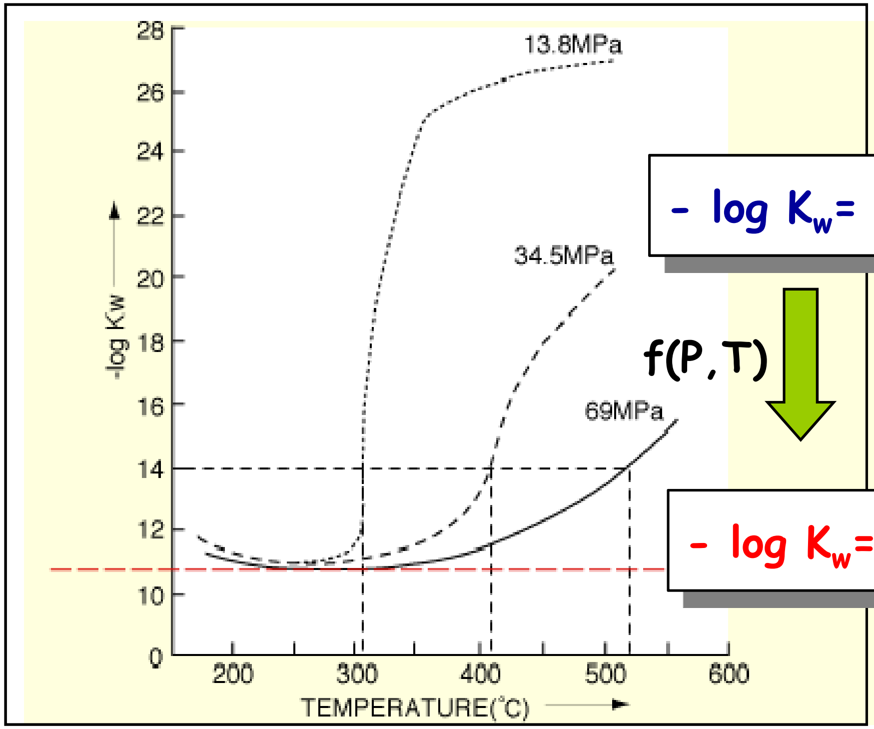
- T_c 374 ^oC; p_c 218 atm.

	H_2O, 374^oC	Hexane
ε	6	1.8
ρ	0.3	0.8

- Organics dissolve; salts precipitate
- O_2 is miscible with H_2O above T_c

The ionic product (K_w)



$-\log K_w = 14$

f(P,T)

$-\log K_w = 11$

As the dissociation proceeds, the nature of the water itself changes. Water becomes an acidic or alkaline catalyst.

$$K_W = [H^+]\,[OH^-]$$

Optimisation of acid/based-catalysed reaction by P and T

Kw depends significantly of the temperature and/or pressures

SCW Gasification

- SC Water miscible with nonpolar organic compounds

- Self dissociation – high OH^-
- Hydrolysis

- 600-800^{o}C (no catalyst)
- 500-650^{o}C (with metal catalyst)
- 220-250 bar – gases produced at pressure

SCW Gasification

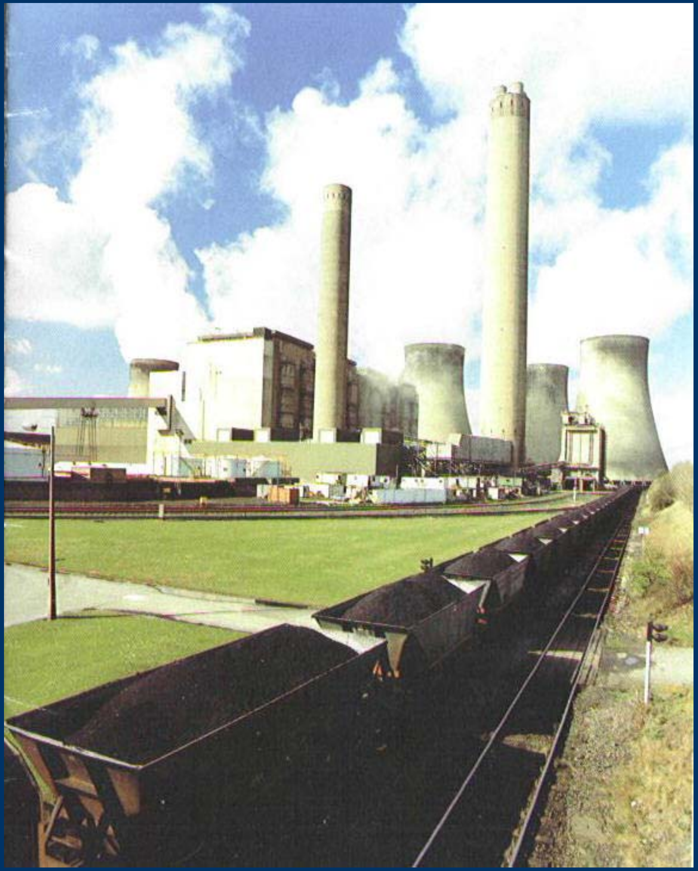
- No need to drive off water

- Suitable for high moisture content materials

- Optimum 700^{o}C, 3% aqueous feedstock
  100% gasification acheivable

- Need energy source for preheating incoming feedstock slurry to ca. 400C

sc Water conditions are routinely in use



- Ratcliffe-on-Soar Power Station
- 4x 500MW Steam Turbines
- 165 bar
- 568°C

Heating Energy

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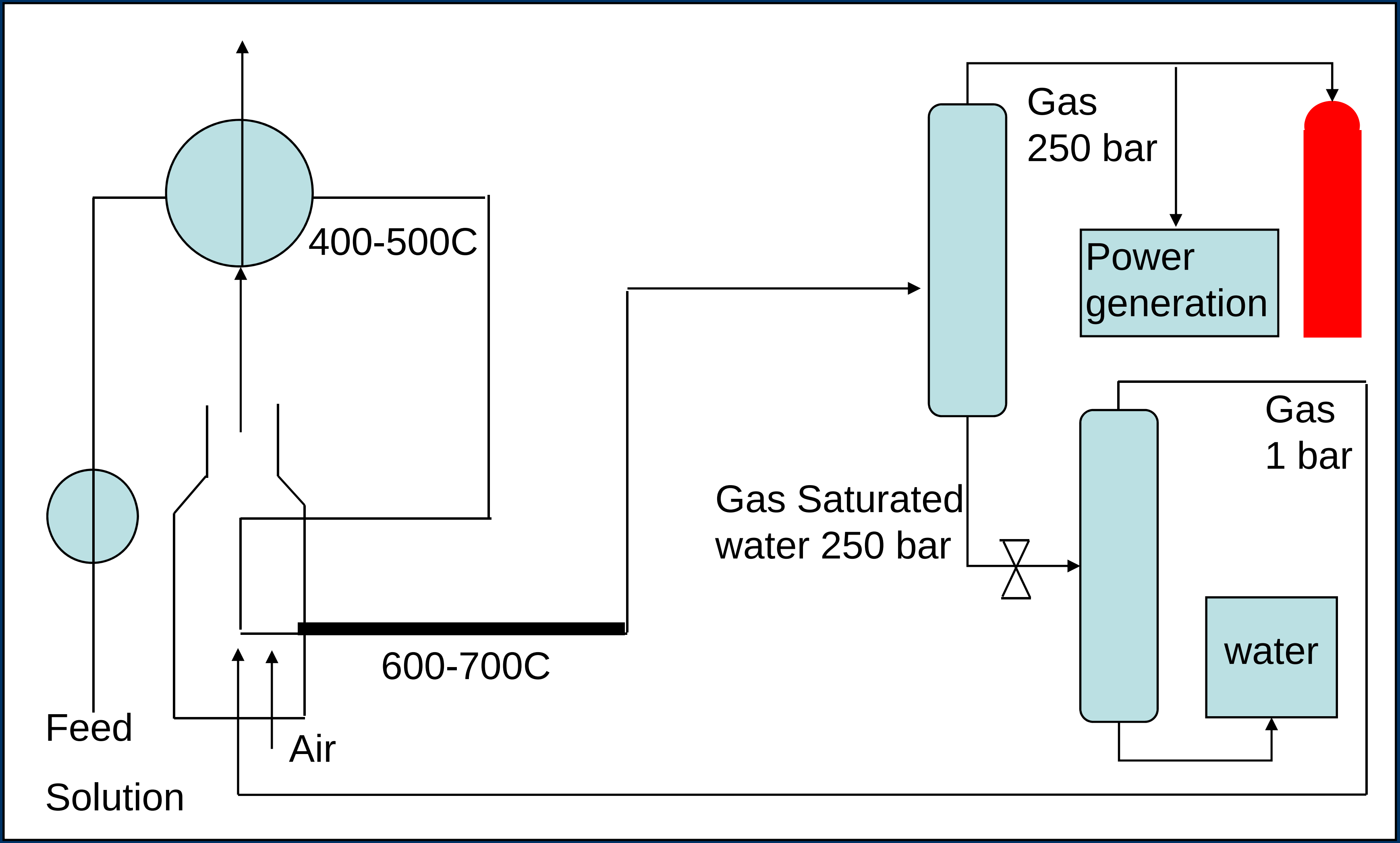
- Externally

  Burn portion of biomass to heat incoming slurry

- Internally

  Inject O_2 in first stage, combust part of feed in SCW

Supercritical Water Gasification Process



Supercritical Water Reactor

Feedstocks

- Dry waste – thermal gasification optimum
- Wet waste – supercritical water optimum

Yoshida et al; Biomass & Bioenergy 25 (2003) 257-272

Bulbs
Cabbage
Cereal residue
Distillers dried grain
Ethanol fermentation residue
Food waste, potato waste
Food packaging
Manure
Sawdust, wood
Straw
Sugarcane bagasse

Chemical Composition

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- Cellulose
- Hemicellulose
- Proteins
- Lignin
  - waste product of paper pulping
  - difficult to process
  - reduces H_2 yield

Feedstocks

Glucose

(Sparqle, NL) Mol%

H_2	54
CH_4	3
CO_2	34
CO	3
C_x	0

Penninger JML et al
J Supercrit Fluids 16: 119-132 (1999)

Trester

(Winegas project) Vol%

H_2	44
CH_4	25
CO_2	22
CO	2
C_x	8

EU Project CRAF-1999-70995

Gas Optimisation

- Hydrogen

  Favoured at higher temperature

  Water – gas shift

- Methane

  Lower temperature

  Ni Catalyst (Kruse, FZK)

Gas Use

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- Gases are pre scrubbed by water
- No SOx, NOx in SCWO;
  (converted to corresponding acids)
- Claimed gases are "turbine suitable"
- At 250 bar, CO_2 sequestration easy

CHOREN Industries Carbo-V Process

Biomass → gas + tar + char [1]

[2] gas + tar → gas

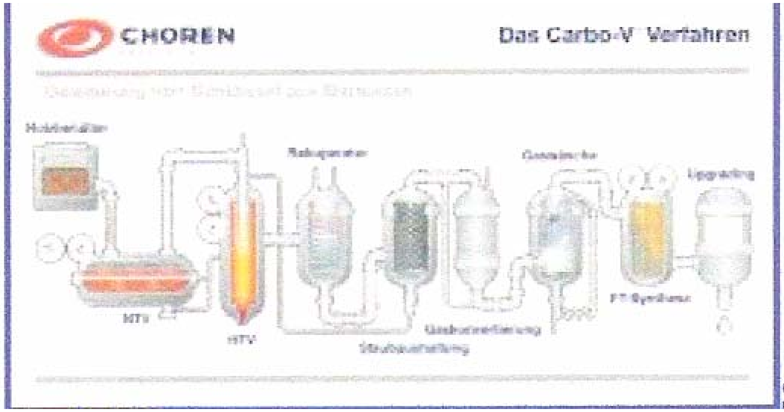
char → pulverisation

[3] gas + pulverisation → syngas

[4] compression

[5] F-T synthesis

Synthetic diesel fuel



www.choren.com

Routes to Syngas

- Steam Reforming: $CH_4 + H_2O \rightarrow CO + 3H_2$
- Partial Oxidation: $CH_4 + 3/2O_2 \rightarrow CO + 2H_2O$
- Water Gas Shift: $CO + H_2O \rightarrow CO_2 + H_2$

Fischer-Tropsch

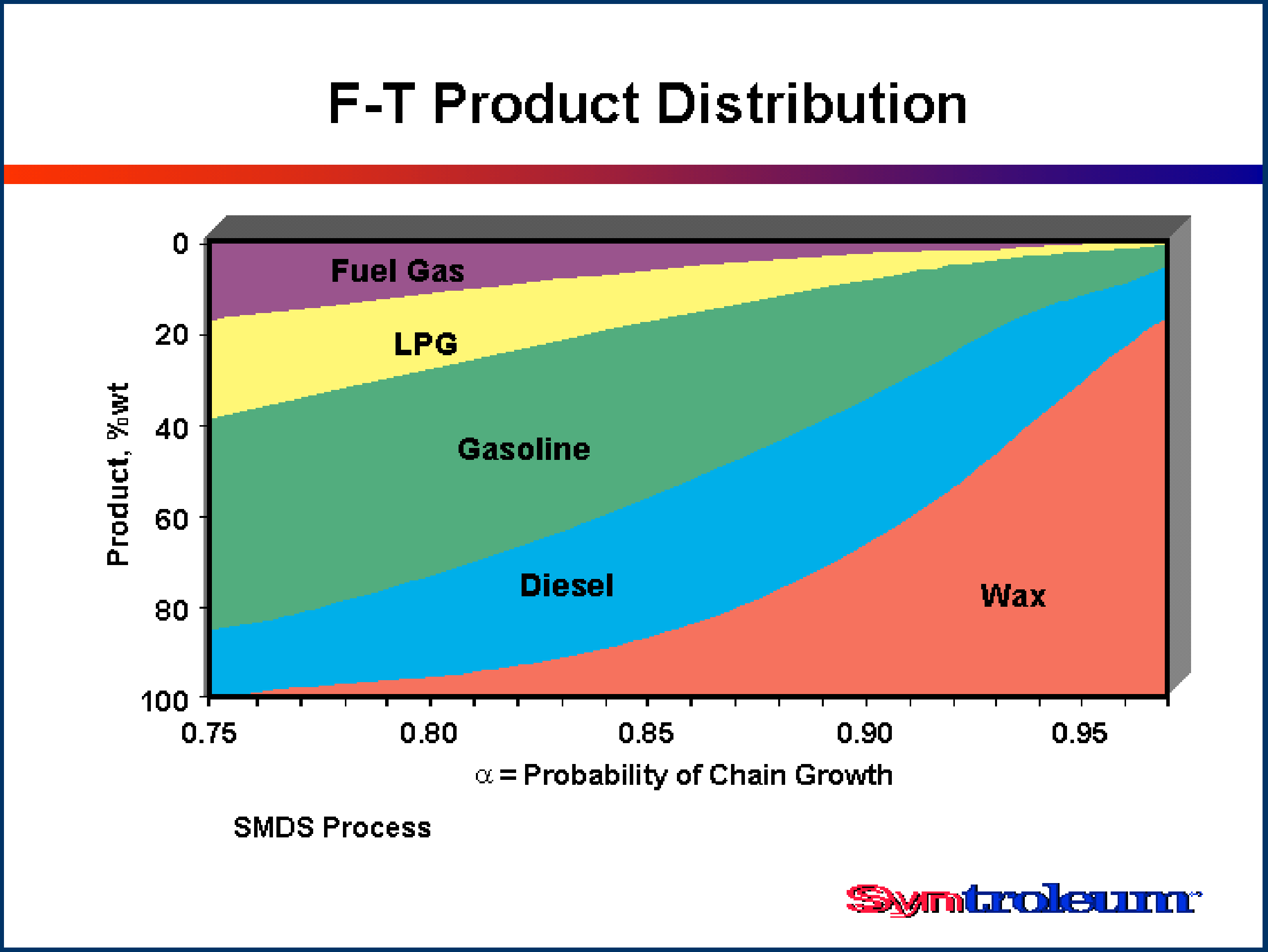
- Step 1
  Production of syngas [CO + H2]

- Step 2
  Syngas to a broad range hydrocarbon stream

  $CO + 2H_2$ -> $[-CH_2-] + H_20$

150,000 barrels/day

www.fischer-tropsch.org/



Who & Where ?

SCW expertise:

- China, Japan
- US – PNW Labs / Hawaii
- EU – Austria, Germany, Holland
- Vienna Institute of Technology
- CHOREN industries
- Sparql
- Univ Twente

UK

- SC Water at Nottingham, Birmingham
  [Hamley, Poliakoff] [Al-Duri]
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