

Gas-to-liquids conversion

Arno de Klerk

Department of Chemical and Materials Engineering
University of Alberta, Edmonton, Canada



Introduction

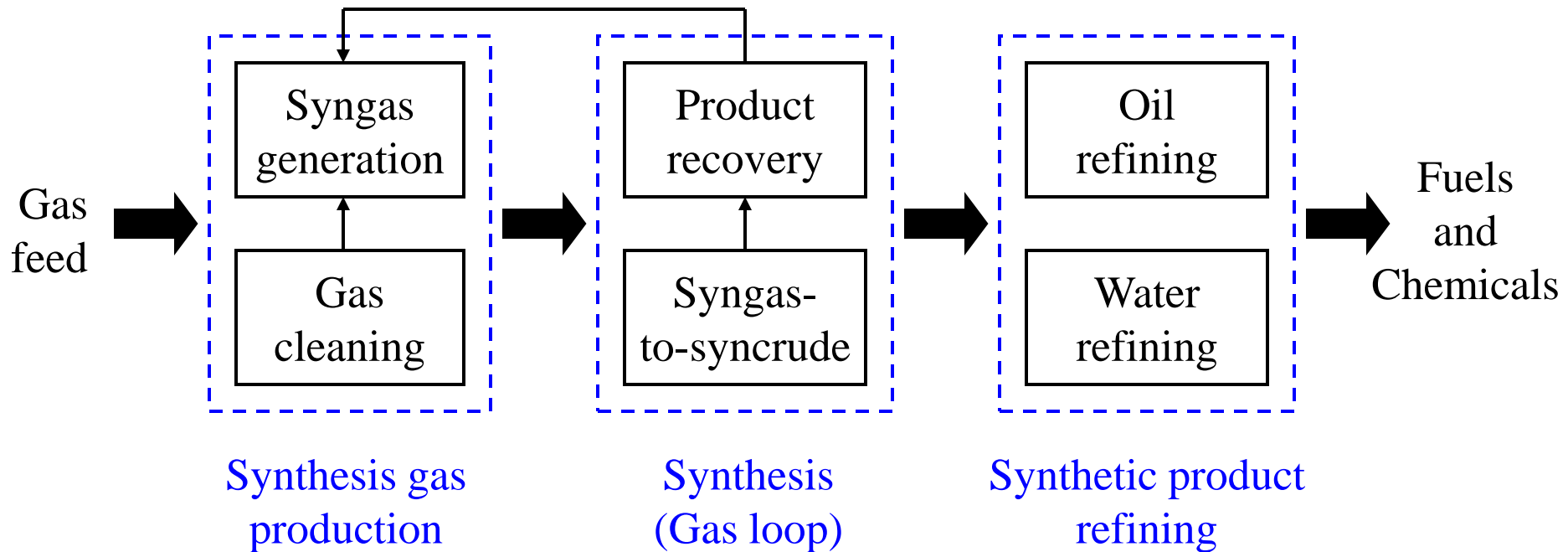


Introduction



Gas-to-liquids overview

Natural gas can be converted into normally liquid products by indirect liquefaction. There are three distinct process steps involved:





Introduction



Industrial gas-to-liquids processes

Industrial GTL facilities are normally classified in terms of the syngas conversion technology that is employed:

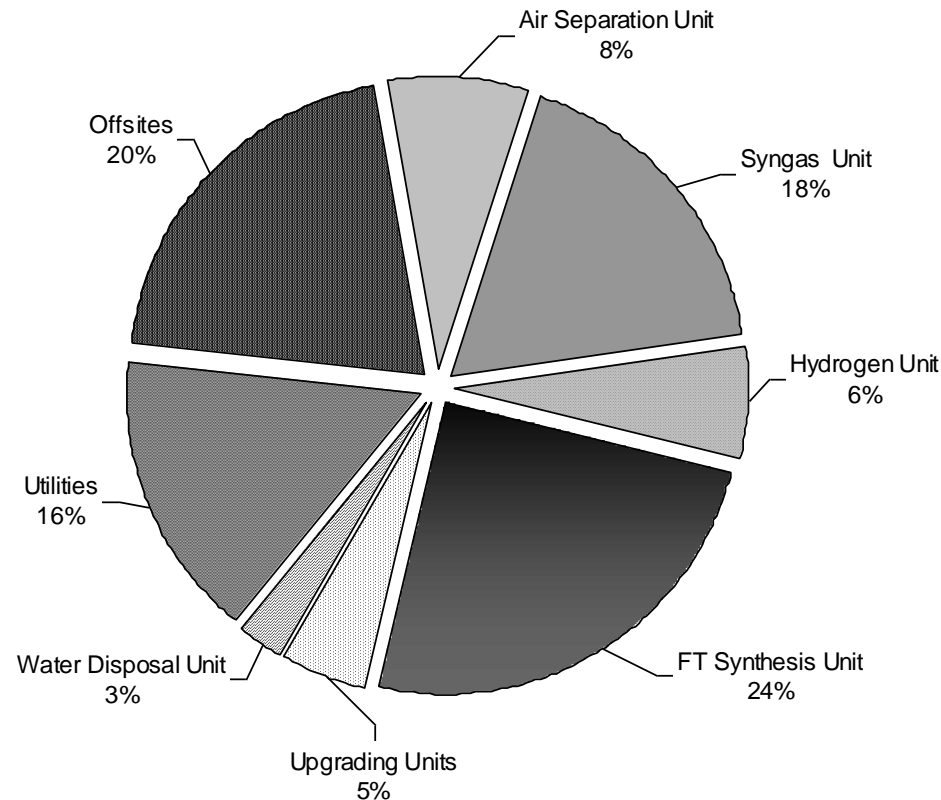
- (a) **Methanol synthesis.**
- (b) **Fischer-Tropsch synthesis.**

The synthesis gas conversion technology is only a small part of the process. GTL is not the syngas conversion technology, but the total integrated process.

In order to advance GTL a wide range of technologies need to be addressed. Some of these themes will have wider reaching benefit than just the advancement of GTL technology.

Gas-to-liquids capital cost

The following 2011 capital cost breakdown was provided for release by Eni.¹



1. Zennaro, R. In *Greener Fischer-Tropsch processes*, Maitlis, P., De Klerk, A. Eds.; Wiley-VCH (to be published)



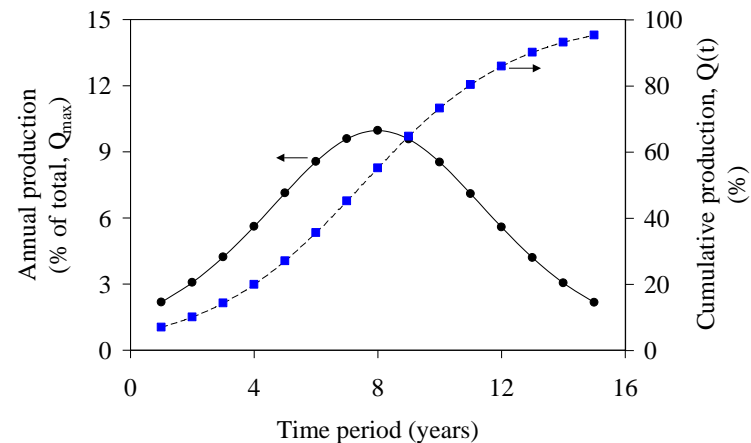
The case for gas-to-liquids

Strategic justification

Crude oil is the main source of transportation fuels at present and demand for crude oil increases year-on-year. Crude oil is also a finite resource. There will be a point in history were:

- (a) Crude oil demand exceeds crude oil supply (peak oil), *or*
- (b) Technology is adopted to **gradually replace crude oil** as feed before crude oil supply becomes constraining.

Gas-to-liquids conversion enables the production of similar products as are presently produced from crude oil.





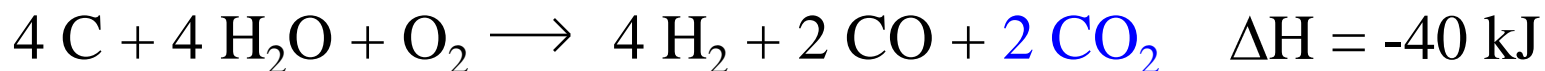
The case for gas-to-liquids



Environmental justification

Natural gas is the **most hydrogen-rich carbon source** available on earth. Even with significant displacement of carbon-based energy carriers (e.g. transportation fuels), not all applications can be carbon-free (e.g. petrochemicals).

When crude oil supply is constrained, indirect liquefaction is a more C-efficient route for alternative C-based products:



The effective feed H:C ratio determines the CO₂ footprint.²



The case for gas-to-liquids



Economic justification

There is an economic incentive for gas-to-liquids conversion when there is a **meaningful price difference** between natural gas and crude oil. This is best illustrated with an example:

Feed material	Feed cost		Efficiency (%) ^a	Effective cost \$/bbl _{equiv}
	\$/bbl _{equiv}	\$/GJ		
Natural gas	28	5	75 ³	37
Crude oil	100	18	89 ⁴	113

^a LPG, gasoline, jet fuel, diesel fuel and fuel oil products

3. Dry, M. E.; Steynberg, A. P. *Stud. Surf. Sci. Catal.* **2004**, *152*, 406-481 (p.436).

4. Gary, J. H.; Handwerk, G. E.; Kaiser, M. J. *Petroleum refining. Technology and economics*, 5ed; CRC Press: Boca Raton, FL, 2007, p.6.



The case against gas-to-liquids



The case against gas-to-liquids



Why is gas-to-liquids conversion so limited?

Despite the justification for gas-to-liquids conversion, there are important **detractors** that limit interest in any alternative carbon feed-to-liquids (XTL) conversion in general:

- (a) Technical **complexity** is high.
- (b) High **capital cost** for XTL facilities.
- (c) Investment **risk**, both financially and technically.

In the US specifically, there is also the burden of the past. The US has a less than stellar track record of proactive and sustained investment in XTL research and infrastructure. This is called the “**hiatus effect**”.⁵

5. Crow, M.; Bozeman, B.; Meyer, W.; Shangraw, R. Jr. *Synthetic fuel technology development in the United States. A retrospective assessment*; Praeger: New York, 1988.

Challenge 1: Technical complexity

One just has to look at the difference in technology necessary to produce conventional versus synthetic crude oil.



Conventional crude oil



GTL synthetic crude oil

The **technical risk** is significant: The company with most production experience in XTL, reported serious technical difficulties during and after commissioning of Oryx GTL.⁶



The case against gas-to-liquids



Challenge 2: High capital cost

In the early 2000's, the capital cost for GTL facilities that was often quoted, was \$ 20,000-30,000/bpd (barrel per day).⁷ Less than 10 years later, **much higher actual capital costs** were reported for GTL facilities:

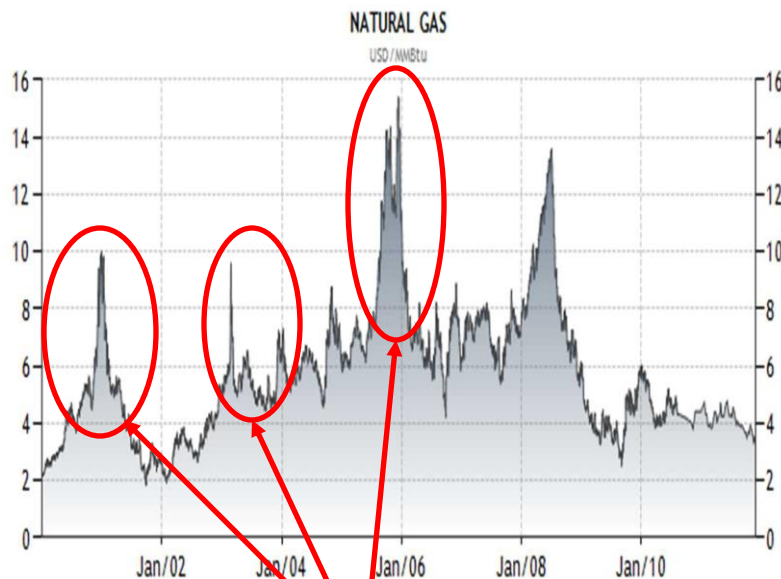
- (a) Pearl GTL (Shell): ~\$ 110,000/bpd [§]
- (b) Escravos GTL (Sasol-Chevron): ~ \$ 180,000/bpd
- (c) Sasol 1 GTL expansion (Sasol): ~ \$ 200,000/bpd

[§] The total project cost is US\$ 19 billion for 140 000 bbl/day GTL and 120 000 bbl/day natural gas liquids. The capital cost split to calculate the GTL contribution was estimated based on refining capital cost.

A 2011 Eni estimate: ~\$ 120,000/bpd for a 17,000 bpd train.¹

Challenge 3: Risk

The financial risk due to complexity and high capital cost is exacerbated by natural gas and crude oil **price volatility**.



Price of natural gas in $\$/\text{bbl}_{\text{equiv}} > \$/\text{bbl}$ crude oil!



The case against gas-to-liquids



Challenge 4: Hiatus effect

Sustained and uninterrupted research and development over a **20 year** period is required for significant cost reductions to occur and for technical risk to be reduced. Breaks in this R&D cycle is the hiatus effect and the following was found:⁵

- (a) On disbanding an R&D team, knowledge loss is high.
- (b) Time of inactivity correlates with knowledge decay rate.
- (c) Significant duplication of research is required after a break and reinitiation efforts are time consuming and costly.

Can the interest in GTL be sustained, or will it follow in the footsteps of US research in direct coal liquefaction (DCL)?



Opportunities to improve GTL



Opportunities to improve GTL



What can be done to improve GTL prospects?

In order to stimulate innovation and enable new technology, one should consider both large and smaller scale GTL facilities. Themes of specific importance are:

- (a) **Reduce complexity**. Robust technology can be optimized, but it is difficult to make already complex technology robust.
- (b) **Reduce capital by innovation**. Stop increasing the size of old technology (“economy of scale”), rather develop new technology based on better understanding of the process.
- (c) **Tackle the difficult problems**. Go back to fundamentals and find solutions to the challenges that undermine progress. This implies research before development.



Opportunities to improve GTL



The small-scale GTL opportunity

The biggest detractor of GTL is risk, both due to complexity and capital cost. There are inherent advantages in stimulating interest in development of small, <2000 bbl/day, GTL plants:

- (a) **Less complex** (out of necessity).
- (b) Requires **smaller capital investment** (due to smaller size).
- (c) **Innovation** fostered by lower risk (less money to lose).
- (d) Response to **learning is faster** (smaller is nimbler).
- (e) More **diversity**, broader interest (less money needed).
- (f) Access to **remote locations** (smaller vessels).



Opportunities to improve GTL



The small-scale GTL opportunity (continued)

- (g) Exploitation of **smaller deposits** of natural gas (capacity of GTL better matched to size of deposit).
- (h) **Scalability** and **robustness** (units in parallel).
- (i) **Modularity** (“mass production” due to smaller size).
- (j) **Mobility** (due to smaller size).
- (k) **Military** applications (due to mobility, modularity and robustness).

Large companies will continue to pursue R&D on GTL if it is important to them, but will likely focus on large-scale GTL applications to exploit economy of scale.



Technical discussion: Opportunities to improve GTL

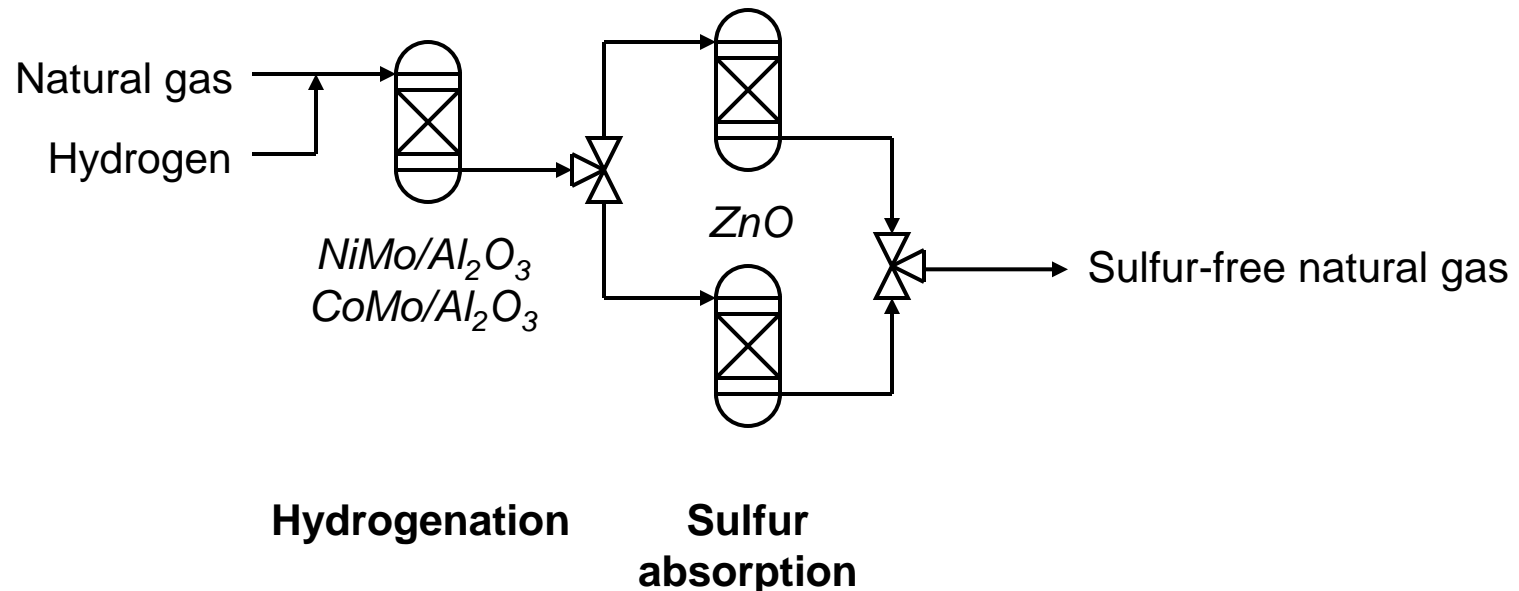


Gas cleaning

Design objective

The natural gas must be **desulfurized**, because S is a catalyst poison for reforming and syngas conversion catalysts.

Typical design





Gas cleaning



Opportunities for improvement

The present state-of-the-art technology is industrially applied and it works well for natural gas sources with a low sulfur content (typically <100 ppm S) where all of the sulfur is present as H_2S , COS or R-SH.

- (a) **Cleaning for high sulfur gas.** Absorption becomes increasingly impractical as the sulfur content increases.
- (b) **Removal of inert gases.** All inert gases (e.g. N_2) that pass through the gas cleaning step increases the size, efficiency and operating cost of a GTL facility. It also limits the extent of recycling of unconverted syngas in the gas loop.
- (c) **Useful/benign spent absorbents.** Small scale applications will likely use absorbents as a disposable product.

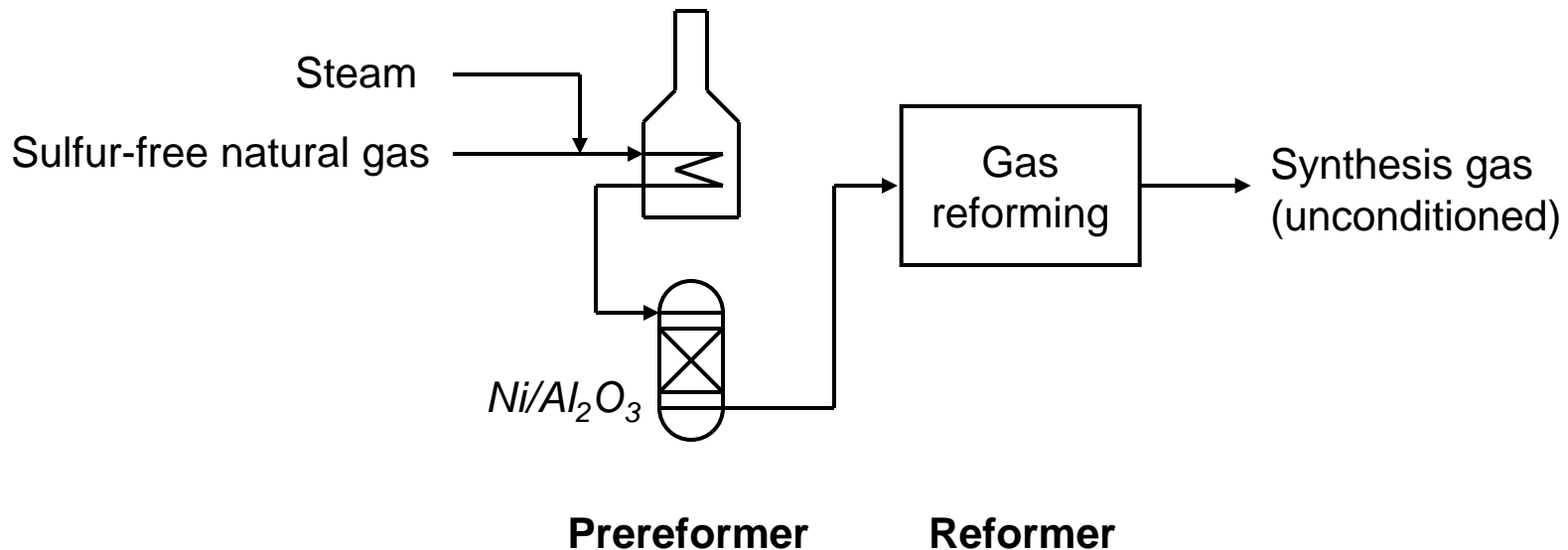


Synthesis gas generation

Design objective

Convert natural gas into **synthesis gas** (H_2+CO), preferably with the desired $H_2:CO$ ratio for the synthesis gas conversion technology.

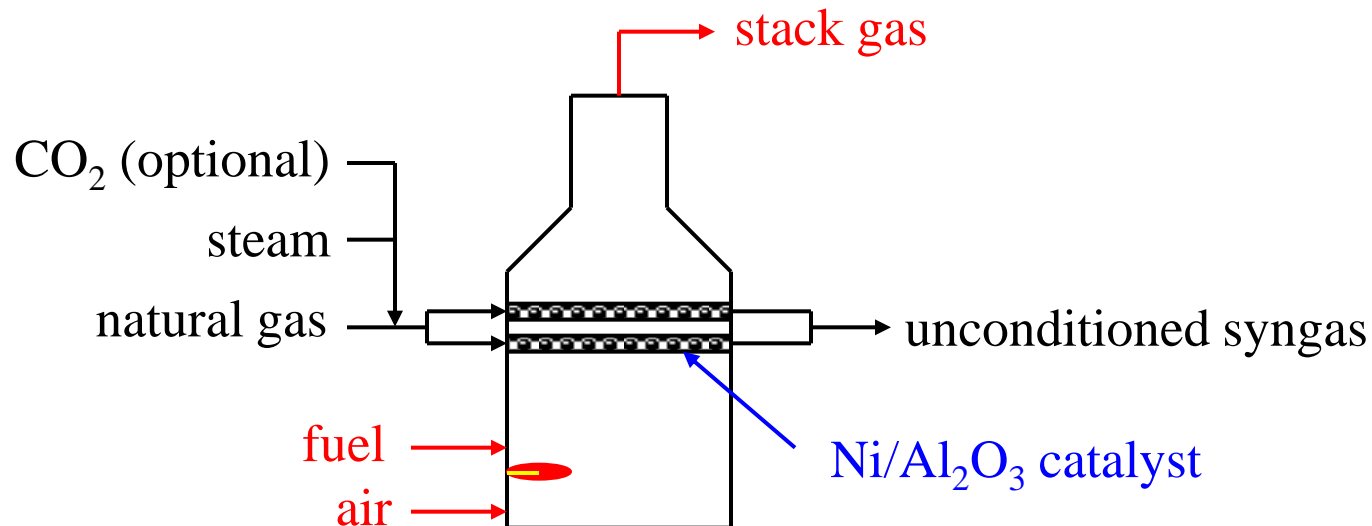
Typical design



Reformer types: Steam reforming

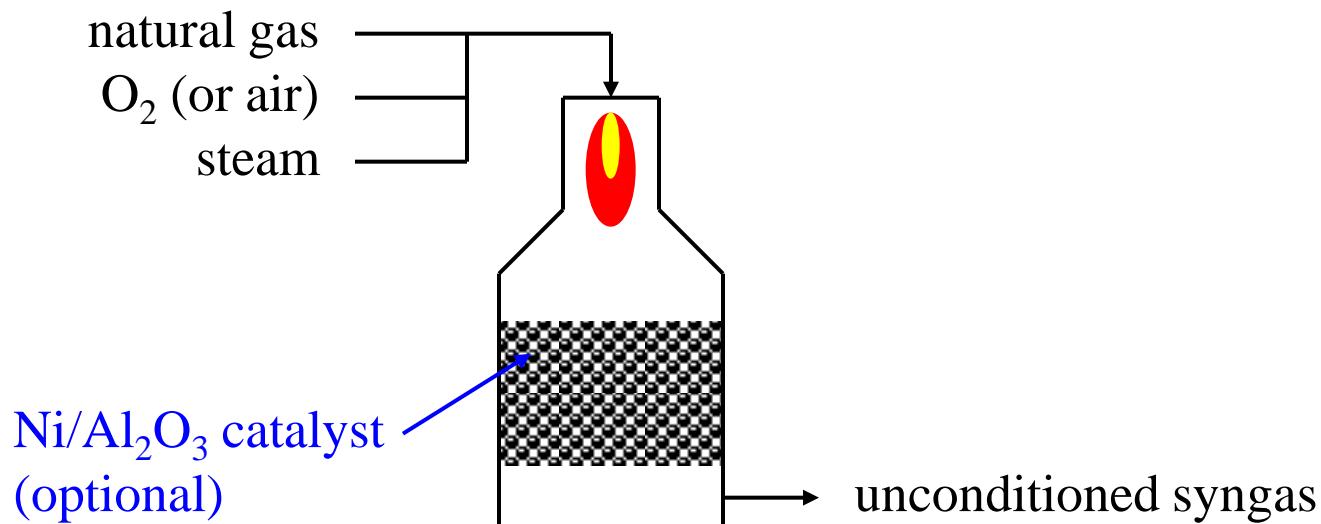
Produces **H₂-rich synthesis gas (H₂:CO>2)**. It can convert C₁ and heavier feed and does not require a pre-reformer.

Reforming is separate from heating and no air separation unit is required. It is physically large.



Reformer types: Adiabatic oxidative reforming

Produces **CO-rich synthesis gas** ($H_2:CO < 2$). It can convert C_1 , but heavier feed requires a pre-reformer. Reforming and heating are combined and an air separation unit is preferred. It is physically more compact.





Synthesis gas generation



Opportunities for improvement

The present state-of-the-art technology is industrially applied and due to wide-spread use, technology for large scale units were optimized over many decades.

(a) **Small scale steam reformers.** Small scale applications require cheaper, more efficient and compact reformers with flexible fuel input for heating and air as oxidant.

(b) **Non-cryogenic air separation.** Applications that want to employ adiabatic oxidative reforming will benefit greatly from from cheaper, robust, non-cryogenic air separation technology. In a GTL facility, ~30 % of the capital cost is due to cryogenic air separation and utilities.⁸ (~10 % for air separation only).¹

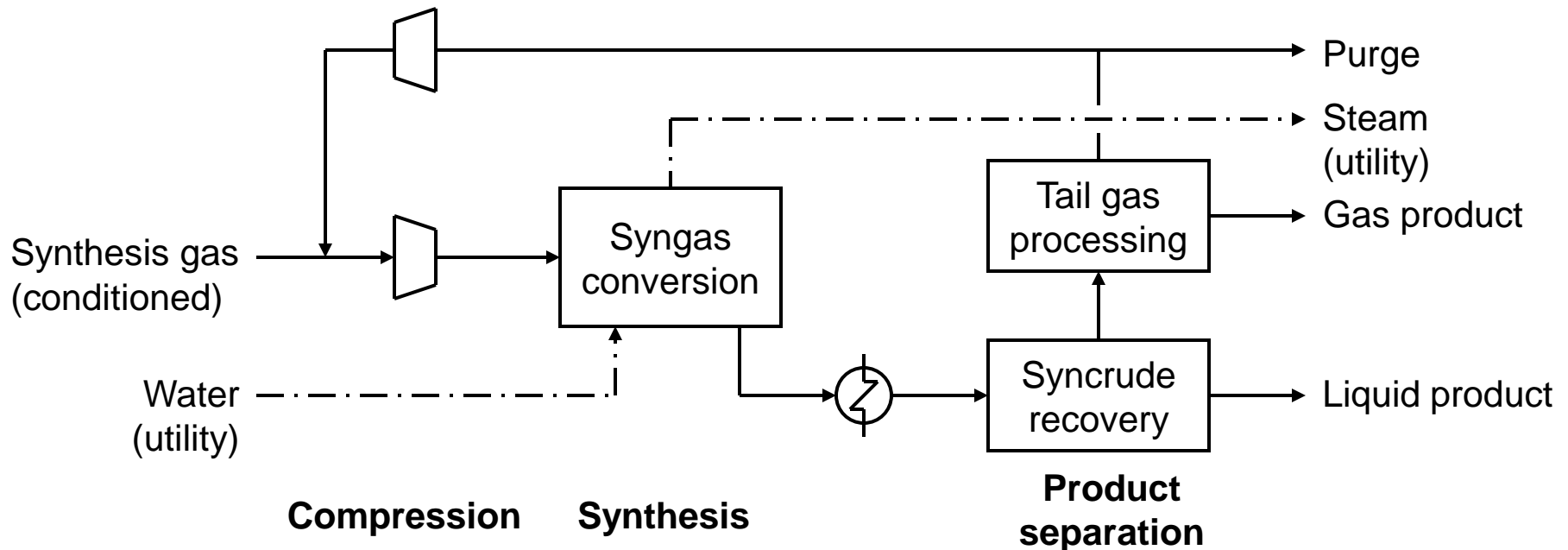


Synthesis gas conversion

Design objective

Convert synthesis gas into **synthetic products** that are related to the **final objective** of the GTL facility.

Typical design





Synthesis gas conversion



Conversion types: Methanol synthesis

Current state-of-the-art is gas phase low pressure conversion using a CuO/ZnO/Al₂O₃ catalyst at 200-300 °C and 3.5-5.5 MPa. Per pass conversion < 35 % to improve selectivity to methanol; **methanol selectivity is > 90 %**. Industrially it is widely applied and there are various technologies available for licensing.



Methanol is one of the seven highest volume **commodity petrochemicals**, with a consumption of more than 40 million ton per year. (At present capacity exceeds demand).⁹



Synthesis gas conversion



Conversion types: Fischer-Tropsch synthesis

Current state-of-the-art involves industrial operation with:

(a) **Low temperature Fischer-Tropsch**, which employs Fe- or Co-based catalysts in either fixed bed or slurry bubble column reactor configurations. Typical operation is at $\sim 220\text{-}240\text{ }^{\circ}\text{C}$ and $2.0\text{-}2.5\text{ MPa}$. Per pass conversion $\sim 60\%$ with recycle or reactors in series to limit catalyst deactivation.

(b) **High temperature Fischer-Tropsch**, which employs Fe-based catalysts in fluidized bed reactors. Typical operation is at $\sim 320\text{ }^{\circ}\text{C}$ and $\sim 2.5\text{ MPa}$. Per pass conversion $> 85\%$.

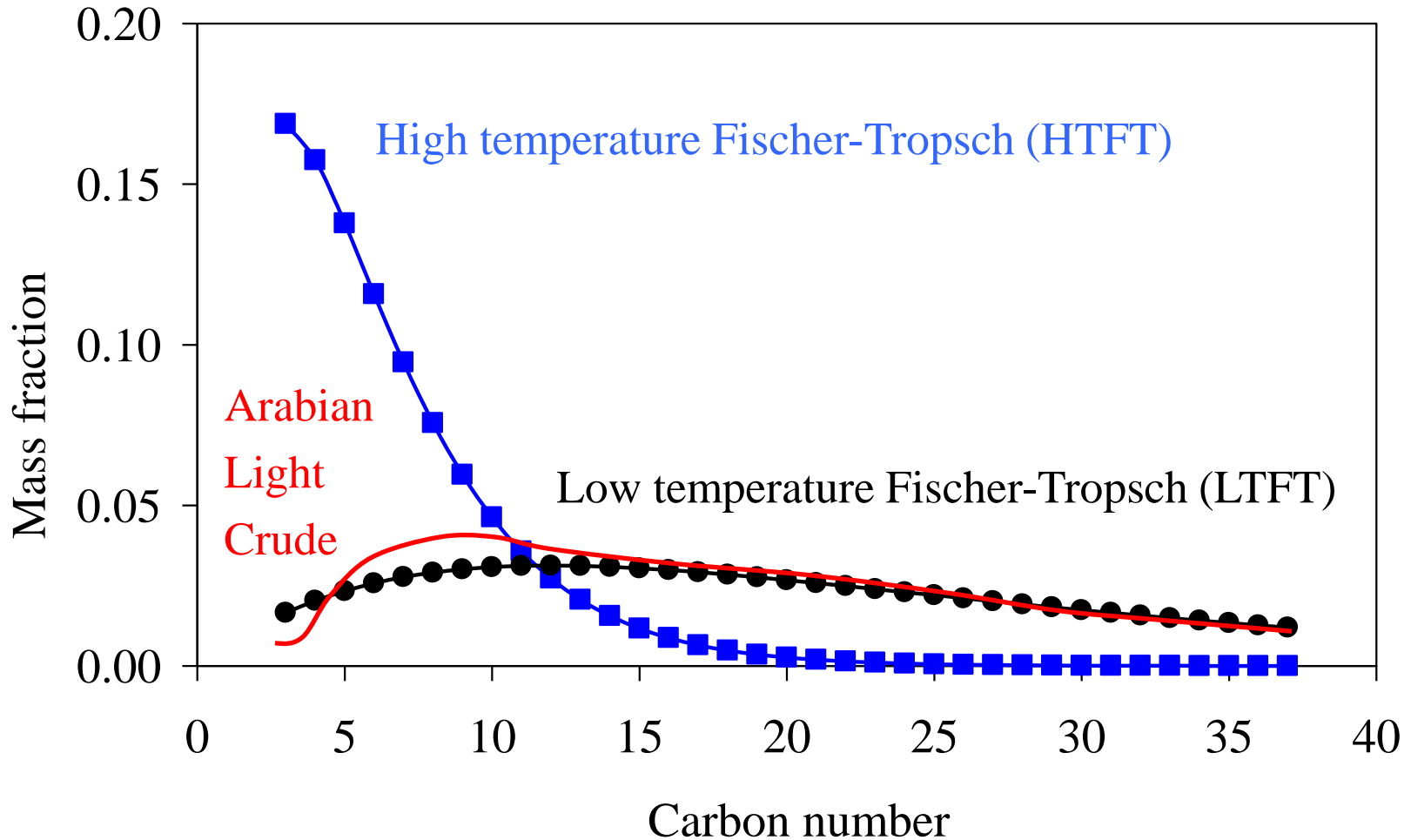




Synthesis gas conversion

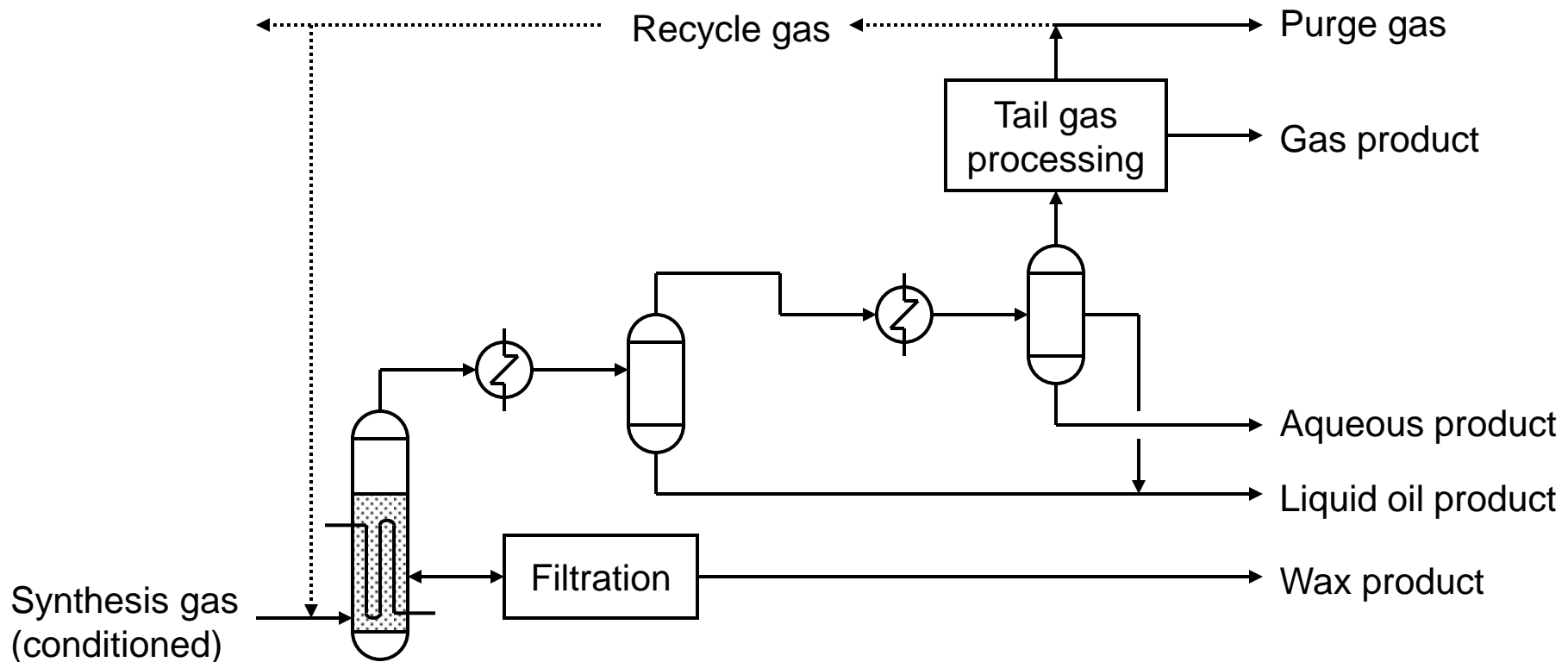


Fischer-Tropsch product distribution (excl. H₂O)



Syncrude recovery after Fischer-Tropsch synthesis

The complexity of **multiphase product recovery** is illustrated using slurry phase low temperature Fischer-Tropsch synthesis.





Synthesis gas conversion



Opportunities for improvement

- (a) **Small scale conversion.** Efficient synthesis at small scale.
- (b) **Lower methane selectivity.** Methane production in GTL is wasteful (methane is the feed). Improvements that lead to lower methane selectivity, especially with time on stream, will increase the overall efficiency of syngas conversion.
- (c) **Non-cryogenic tail gas separation.** The size of the purge gas stream depends on unconverted syngas recovery.
- (d) **Product specific synthesis.** One size does not fit all.

Many other improvements that are possible, e.g. incorporate distillation in product recovery not just flash separation; improve reaction engineering for better once through yields.



Synthetic product refining



Synthetic product refining



Design objective

Convert synthetic products into **transportable** and **marketable** products, preferably as large volume final products.

Typical refinery designs

Crude oil and synthetic refineries are designed with specific feed (synthetic product) and refined products in mind. E.g.:

- (a) Final on-specification transportation fuels.
- (b) Petrochemicals and lubricants.
- (c) Intermediate products and blend stocks.
- (d) Mixed refineries, with fuel and petrochemical products.



Synthetic product refining



Key conversion processes

Although methanol and Fischer-Tropsch syncrudes can be refined to similar products as crude oil, refinery designs, key conversion processes and technology selection are different:

- (a) Olefin dimerization / oligomerization
- (b) Aromatic alkylation
- (c) Isomerization
- (d) Aromatization / naphtha reforming
- (e) Cracking (all types: thermal, acid and hydrocracking)
- (f) Oxygenates conversion
- (g) Hydrotreating (olefins and oxygenates)



Synthetic product refining



Synthetic product refining myths

There are a number of persistent myths about the refining and refined synthetic products:

- (a) Refined synthetic products are different from petroleum products. **WRONG.** Refined on-specification synthetic products fall within the range of petroleum product diversity.
- (b) Fischer-Tropsch synthesis produces a high quality diesel fuel in high yield. **WRONG.** Hydrocracking of LTFT wax produces a high yield of distillate blending stock.
- (c) HTFT synthesis is for gasoline and LTFT synthesis for diesel. **WRONG.** Any Fischer-Tropsch syncrude can be refined to gasoline, jet fuel, diesel fuel and petrochemicals.

Opportunities for improvement

- (a) **Synthetic product specific refining.** The reactivity of the synthetic products enables more selective, efficient and lower energy refining, but requires syncrude specific technology.¹⁰
- (b) **Tail gas to liquid conversion.** Direct conversion of C₂-C₄ hydrocarbons into liquid products (not via syngas) will aid tail gas processing and improve efficiency. Useful especially in remote areas and locations far from petrochemical markets.
- (c) **Aqueous product refining.** The dilute nature of the water product poses challenges to refining, especially for acids.
- (d) **Regulatory guidance.** Provide technically justified fuel specifications for synthetic fuels - jet fuel in particular.



Threats



Threats



Premature demonstration

There is a design adage (that is mostly true) stating: “**All the really important mistakes are made on the first day.**”¹¹

The development of a process is to a large extent based on the level of understanding on the “first day”. In fact, about 70 % of the life-cycle costs are committed after 1 % of the project development cost.¹¹

Too much development with not enough research leads to a premature commercialization effort and **failure** to demonstrate **competitive viability** of the technology in the free market.⁵



Threats



Lessons from the past

There is a good body of literature on the US development of synthetic fuels.^{5,12-14} It is important to learn from history and to have realistic expectations. Some general points:

- (a) Pioneering processes are not conventional processes and it requires **time to become competitive**.
- (b) Unless GTL is developed as **strategic initiative**, it will be a competitive failure when the gas-oil price difference shrinks.
- (c) Not all technology can be bought or developed within the **timeframe** ordained by managers and politicians.
- (d) **Skilled people** can quickly become a key constraint.

12. *The emerging synthetic fuel industry*; Thumann, A. Ed.; Fairmont Press: Atlanta, 1981.

13. Harlan, J. K. *Starting with synfuels. Benefits, costs, and program design assessments*; Ballinger Publishing Co.: Cambridge, MA, 1982.

14. Hoffman, E. J. *Synfuels. The problems and the promise*; Energon Co.: Laramie, 1982.



Threats



“Predictable surprise”

One of the hallmarks of a predictable surprise in the making is that the **problem is known**, but it has **real present cost** to address the problem, but with an **uncertain future benefit**.¹⁵

To quote the 1988 assessment of US synfuels development:⁵
“The ultimate need for synthetic fuels seems a certainty. ... [Yet,] it is likely that there won’t be twenty to twenty-five years of lead time to any long-term oil supply interruption, [and] it is fair to conclude that highly inefficient [liquefaction] options will be our only means of meeting the need.”

15. Bazerman, M. H.; Watkins, M. D. *Predictable surprises. The disasters you should have seen coming and how to prevent them*; Harvard Business School Press: Boston, 2004.



Conclusions



Conclusions



Key challenges to GTL development

- (a) **Complexity** - technical level of difficulty is high.
- (b) **Capital cost** - high barrier to entry; difficult to finance.
- (c) **Risk** - volatile gas/oil prices; high cost; complexity.
- (d) **Hiatus** - sustained interest is required for progress.

Key opportunities

- (a) **Small-scale GTL** - lower risk and cost, enables innovation and participation, and out of necessity reduces complexity.
- (b) **Non-cryogenic gas separation** - improves overall gas loop, enables more efficient small-scale GTL and it has application possibilities beyond GTL.



Conclusions



Key opportunities (continued)

(c) **Compact “fired” heaters** - utility heating >240 °C requires fired heaters that are large/expensive. It is an obstacle to small-scale GTL and has efficiency benefits beyond GTL.

(d) **Selective synthesis** - reduced methane selectivity and product specific synthesis can improve overall efficiency and enable easier refining to higher value products.

(e) **C₂+ gas to liquids** - simpler and more efficient gas loop for small-scale GTL and improved refining efficiency for applications that generate light hydrocarbon gases.

(f) **Water refining** - recovery of organics from dilute aqueous mixtures; useful for all organic contaminated wastewaters.



Thank you