

HIGHBIO - INTERREG NORD
2008 - 2011



*Högfördädlade bioenergiprodukter via förgasning
Korkeasti jalostettuja bioenergiatuotteita kaasituksen kautta*

EUROPEAN UNION
European Regional Development Fund

FISCHER-TROPSCH AT THE KOKKOLA UNIVERSITY CONSORTIUM CHYDENIUS

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HIGHBIO LULEÅ MAY 2009



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Fischer-Tropsch Background

- Fischer-Tropsch process discovered already in 1923
- Converts H_2 and CO to aliphatic hydrocarbons (FT-fuels etc.)
- Mostly used catalysts Co, Fe and Ru
- H_2 and CO (syngas) derived from coal, methane or [biomass](#)
- Lack of oil → FT process (CTL) used in WW2 and in South Africa (Sasol)



Franz Fischer



Hans Tropsch

F-T Apparatus at the Kaiser-Wilhelm Gesellschaft, 1930

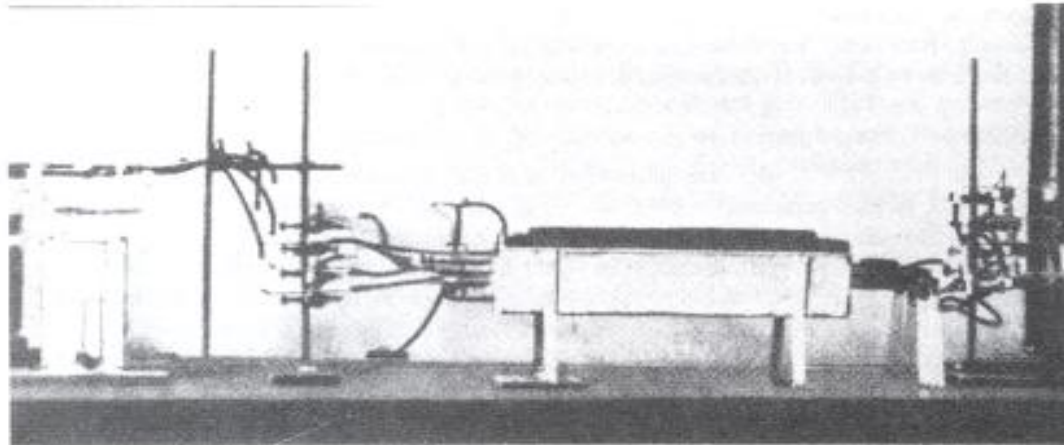


Fig. from Fischer-Tropsch Archive,
<http://www.fischer-tropsch.org/>

Gasification - Options for Bio-based Products

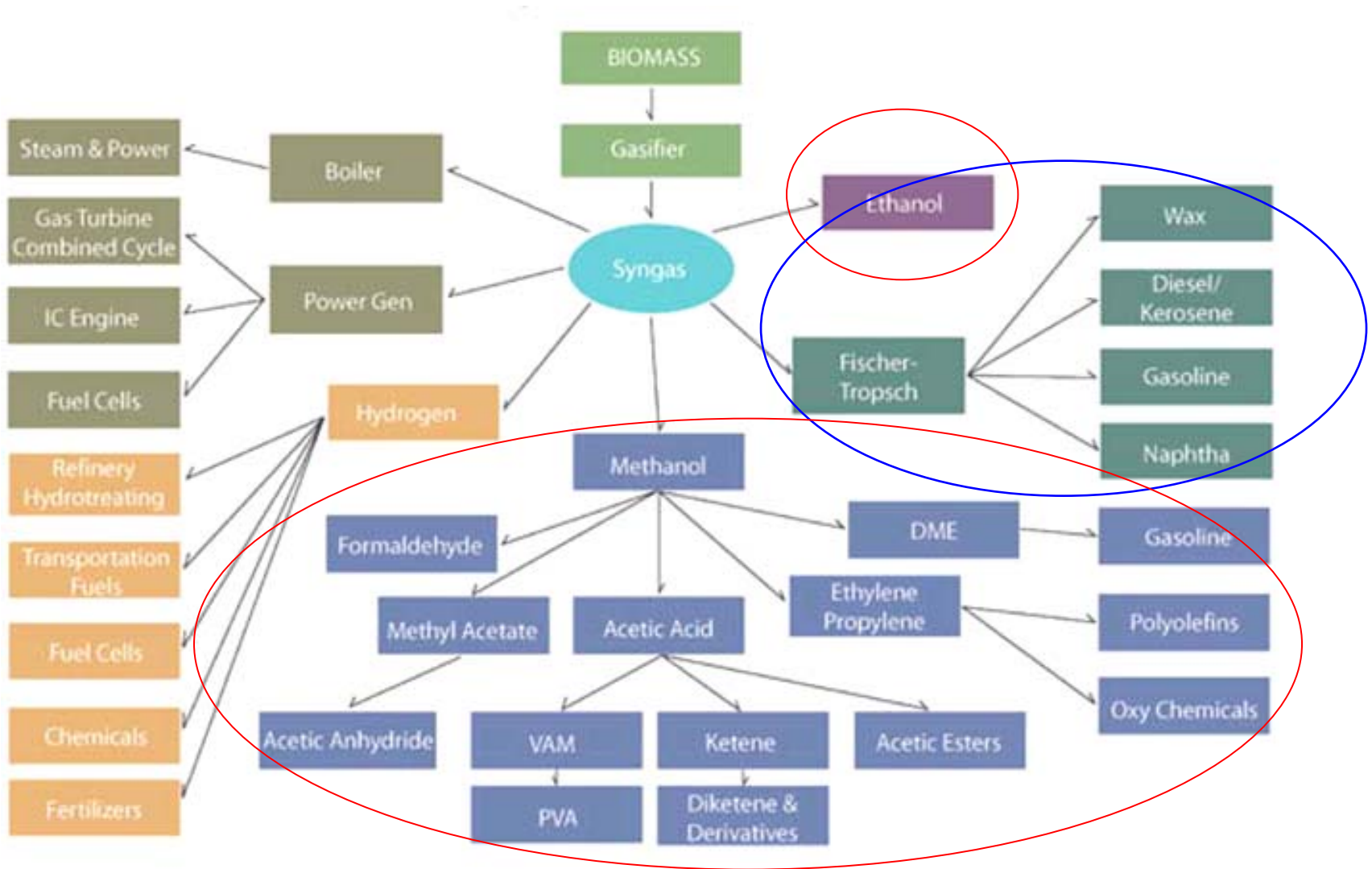


Fig. from Biomass Magazine, Syngas 101, January 2009, www.biomassmagazine.com

Fischer-Tropsch Reaction

- Basic FT: $2 \text{H}_2 + \text{CO} \xrightarrow{\text{Catalyst}} \text{-CH}_2\text{-} + \text{H}_2\text{O}$
- $\Delta H_r = -165 \text{ kJ/mol} \rightarrow$ highly exothermic
- Stoichiometric Ratio: $\text{H}_2/\text{CO} = 2/1$
- If H_2/CO lower than 2/1 then water-gas-shift (WGS) is needed
- WGS: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$
- Pressure 5 - 60 bar
- Temperature $\sim 200 - 400 \text{ }^\circ\text{C}$

Reaction steps in the catalytic reaction Fischer-Tropsch synthesis (Co and Fe catalyst):

- Adsorption of CO on the catalyst surface $\text{CO}_{(g)} \longrightarrow \begin{array}{c} \text{O} \\ || \\ \text{C} \\ | \\ \text{---} \end{array}$
- Breakage of a C-O bond $\begin{array}{c} \text{O} \quad \text{C} \\ || \quad ||| \\ \text{---} \end{array}$
- Dissociative adsorption of two H_2 molecules on the catalyst surface $2\text{H}_2 + \text{---} \longrightarrow \begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ | \quad | \quad | \quad | \\ \text{---} \end{array}$
- Bonding of two hydrogen atoms with an oxygen atom resulting in the formation of a water molecule, H_2O $\begin{array}{c} \text{O} \\ || \\ \text{---} \end{array} \xrightarrow{+\text{H}_{(ads.)}} \begin{array}{c} \text{H} \\ | \\ \text{O} \\ | \\ \text{---} \end{array} \xrightarrow{+\text{H}_{(ads.)}} \begin{array}{c} \text{H}_2 \\ | \\ \text{O} \\ | \\ \text{---} \end{array}$
- Desorption of water $\begin{array}{c} \text{H}_2 \\ | \\ \text{O} \\ | \\ \text{---} \end{array} \longrightarrow \text{H}-\text{O}-\text{H}$
- Bonding of two hydrogen atoms with a carbon atom resulting in the formation of CH_2 $\begin{array}{c} \text{C} \\ ||| \\ \text{---} \end{array} \xrightarrow{+\text{H}_{(ads.)}} \begin{array}{c} \text{H} \\ | \\ \text{C} \\ ||| \\ \text{---} \end{array} \xrightarrow{+\text{H}_{(ads.)}} \begin{array}{c} \text{H}_2 \\ | \\ \text{C} \\ || \\ \text{---} \end{array}$
- Formation of a new C-C bond $\begin{array}{c} \text{H}_2 \\ | \\ \text{C} \\ || \\ \text{---} \end{array} + \begin{array}{c} \text{R} \\ | \\ \text{CH}_2 \\ | \\ \text{---} \end{array} \longrightarrow \begin{array}{c} \text{R} \\ | \\ \text{CH}_2 \\ | \\ \text{CH}_2 \\ | \\ \text{---} \end{array}$

Products from the Fischer-Tropsch process

Carbon number:	Name:
C1-C2	SNG *
C3-C4	LPG **
C5-C10	Petroleum
<i>C5-C7</i>	<i>Light</i>
<i>C8-C10</i>	<i>Heavy</i>
C11-C20	Middledestillate
<i>C11-C12</i>	<i>Kerosine</i>
<i>C13-C20</i>	<i>Diesel</i>
C21-C30	Softwax
C31-C60	Hardwax

*SNG = Synthetic Natural Gas

**LPG= Liquefied Petroleum Gas

Preparation of the Co catalysts

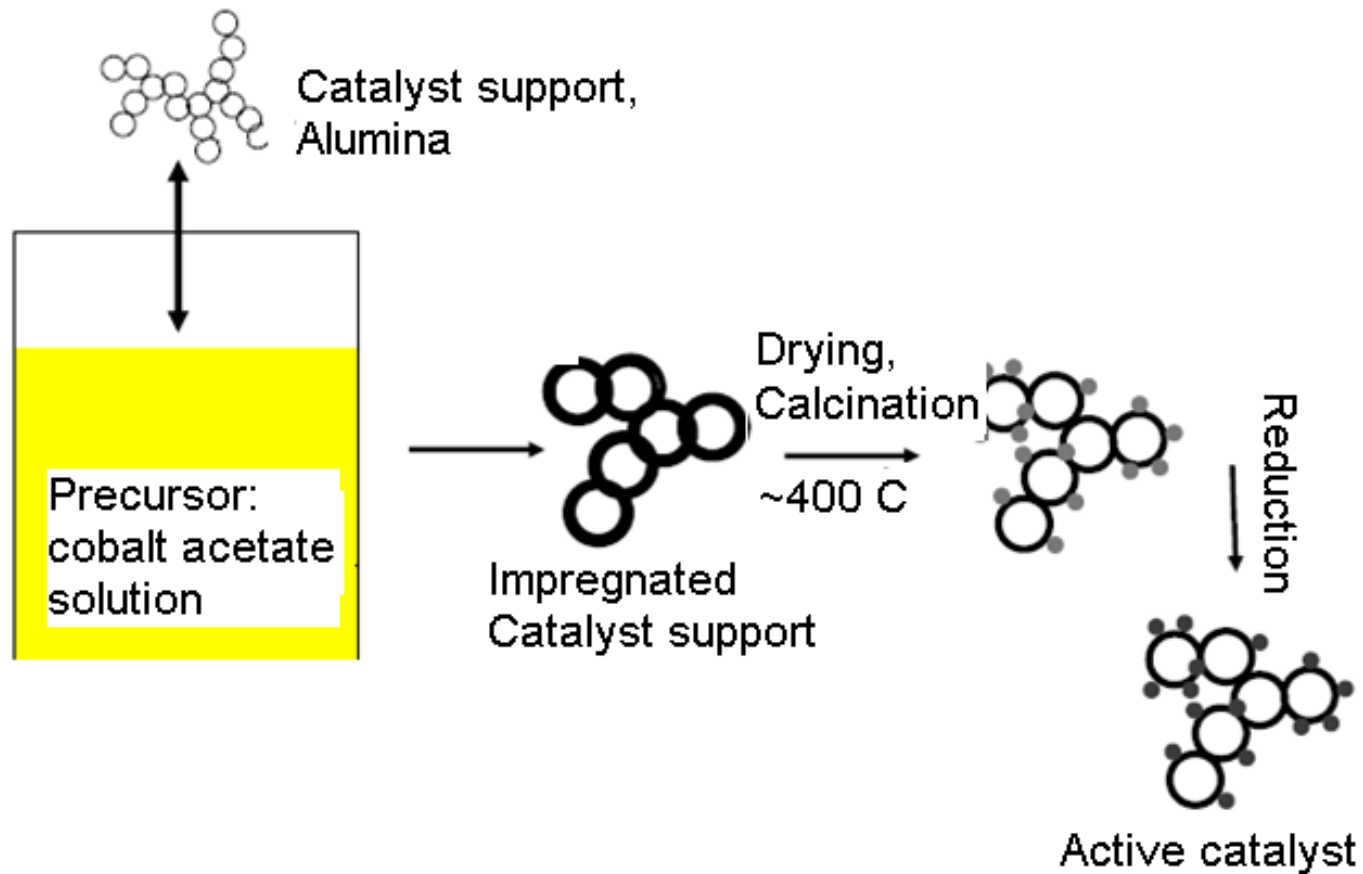


Fig. from HighBio project INFO done by Kirsi Partanen and Ulla Lassi

FT reactors

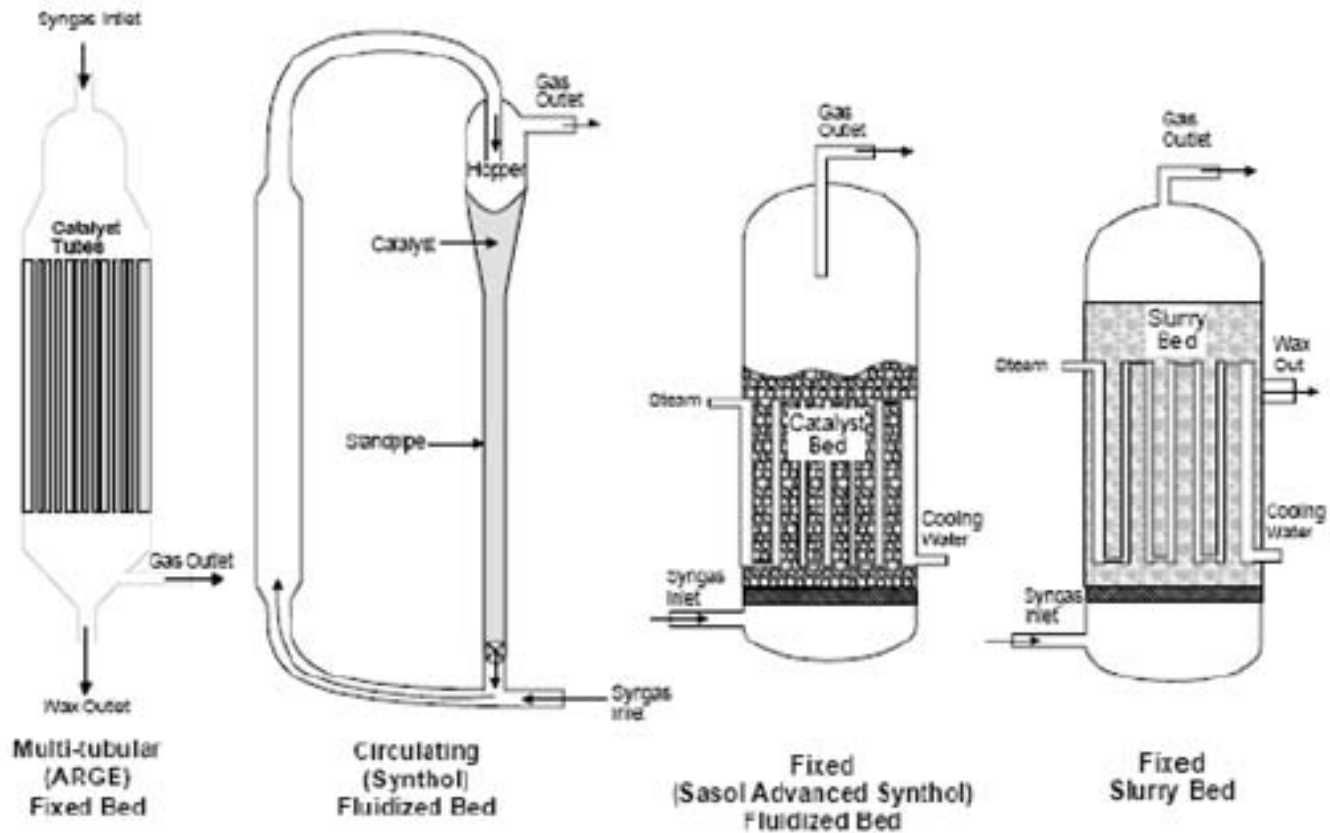
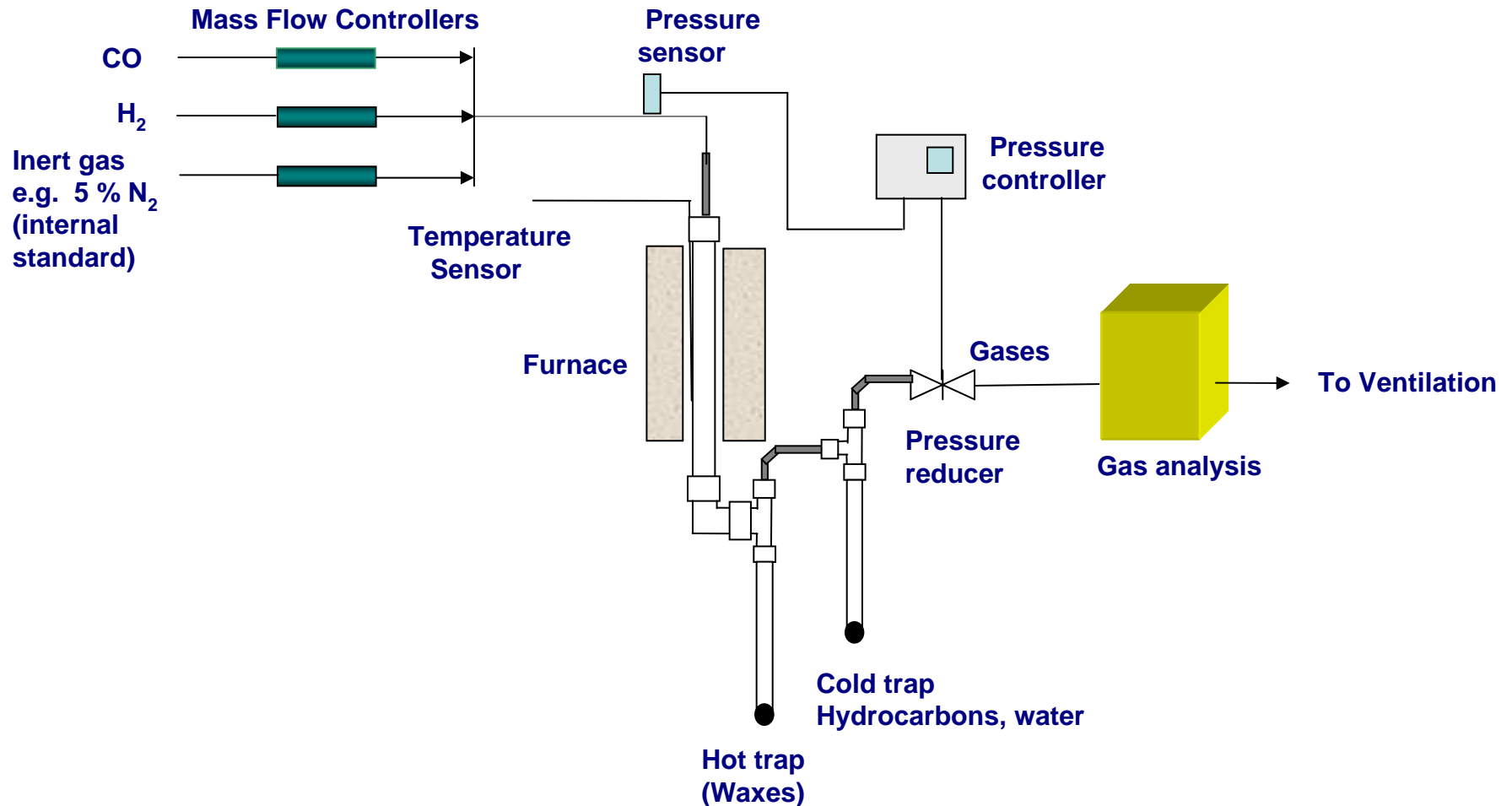


Fig. from <http://www.zero.no/transport/bio/fischer-tropsch-reactor-fed-by-syngas>

Reactor Configuration in Kokkola for the Conversion of Syngas; Testing (activity and selectivity)



Kokkola Fischer-Tropsch reactorsystem



Conclusions

- FT synthesis over Co catalysts has been preliminary tested
- Some hydrocarbons (mixture) are formed
- System will be further developed e.g. for continuous gas analysis (from inlet and outlet flows)
- M.Sc. Thesis (Riikka Lahti) will start (in August) on that topic
- Currently two B.Sc. theses under preparation;
Tong Shu: Preparation of heterogeneous Co catalysts
Leena Saukkonen: Kobolttikatalyyttien sovellukset ja epäpuhtauksien vaikutus

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THANK YOU FOR YOUR ATTENTION !



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