A FT-GTL technology for small-scale applications

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Material and Process Synthesis (MaPS) A Research Unit @ UNISA
MaPS Engineering is a newly formed research unit based at the Science campus in Florida, with the vision of utilizing the resources in universities to serve industry, especially in the field of alternative energy.

MaPS has 20 permanent staff, among them over 10 holding a PhD’s in Engineering or Science, and has over 20 postgraduate students.

Team members were all from the group winning the NST-BHP Billiton award for research for innovations through an NGO, NP, or CBO 2009-2010.
XTL services provided

• XTL process design and optimization
  • Biomass-to-Liquids (BTL)
  • Coal-to-Liquids (CTL)
  • Gas-to-Liquids (GTL)
  • Waste-to-Liquids (WTL)

• Evaluation of the available XTL technologies

• XTL projects engineering
  • Opportunity Analysis and Business Proposals
  • Feasibility Study
  • Front End Engineering Design
  • Commissioning of the Fischer-Tropsch section
Conventional Fischer Tropsch Process

- Modern Fischer Tropsch process has been used only in MEGA plants
  - Secunda CTL: 160,000 bpd
  - PetroSA GTL: 36,000 bpd
  - Oryx GTL: 34,000 bpd
  - Pearl GTL: 140,000 bpd
  - Ningdong CTL: 90,000 bpd (under construction)
Mega Plants

• Mega plants perform at high efficiency within the
  – Flow sheet
  – Equipment used
  – Product they are designed to produce
• Rely on economy of scale to improve profitability
Is it too big?

- Huge investment involved
  - Sasol Two: R 2.5 B (8% of GDP of SA in 1976)
  - Sasol Three: R 3.3 B (7% of GDP of SA in 1979)
  - Pearl GTL: USD 18–19 B (11% of GDP of Qatar in 2010)
  - Long time for financing
  - Lots of politics involved
  - Long time to bring into market

- Flow sheet chosen normally conservative
  - To minimize the risk
  - Difficult to implement the latest research development

- Large amount of carbon resources needed
  - Billion tons of reserves needed to secure a long time life time
  - Large amount of CO$_2$ emitted from a single plant in the case of CTL
Is there a reason to think small-scale?

Massive Reserves
Potential global natural gas deposits, in trillions of cubic meters
Source: German Federal Institute for Geosciences and Natural Resources (BGR), 2009

- **Conventional**
  - Natural gas production without fracking
- **Unconventional**
  - Occurrences in dense rocks (tight gas and shale gas), coalbed methane and natural gas from aquifers and gas hydrates
  - Including natural gas from porous rocks

By comparison: global natural gas consumption in 2010 3.2 trillion m³
Why think small-scale?

World's largest natural gas reserves

15 countries hold 87% of the world's proved reserves. 2012 natural gas consumption worldwide was 114 tcf.
There are some reasons to think small

• There are many carbon resources that are not as big
  – Small carbon reserves
  – Coal bed methane
  – Coke oven gas
  – Underground coal gasification
  – Landfill gas
  – Flare gas
  – Soluble methane
  – Biomass
  – Municipal solid waste
  – etc.

• Smaller investors want to be involved

• Shortage of engineers and skilled-labor, especially in many developing countries

• Short project startup time gives a faster response to market

• Lower financial risk as investment is smaller

• To implement latest development from research
Modular Approach?

• A new approach is to build smaller modular plants.
• These have the advantages of being
  – less capital intensive
  – more flexible and
  – having a faster time-to-market
• Start giving returns on expenditure much sooner
• Later modules can incorporate newer ideas
• Good for managing risk
• Get higher efficiency by being able to incorporate new ideas
• Need a new flow sheet to make it work
Development of Conventional GTL Process: Reactions

• **Reforming:**
  – Methane / Natural Gas feed to produce Synthesis Gas (“Syngas”):
    • $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3 \text{H}_2$
    • $\text{CH}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{CO} + 2 \text{H}_2$
    • $\text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O}$

• **Fischer Tropsch:**
  – Syngas converted to hydrocarbons and water:
    • $\text{CO} + 2 \text{H}_2 \rightarrow -\text{CH}_2 - + \text{H}_2\text{O}$
Development of Conventional GTL Process: Produce the Right Syngas

- **Pure O₂ is required**
  - Need an Oxygen Plant

- **H₂/CO is wrong**
  - Corrected by water gas shift reaction
  - \[ CO + H₂O \rightarrow CO₂ + H₂ \]

- **High moisture content in syngas**
  - Water is to be knocked out

- **Feed stock is always dirty**
  - Syngas is also dirty, clean up is needed to protect downstream catalyst and for easy operation
Development of Conventional GTL Process: Produce the Right Products

- The Fischer Tropsch reaction unable achieve 100% conversion and produces a wide range of hydrocarbons from C$_1$ to C$_{\text{many}}$
  - Normally Only C$_{5+}$ are needed for fuel
    - Naphtha, Kerosene, Diesel, Fuel oil, Wax
  - Light hydrocarbons are useful chemicals
    - Ethylene, Propene, Butene, etc.
  - Unreacted syngas and light hydrocarbons can be recycled through reforming process
    - CO$_2$ need to be knocked out during gas conditioning

- Need for Separation and Product Workup
Development of Conventional GTL Process: Consider the Start-up and Activation

- **Inert gas needed for start-up**
  - Normally N$_2$ is used, which is also produced from the oxygen plant

- **Hydrogen needed for catalyst reduction/activation, and product workup**
  - H$_2$ can be produced from syngas via water gas shift reaction

![Diagram of the conventional GTL process](image)
Development of Conventional GTL Process: And Utilities

**STEAM SYSTEM**

- Natural Gas
- Air
- Oxygen plant
  - Oxygen
- Steam
- Reforming
- Raw Syngas
- Gas Conditioning
  - Clean Syngas
  - Waste water, CO₂
- Fischer Tropsch
  - HCs, Water
- Separation
  - Hydrocarbons
- Workup
  - Fuel & chemicals

**COOLING WATER SYSTEM**

- Waste water, CO₂
- Reaction Water
- Hydrogen plant
  - H₂
- Unreacted syngas, Light hydrocarbons
- Clean Syngas
Development of Conventional GTL Process: A Real Case
Small-scale approach: Can we simplify it?

- **Do we need a recycle?**
  - By pushing conversion & heavy hydrocarbon selectivity higher, recycle can be removed
  - Unconverted syngas and light hydrocarbons can be used to provide energy (heat or electricity)
As there is no recycle, we don’t have to use pure oxygen for reforming
  – Air plant can be smaller or be removed
We can tolerate more CO\(_2\) in the FT section
  – Removing CO\(_2\) in gas conditioning is not a must
Is producing syncrude sufficient?

- Produce syncrude and sell to refineries
Small-scale approach: Can we simplify it?

- **Is Hydrogen a must?**
  - By developing new catalyst, catalyst can be reduced by syngas, thus no need for Hydrogen
Small-scale approach: Can we simplify it?

- **Is Air Separation necessary?**
  - By developing new catalyst, it can be dried by syngas
  - Reactor can be flushed with clean natural gas in shutdowns
Now we have a simplified process

- More Robust, modular, once-through
- Less Capital intensive
- Request for catalyst:
  - Active at low syngas partial pressure
  - High heavy hydrocarbon selectivity
  - Tolerant to CO₂
  - Reduction using syngas
  - Easy to regenerate

**Diagram:**
- **Natural Gas** → **Gas Clean-up** → **Reforming** → **Gas Conditioning** → **Fischer Tropsch** → **Separation** → **Produce Energy**
- Air separation
- N₂
- Enriched O₂

**Processes:**
- Syncrude
- Unreacted syngas, Light hydrocarbons
- HCs, Water
- Reaction Water
- Waste water

**Reforming Fischer Tropsch**
- Raw Syngas → Clean Syngas
- HCs, Water
500bpd GTL: Feasibility Study

• Request from client:
  – Conduct a Feasibility Study of a 500bpd GTL demo unit
  – Location: USA
  – Feed: pipeline gas
  – Required products: Syncrude & Wax
  – MaPS responsibility: FT Section (using modular approach)
  – Rest of plant to be done by client-chosen vendors
500bpd GTL: Feasibility Study

• Feasibility Study included:
  – Concept design
    • Operating conditions (T, P, syngas ratio, etc.)
    • Catalyst selection (Fe vs Co)
    • Environmental considerations
  – Equipment listing and sizing
  – Cost estimates and quotes
  – Syncrude and Wax Product offtake
Flow Sheet

- Flow sheet of entire plant:
  - Choose ATR conditions
  - Enriched O₂ VS Air
  - Minimize utilities required
  - No heat/electricity needed (by client): thus flare tail-gas
Economics

- CAPEX comparison with a recent large-scale (96,000bpd) GTL case for USA (feasibility study, 2012)
Problems encountered

• Products – what to do with them?
  – Refineries?
  – Other end users?
• Process Engineering aspect has progressed for small-scale modular plants. Other engineering disciplines need to also. This is vital to the economics
• The large-scale design and manufacturing approach can not be applied
Biomass to Liquid Pilot Plant

- Funded by SA NRF and China MoST
  - Capacity: up to 1 L syncrude production a day
  - Collaboration with Hebei Academy of Agricultural and Forestry Sciences
    - In Shijiazhuang, Hebei, China
- Full demonstration of biomass to syncrude process
  - Air blow biomass gasification
  - Syngas conditioning
  - Fischer Tropsch Synthesis
- Successful commissioned in 2012
Gasification

Down draft air blow ambient pressure biomass gasification unit
Load: 50 kg of compressed wood
Capacity: 10 Nm³/hr
### Typical gasification results (v%)

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<th>( \text{CH}_4 )</th>
<th>( \text{CO} )</th>
<th>( \text{H}_2 )</th>
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Guard Bed

- Remove $\text{H}_2\text{S}$
- Hydrolysis
- Remove $\text{H}_2\text{S}$
- Remove $\text{O}_2$
- Drier

- Total S level is lowered
  - From $\sim 10$ ppmv to $< 10$ ppbv
- $\text{O}_2 < 0.1$ v%
- Over 2000+ hrs operation experience achieved
  - No deactivation observed
Fischer Tropsch Synthesis

• Single tube fixed bed reactor
  – i.d. 50 mm
  – Length 900 mm
  – Max catalyst bed 600 mm
    • 1.2 L

• Heated by
  – heating oil (< 260 C)
  – Nitrogen (250 – 400 C)

• Reaction pressure up to 4 MPa

• Two steps products separation
  – Step one: 150-190 C
  – Step two: 4 C
Liquid products
Simulation results based on pilot data

- At the right operation condition, 1 barrel of syncrude (including wax) can be produced using 1 ton of biomass (LHV ~ 20 MJ/kg), without energy input from outside.
- More fuel can be produced if electricity is provided from grid
Current and future work

• Container scale waste to liquid demonstration plant in design phase
  – 1 barrel syncrude production a day from municipal solid waste
  – Collaboration with Nuclear Energy Cooperation South Africa (NECSA)
  – To be constructed later 2014
  – Targeting
    • Fully independent plant, or
    • Maximum fuel production

• Further simplify the process by looking at the utility requirement
Thank you