GTL - Gas to liquids
Biomass-to-liquids (BTL)

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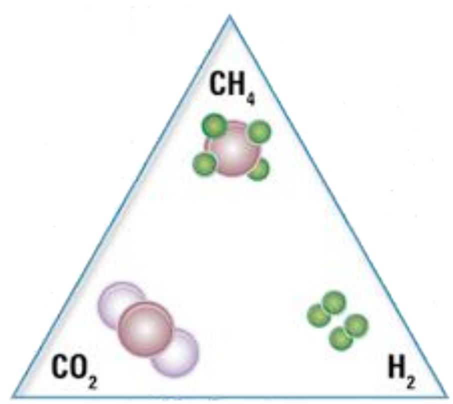

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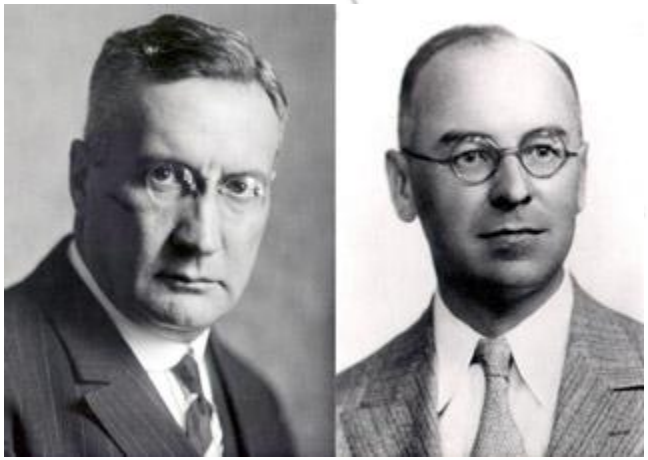
Plan

- Innledning
- Fischer-Tropsch og GTL
  - Bakgrunn
  - Eksempler fra vår forskning
- Biodrivstoff
  - BTL
  - BTL og Fischer-Tropsch
  - Eksempler
- Synergi BTL-GTL?
- ?



Fischer, Tropsch

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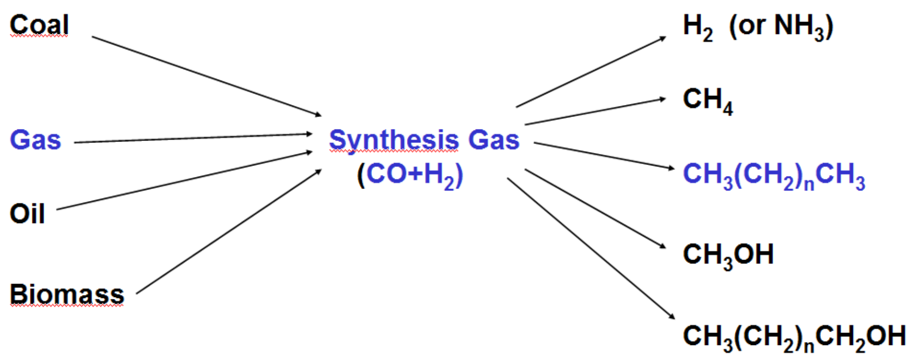
XTL

- XTL X = ?
  - GTL: Gas to Liquids
  - CTL: Coal to Liquids
  - BTL: Biomass to Liquids

Kommersiell teknologi

Under utvikling

- Kort prinsipp
  - Hydrokarboner (drivstoffer) fremstilles i en fler-trinns prosess med <u>syntesegass</u> som mellomprodukt
    - Nøkkelteknologi: Katalyse
    - Flere synteseruter mulig - Fischer-Tropsch meget aktuell prosess
  - Uavhengig av råstoffet er produktet mellomdestillater (diesel, kerosin) av meget høy kvalitet - svovelfri, uten aromater, meget gode forbrenningsegenskaper



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Eksempel på storskala GTL: Pearl

QP/Shell's "Pearl"-anlegg under bygging i Qatar. Oppstart 2011

- Qatar – Ras Laffan
- Kapasitet 140000 fat/dag
- Total investering estimert til å være > 20 milliarder US$
- Andre anlegg
  - Mossgas (Petro SA) (36000 fat/dag (1987)
  - Bintulu Malaysia (15000 fat/dag) (1992)
  - ORYX (QP/Sasol) Qatar (70000 fat/dag) (2007)

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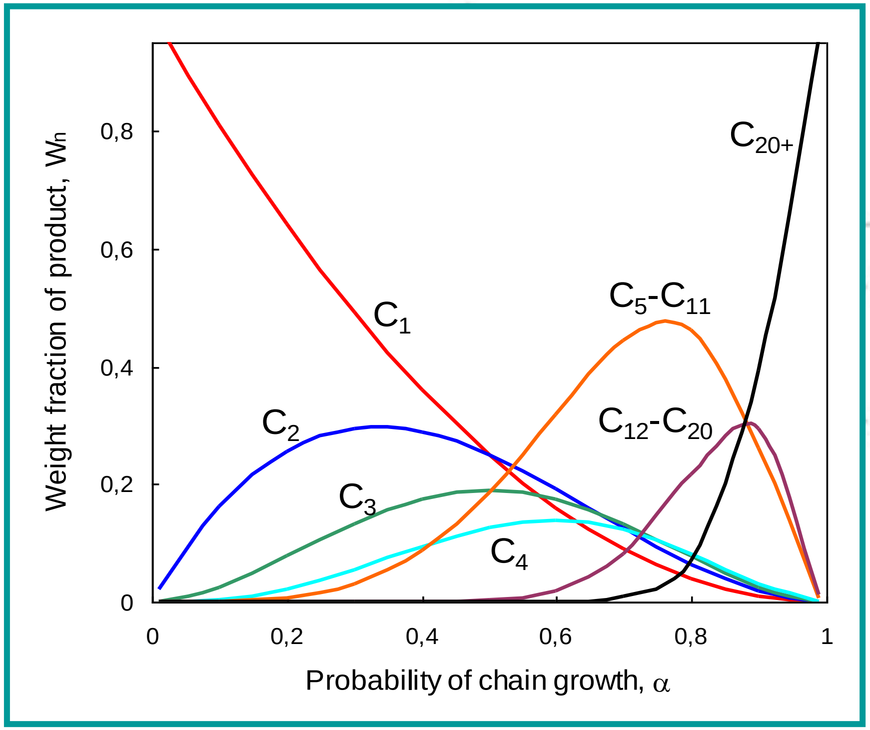
GTL via Fischer-Tropsch synthesis

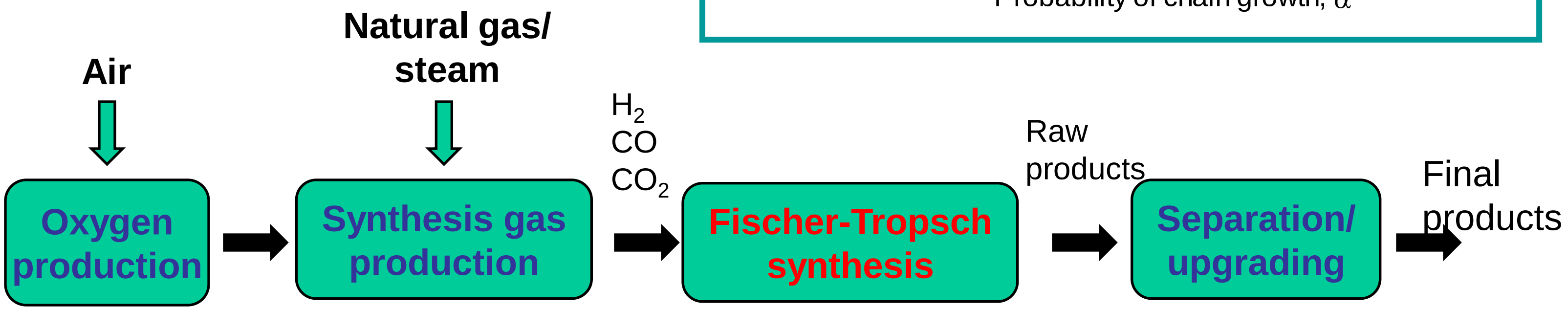
$$CO + 2H_2 \rightarrow -(CH_2)_n- + H_2O$$

Catalysts: Co, Fe, Ru

Temperature: 180-350° C

Pressure: 1-50 atm

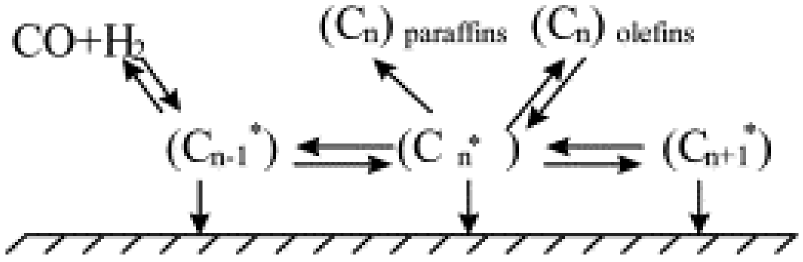




- Chain growth polymerization mechanism explains the typical product distribution
  - Stepwise addition of single carbon atom units
  - Chain length determined by a single parameter α; the probability of chain growth

$$\ln\left(\frac{S}{n}\right) = n\ln(\alpha) + \ln\left[\frac{(1-\alpha)^2}{\alpha}\right]$$

  - α varies with catalyst and conditions (T, H_2:CO ratio etc. .)



- Catalysts
  - Ru
    - Highest activity, selectivity, low WGS
    - Not available for commercial use
  - Fe
    - ”Cheap”, reasonable activity, but usually operated at ”high” T
    - Oxygen out as CO_2 (WGS close to equilibrium)
  - Co
    - High activity, good selectivity
    - Low T operation
    - Very low WGS activity – oxygen out as H_2O
  - Ni
    - Methanation only
- Modern Co catalysts
  - Supported on inorganic support
    - alumina-, silica- or titania-based
  - 220-230 ° C, 20-30 bar
  - $\alpha \geq 0.90$ (S_{C5}^{+} ~ 90%)

Fischer-Tropsch i Norge

- Statoil har utviklet egen teknologi (videreføres nå i selskapet GTL.F1 hvor Statoil er medeier)
  - Koboltbasert katalysator
  - Slurry boblekolonne reaktorteknologi
  - Demonstrert (1000 fat/dag), kommersielt tilgjengelig
- Kritiske faktorer (områder hvor NTNU/SINTEF har bidratt)
  - Katalysator
    - Kjemiske egenskaper (aktivitet, selektivitet)
    - Mekaniske egenskaper
  - Reaktor
    - Hydrodynamiske forhold
    - Separasjon/filtrering av voks/katalysatorpartikler

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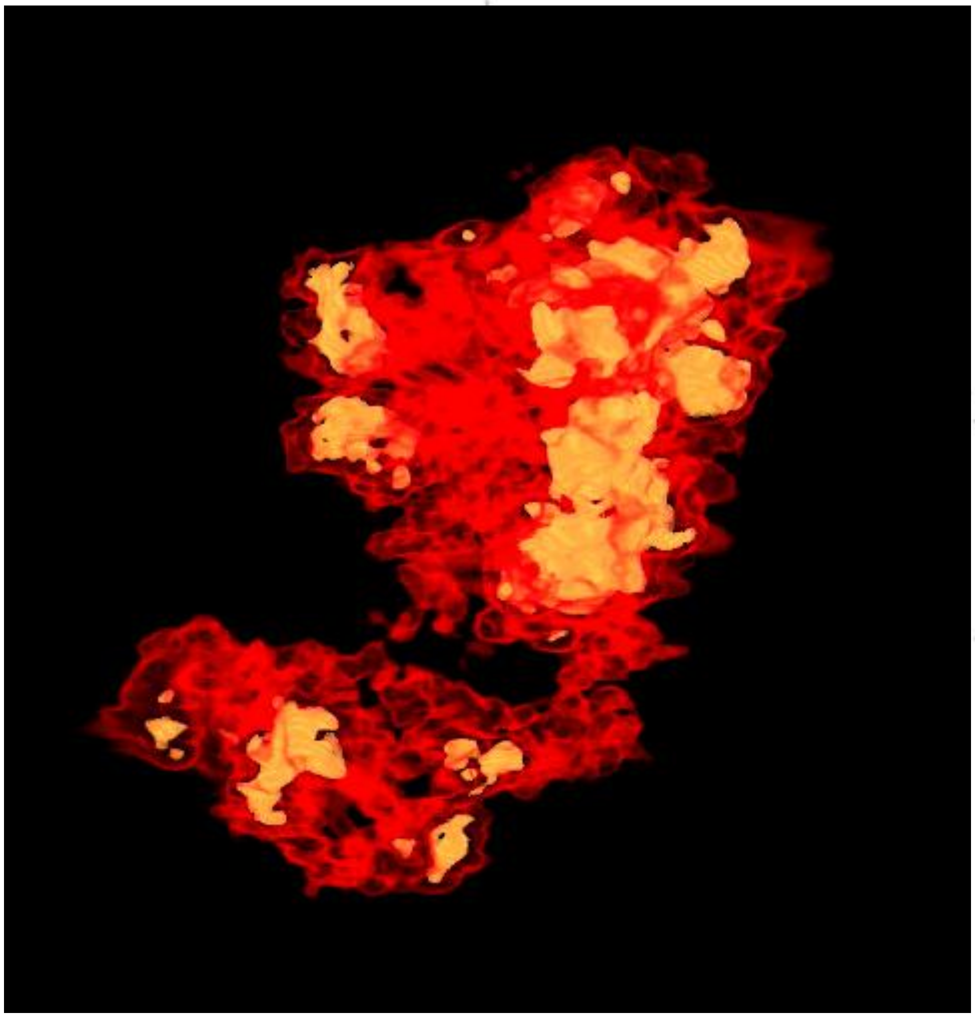
Katalysatorutvikling

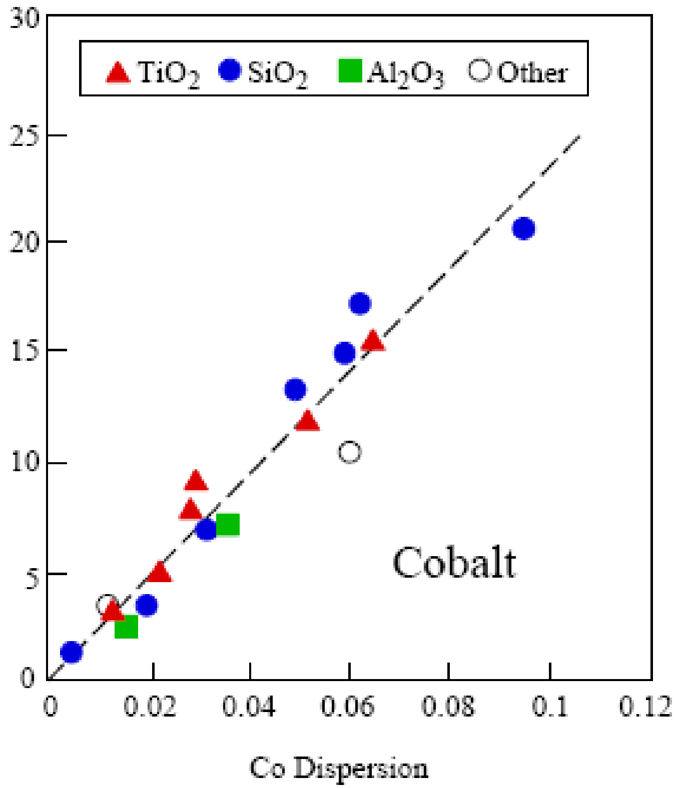
- Kobolt/bærer
  - Nanopartikler av kobolt
  - Kontrollert partikkelstørrelse
  - Kjemisk sammensetning (promotorer)
  - Interaksjon med bærer
- Nøkkelegenskaper
  - Aktivitet (tilgjengelig kobolt metalloverflate)
  - Selektivitet – kjedevekst
  - Stabilitet –deaktivering
    - Effekt av vann

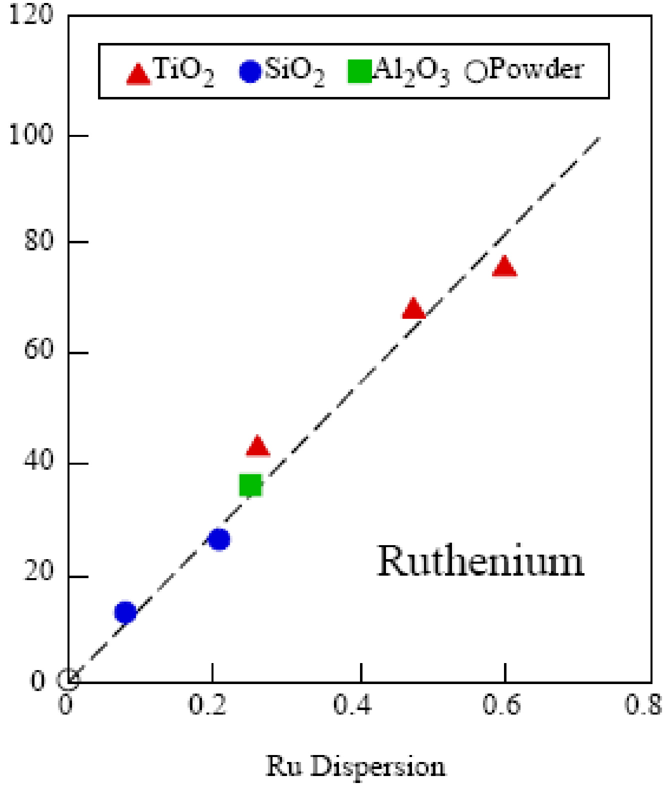


Arslan et al., JACS 130(2008) 5717.

Particle size is important

"Normal" cobalt catalyst: TOF is constant

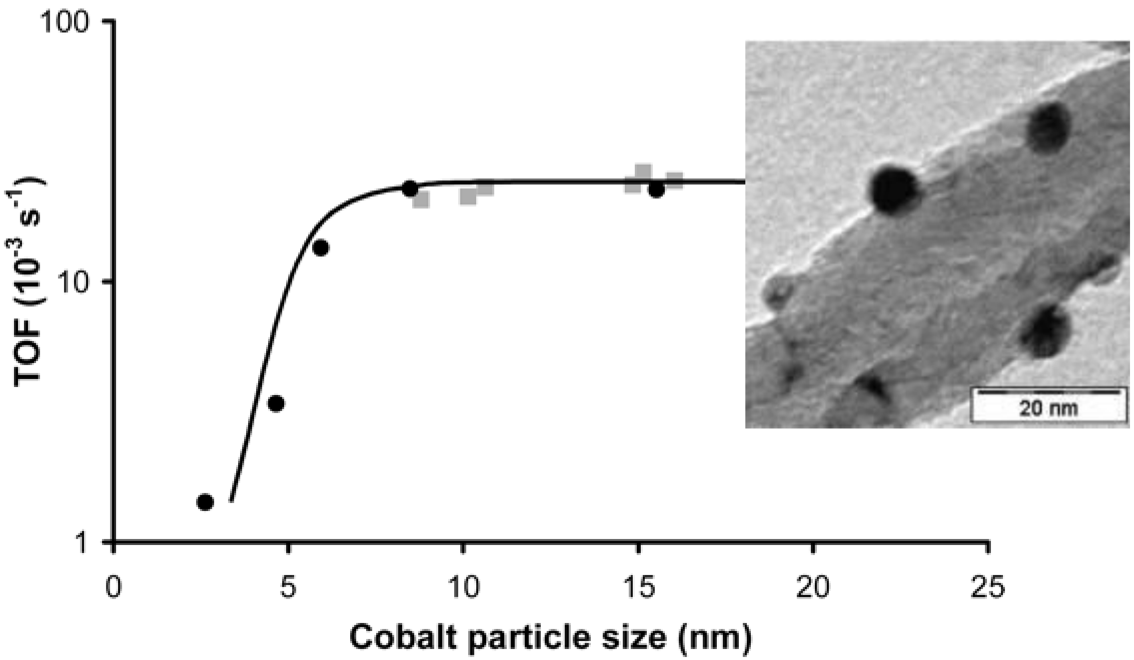




Conclusion: TOF or site-time yield is independent of dispersion.

Iglesia et al., J. Catal., 137 (1992) 212

Smaller particles behave differently

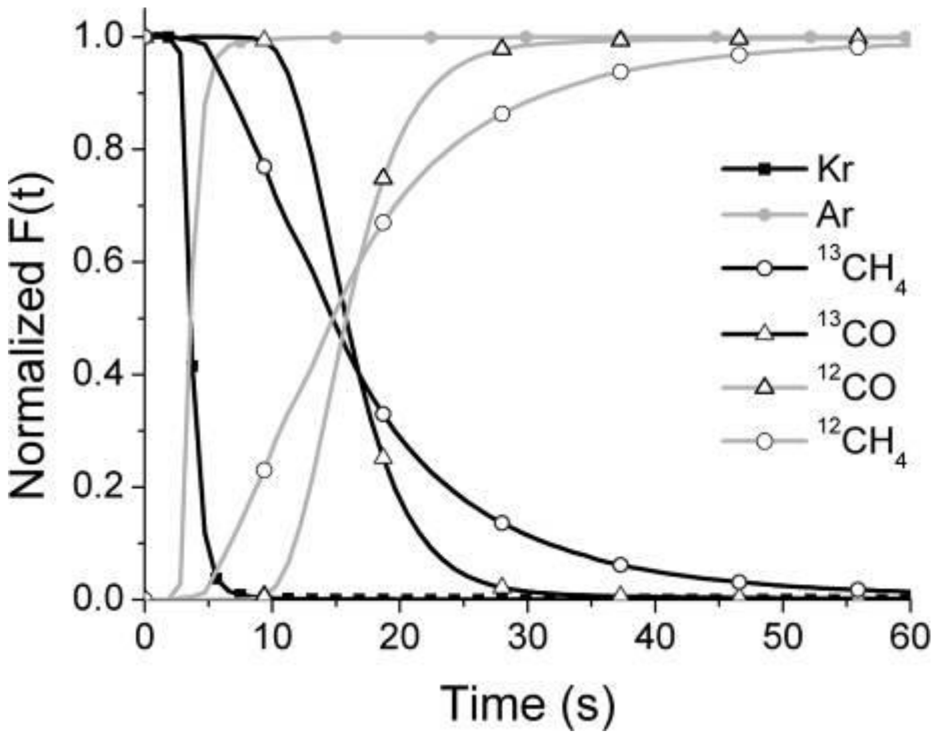


- Co/CNF
- 35 bar, H_2:CO = 2
- Grey points from Iglesia et al. (previous slide)

- De Jong and coworkers in Utrecht showed systematic change in behaviour below 6-8 nm, smaller particles give
  - Lower specific activity
  - Poorer C_{5+} selectivity, especially due to higher methane selectivity
- What is the origin of this behaviour?
  - Non-classical particle size effect

Bezemer et al. J. Am. Chem. Soc., 128 (2006), 3956.
(The idea presented at NGCS VII in Dalian 2004; Bezemer et al. Stud. Surf. Sci. Catal. 147 (2004), 259.)

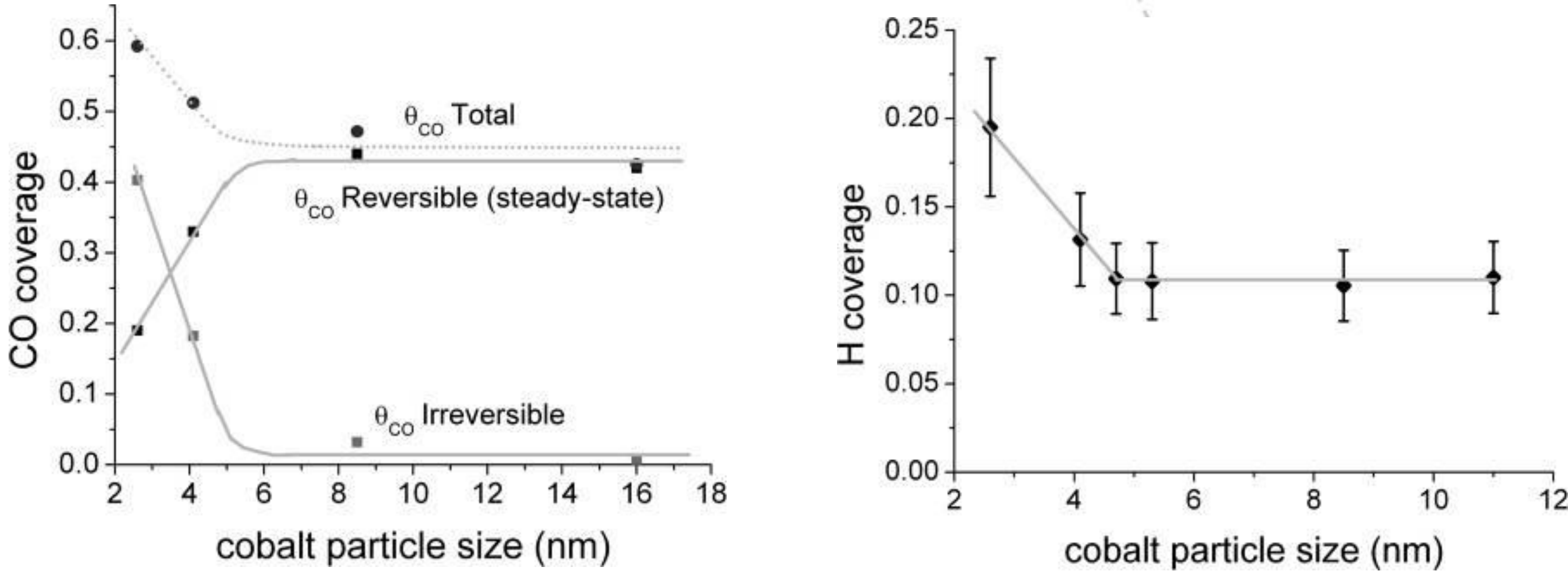
SSITKA gives a clue



- Experiment:
  - Switch between isotopically marked but chemically identical CO (e.g. $^{13}CO \rightarrow ^{12}CO$ and follow development of products by QMS)
- SSITKA allows the separate determination of the coverage of intermediates and their intrinsic reactivity (surface residence time)

den Breejen et al, JACS, 131 (2009), 7197.

Small particles have different surface coverages

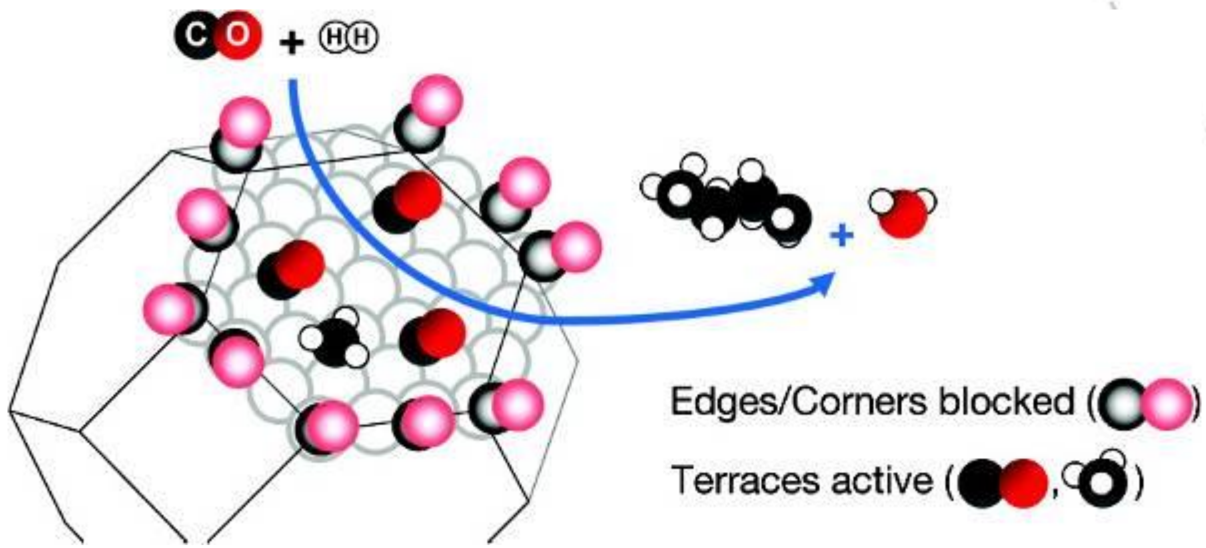


SSITKA demonstrates that small particles have

- Higher coverage of ”irreversible” CO (blocks the surface, leads to lower activity)
- Higher coverage of H (leads to more methane)

den Breejen et al., *JACS 131* (*2009*), 7197.

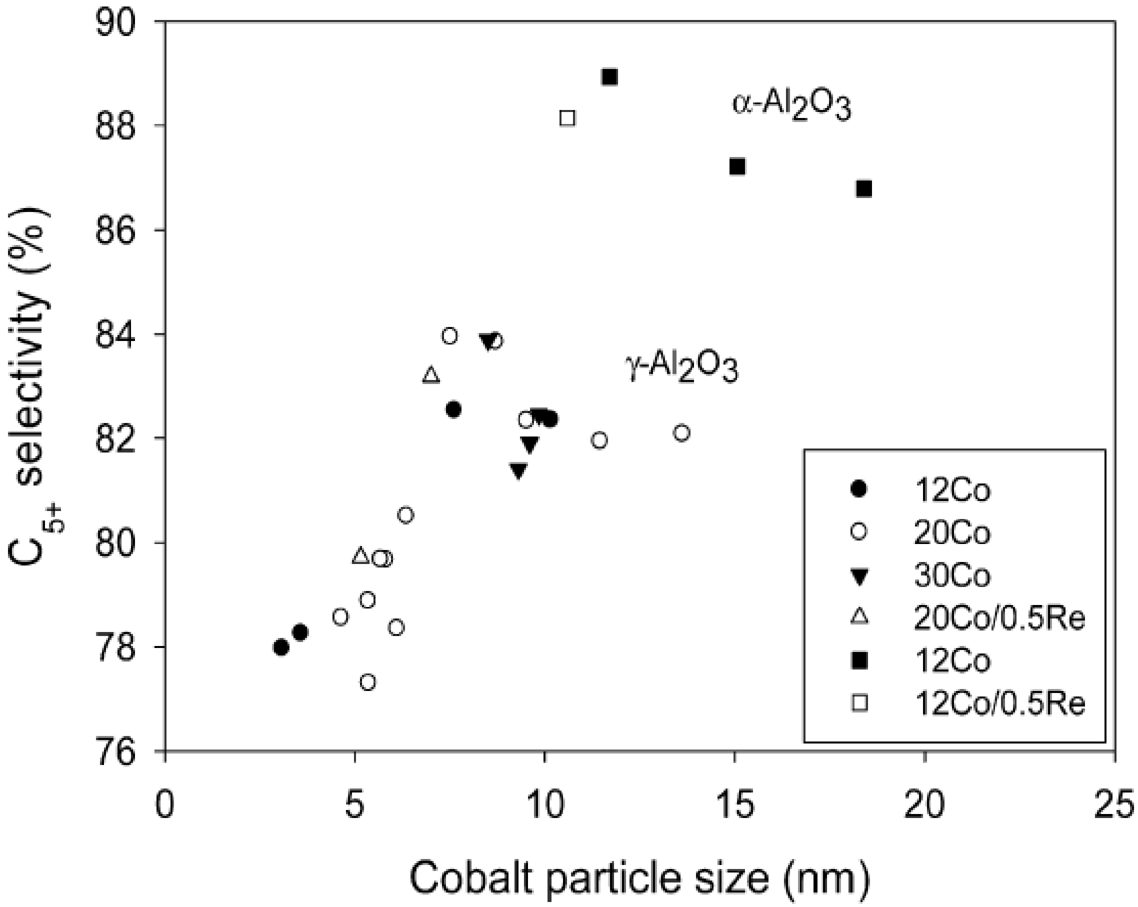
Proposed mechanism



- Cobalt modelled as cubo-octahedral particle
- Smaller particles have larger fraction CUS atoms
- Also affects terrace sites

den Breejen et al., *JACS 131* (*2009*), 7197.

Eksempel 2: Selektivitet



Ø. Borg et al., J. Catal. 259 (2008) 161.

- Selektivitet (til C_5^{+}) avhenger av kobolt partikkelstørrelse og bærer
- Optimal partikkelstørrelse: 6-8 nm
  - Gir best C_5^+ selektivitet
  - Gir optimal dispersjon uten at TOF faller

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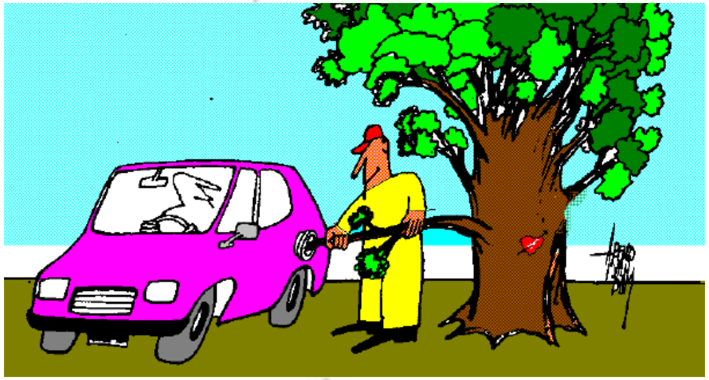
Biomasse - biodrivstoff



- Hvorfor biodrivstoff?
  - CO_2!
  - Peak oil – oljen tar slutt
  - Nasjonal/regional forsynings-sikkerhet, uavhengighet av oljeimport
  - Landbrukspolitikk!
  - I Norge: EU-direktiv, klimaforlik
- 1.generasjon biodrivstoff
  - Etanol (USA, Brasil)
  - Biodiesel (metylester av ulike oljeprodukter)
  - I Norge
    - B5 (B7) diesel – lav innblanding av biodiesel i all diesel (RME)
    - B30 (30% biodiesel) – selges på enkelte stasjoner – i hovedsak tyngre kjøretøy
    - B100 (ren biodiesel)
    - E5 bensin (5% etanol) selges som vanlig 95 oktan
    - E85 (85% etanol -15% bensin) krever tilpasset motor/drivstoffsystem

•Landbruksprodukter!
•Konkurranse med mat-produksjon
•Økende matpriser:
  •Mais
  •Oljeprodukter

Not a new idea: Wood as fuel

Illustration: Lars Stigsson: Oral presentation, Biofuels From The Forest, 20 Nov. 2008, Trondheim, Norway.

- 1 liter gasoline replaced by about 2,5 kg wood (often in the form of small pellets called "knott")
- The wood was gasified in a small chemical plant
- The driver and his helper (a lot of manual work involved in stoking and cleaning the apparatus) usually covered in soot!

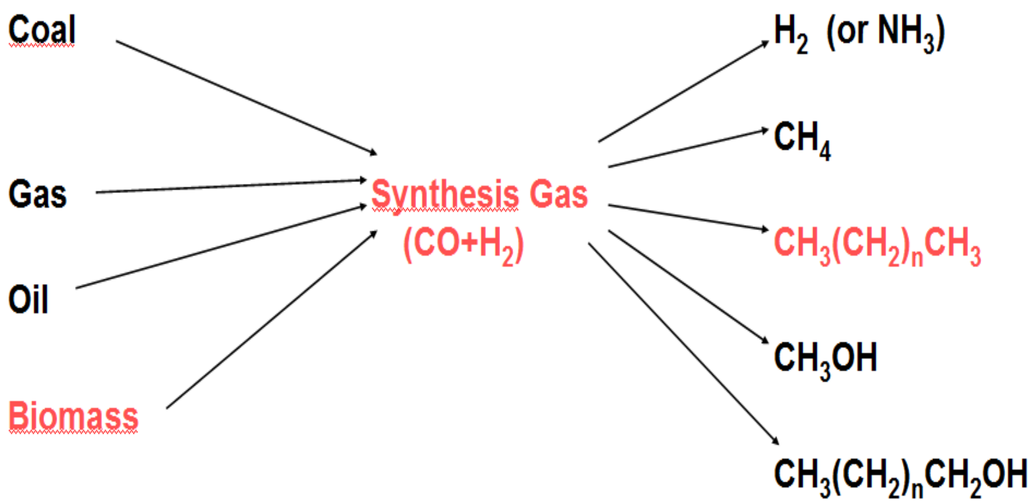
2. generasjon biodrivstoff

- Lignocellulose danner grunnlaget for 2.generasjons biofuel (2G)
- 2 hovedveier
  - Termokjemi
    - Pyrolyse eller gassifisering fulgt av oppgradering eller syntese
  - Biokjemi
    - Etanol
    - Biobutanol
- 3. generasjon: Alger
  - Langt frem! Lite realistisk innen overskuelig fremtid

Fischer-Tropsch-basert BTL

Krevende prosess:

- Logistikk
  - Biomasse er spredt over store områder
  - Kostbar innhøsting og transport, lav energitetthet
  - Storskala umulig?
- Vanskeligere råstoff
  - Inneholder mange elementer som forgifter katalysatorer
  - Rensing av gass
    - S, alkali,



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Step 1: Gasification of biomass

- Reaction between solid and steam and/or oxygen/air to produce synthesis gas (syngas)
- Synthesis gas
  - Mixture of CO, H_2, CO_2, CH_4, and N_2
  - Used in production of methanol, hydrogen, Fischer-Tropsch liquids
  - Currently produced industrially from coal or natural gas (or heavy oil)
- Reactions
  - Pyrolysis: thermal decomposition in inert atmosphere
  - Partial oxidation: combustion in oxygen-lean atmosphere
  - Steam reforming: react with steam to produce CO, CO_2, and H_2
  - Water gas shift and methanation
- Complex chemistry (complex feed!)
  - Reactions in gas, liquid and solid phases
  - Heat to drive the process usually generated in situ
- Syngas cleanup issues, gasifier raw gas contains
  - Particulates
  - Tar and hydrocarbons
  - Sulfur
  - Chlorine (HCl)
  - Metals (Na, K, ..)
  - Other inorganics

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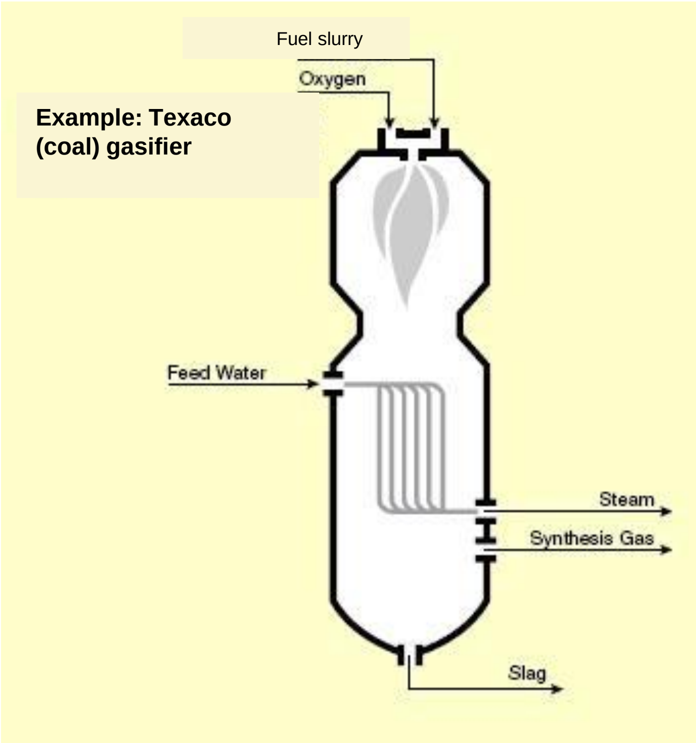
Entrained flow gasifier



- Entrained (Norw. ”medrevet”) flow of fuel particles with oxygen (and in some cases steam)
- High T, above slagging temperature
- No tar in product gas
- Typical gas composition:
  - H_2: CO = 1 -1.5
  - Traces of sulfur, alkali
  - Gas cleanup needed

Probably the best technology for large BTL plants

Step 2: Fischer-Tropsch synthesis

- $CO + 2H_2 \rightarrow -(CH_2)_n- + H_2O$
  - Ideal ratio: H_2: CO ≈ 2
  - Adjustment: Shift reaction
- Improved catalysts and reactors needed
  - Not optimal H_2:CO ratio
    - Separate or intrinsic WGS ?
  - Tolerance to pollutants (alkali, sulfur, others?)
    - Gas cleanup essential
  - Scale of operation
    - FTS benefits from economy of scale
    - BTL size limited by available feedstock
    - Can different reactor technology change the game?

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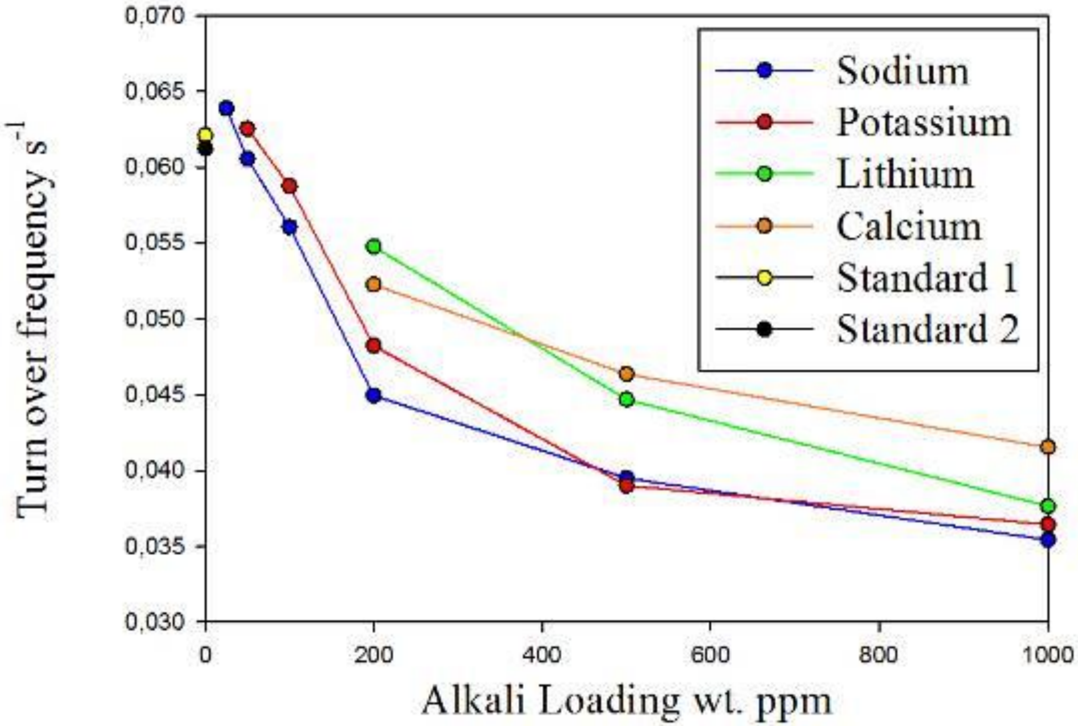
Example 1: Effect of alkali on FTS catalyst



- Alkali and alkaline earth pollution has detrimental effect on catalyst activity (here reported as turnover frequency)
  - Cause: Probably due to electronic effect on active cobalt sites (no change in available cobalt surface area was observed)

(Ongoing work by A.H. Lillebøe at NTNU.)

Example 2: Microstructured reactors

- Microstructured reactors:
  - Large number of small, parallel channels
    - enhanced mass transfer properties
    - intensified heat transfer
    - could make FTS economical at a smaller scale?
  - Compact and modular
    - Suggested for offshore use, biogas conversion etc.
- Suitable for FTS?
  - Catalyst introduction
    - Wall coating
    - Packed bed
    - Structured systems
  - Pressure drop and stability issues?
- Ongoing research topic at NTNU/SINTEF

Example: Oxford Catalysts (Velocys) unit

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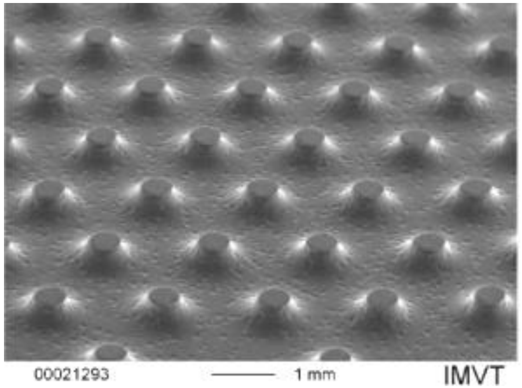
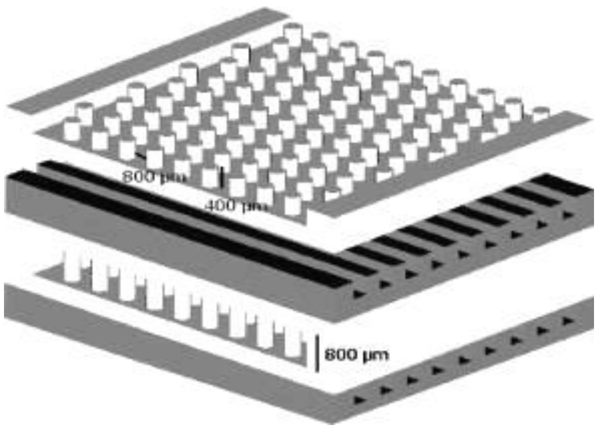
Micro-channelled reactor (SINTEF Trondheim)



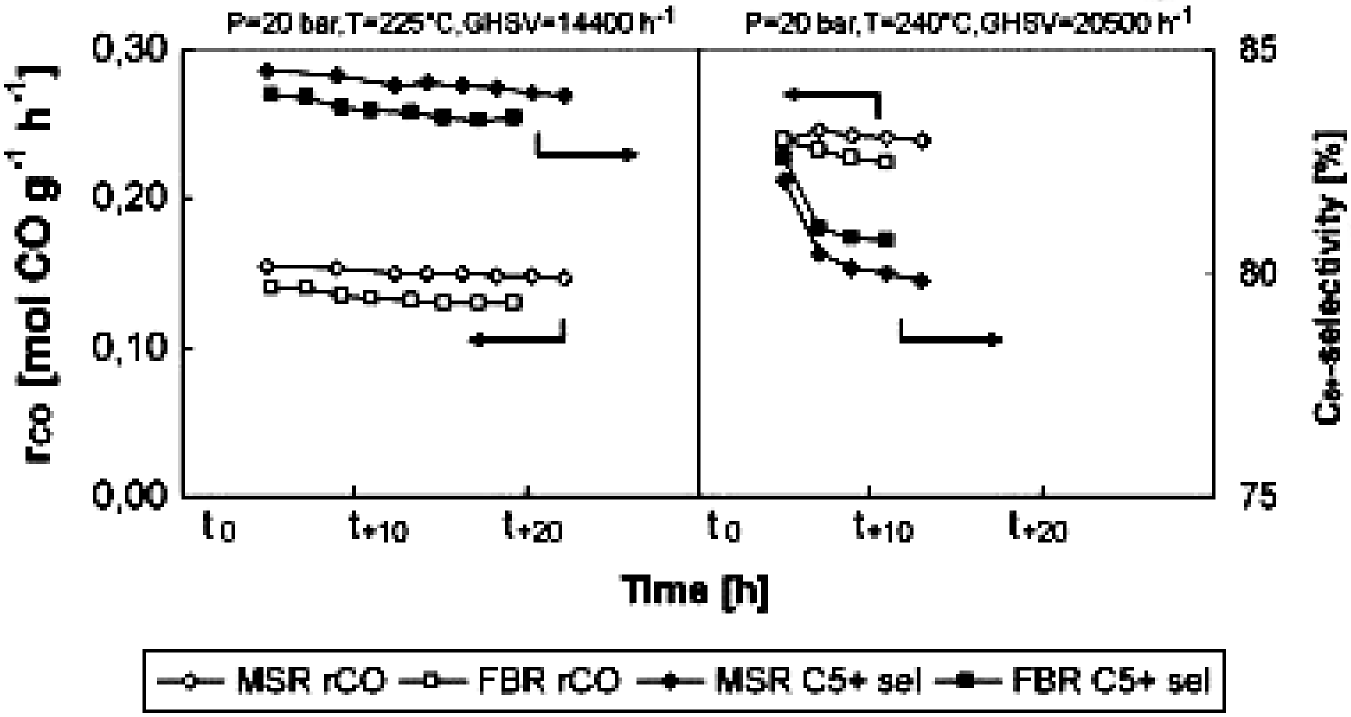


Steel microstructured reactor (FZK, Karlsruhe)

- 8 sections with 800 μm channel height
- Channels formed by stacking of foils etched with a pillar structure
- Cross-flow oil-channels between catalyst layers (cooling)
- Unit (2 cm^3) placed in tube fitting
- Filled with catalyst (high loading Co/Al_2O_3, particle size 53-75 μm
- Compared with same catalyst in FBR (diluted 1:20 with SiC to ensure uniform temperature, Δ <1 K

R. Myrstad et al. Catalysis Today 147S (2009) S301.

Microchannelled system compared to FBR



- The catalyst activity and selectivity is comparable in the two systems
- T measurements indicates some axial gradient, probably due to the effect of heat loss to surroundings (modelling indicates isothermal operation)'
- No increased deactivation even at 240 ºC confirms isothermal operation

Myrstad et al. Catalysis Today 147S (2009) S301.

Comparison Biomass – Natural Gas

- Biomass
  - – Low H : C ratio
  - – Limited energy density
  - – Limited availability
  - – Requires complex chemical plants of small to moderate size
    - Very high investment cost per produced unit
    - Poor thermal efficiency
    - At present at the development stage
  - \+ CO_2 neutral

- Natural gas
  - \- Fossil fuel
    - \- CO_2 issues!
  - \- Low C : H ratio
    - \- Syngas composition depends on choice of technology
  - \+ Available in large quantitites on several sites
  - \+ GTL (via Fischer-Tropsch) is established technology
    - \+ Products with excellent properties

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Possible synergies from a combined plant

- Chemical composition
  - Combining a hydrogen rich feedstock (natural gas) with a hydrogen-poor feedstock (biomass) seems obvious
    - But: This introduces a range of new design and operational issues
- Politics
  - Introducing biomass would balance some of the CO_2 issues
    - If CCS is employed the plant could even be an overall CO_2 sink
- Scale
  - A combined plant would have the necessary size to benefit from economy of scale
    - But: The plant would be more complex, would have all the drawbacks of biomass operation (impurities)
- Good idea?

Sammendrag

- ”XTL” med syntesegass som mellomprodukt kan produsere drivstoff med utmerket kvalitet fra alle C-holdige råvarer
- ”GTL” er etablert teknologi
  - Flere anlegg og tilbyderer av kommersielle prosesser
  - Deriblant norskutviklet prosess demonstrert av Statoil
- ”BTL” kan gi etisk forsvarlig produksjon av biodrivstoff (ingen konkurranse med matproduksjon)
  - Biomasse introduserer en rekke utfordringer
  - Omfattende utviklingsarbeid gjenstår
  - Kombinasjon med naturgass KAN gi synergier (i hvert fall sett fra skrivebordet)

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