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Partial Oxidation Gas-Turbine Based Turbo-POx Syngas Generation Technology for GTL Applications

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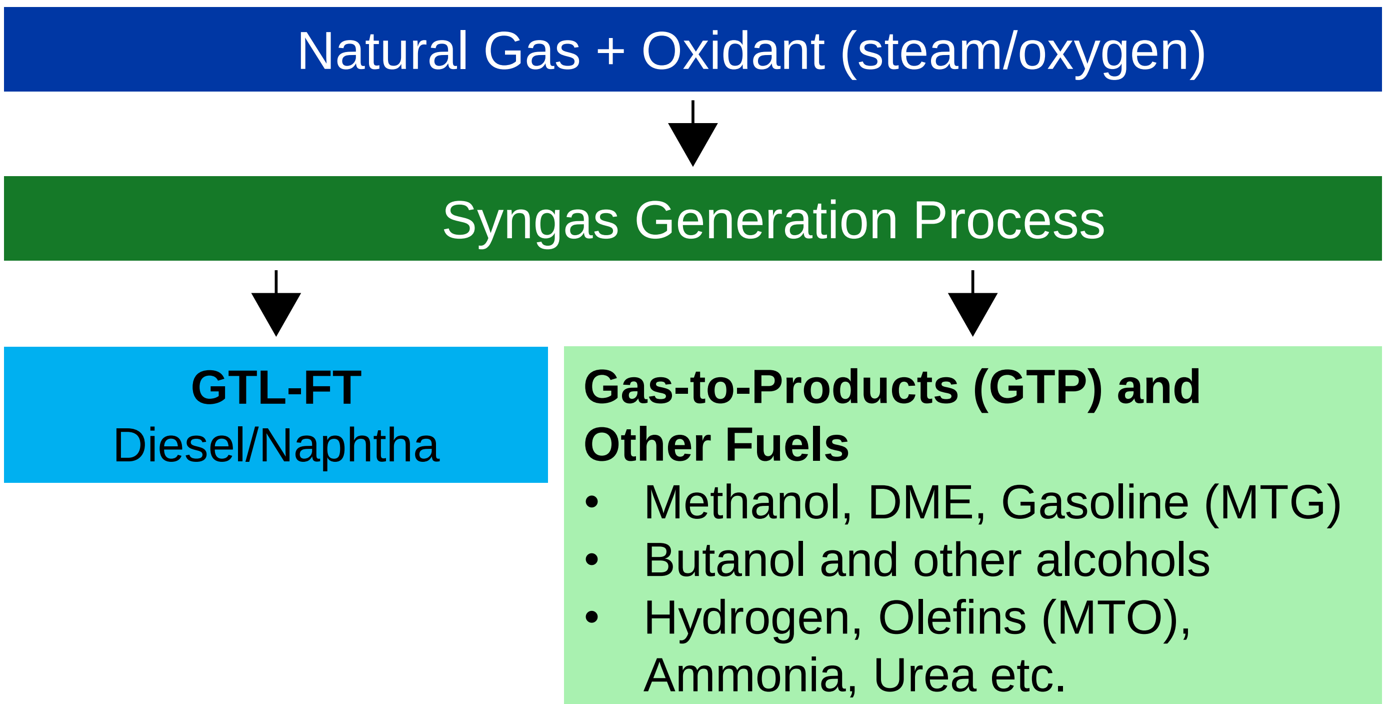
Syngas Generation Process

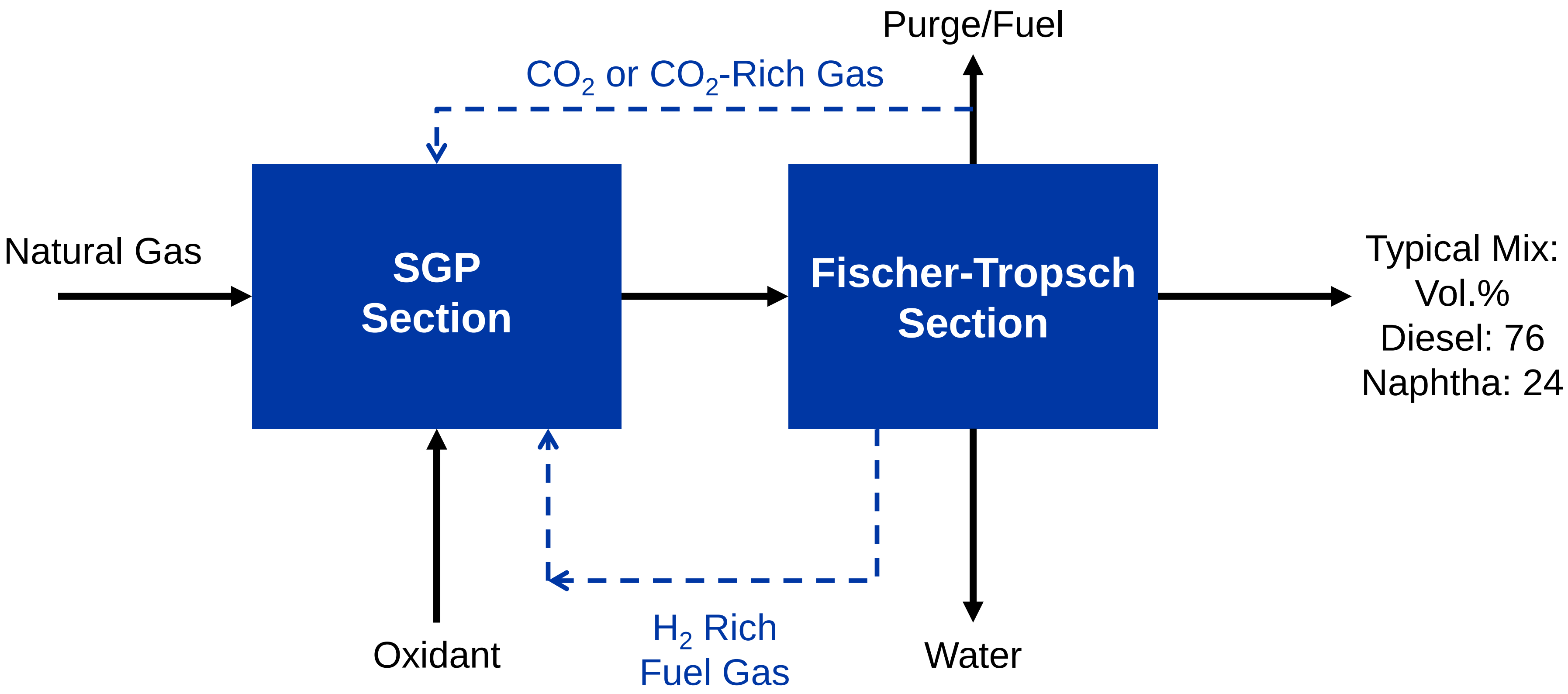
- Key step in current commercially proven GTL/GTP technologies – relatively high CAPEX



TYPICAL PROCESS FLOW DIAGRAM

Fischer-Tropsch (FT) GTL Process

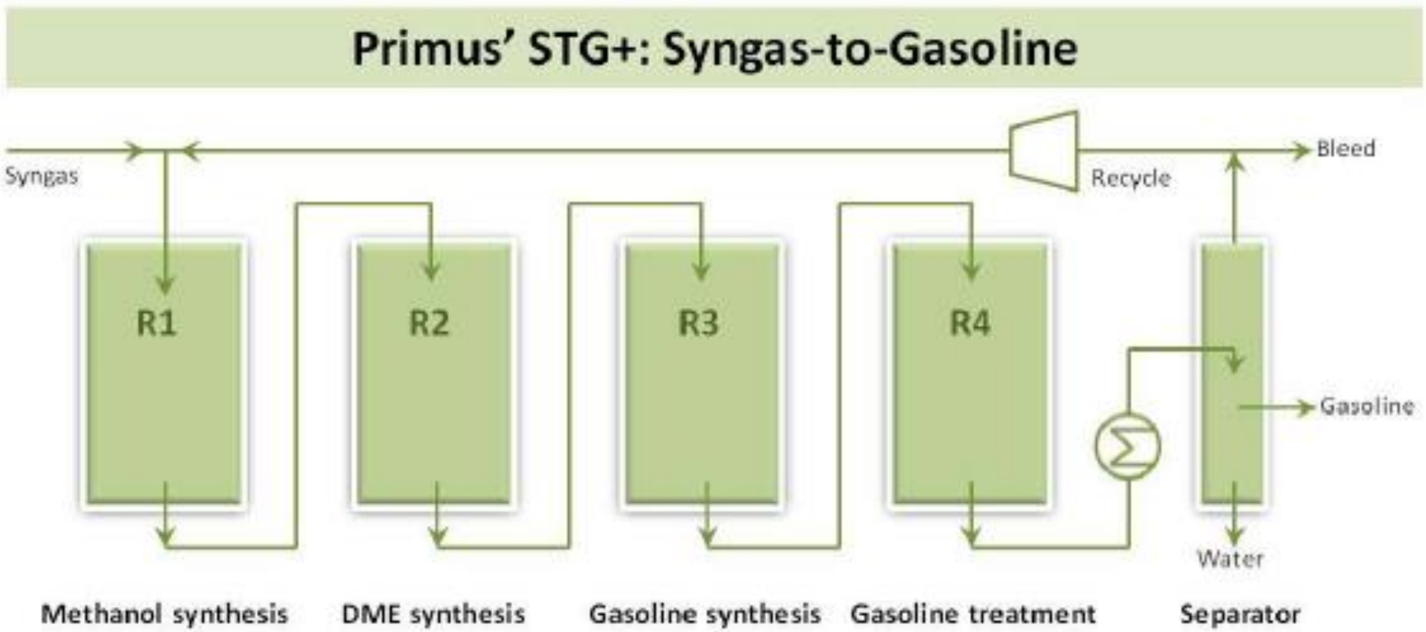
> Typical H_2/CO molar ratio in syngas feed to FT Section should be ~ 1.7-2.0



TYPICAL PROCESS FLOW DIAGRAM

Primus' Syngas-to-Gasoline (STG+) Process

- Typical syngas Module Factor M $((H_2 - CO_2)/(CO + CO_2))$ for MTG or STG+ type processes should be ~2.0-2.5

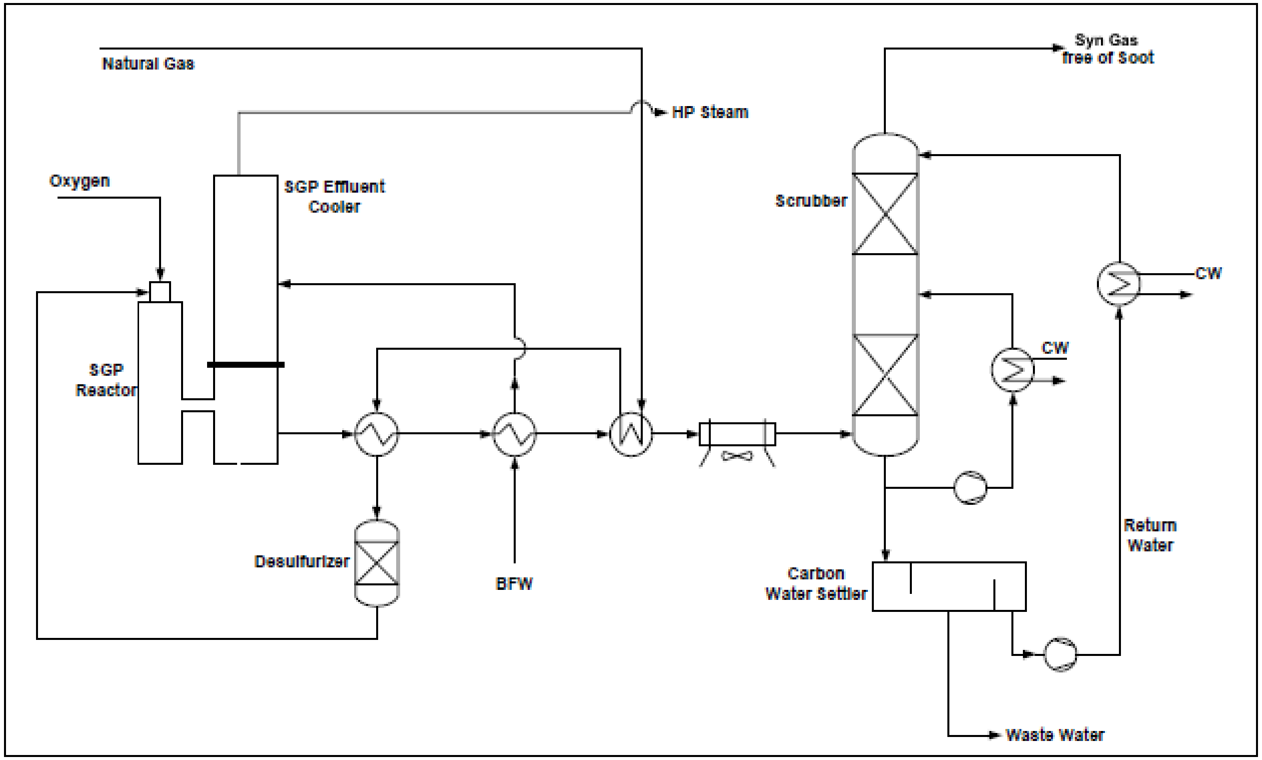


Ref. Eli Gal et al., "Comparison of STG+ with other GTL Technologies", Primus Green Energy, www.primusge.com

TYPICAL PROCESS FLOW DIAGRAM

Shell Non-Catalytic POx Technology for FT

> **Near-optimum H_2/CO molar ratio** (~1.7-2.0) for FT with very low S/C ratio usage; however, there is a significant loss of overall thermal efficiency due to the use of water quench

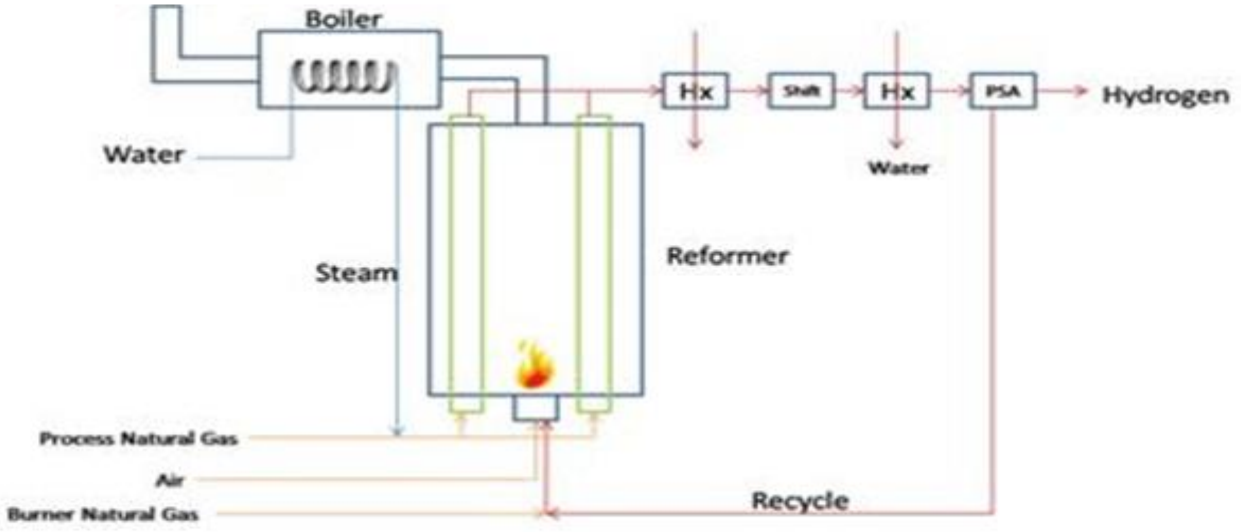


TYPICAL PROCESS FLOW DIAGRAM

Conventional Steam Methane Reforming for H_2

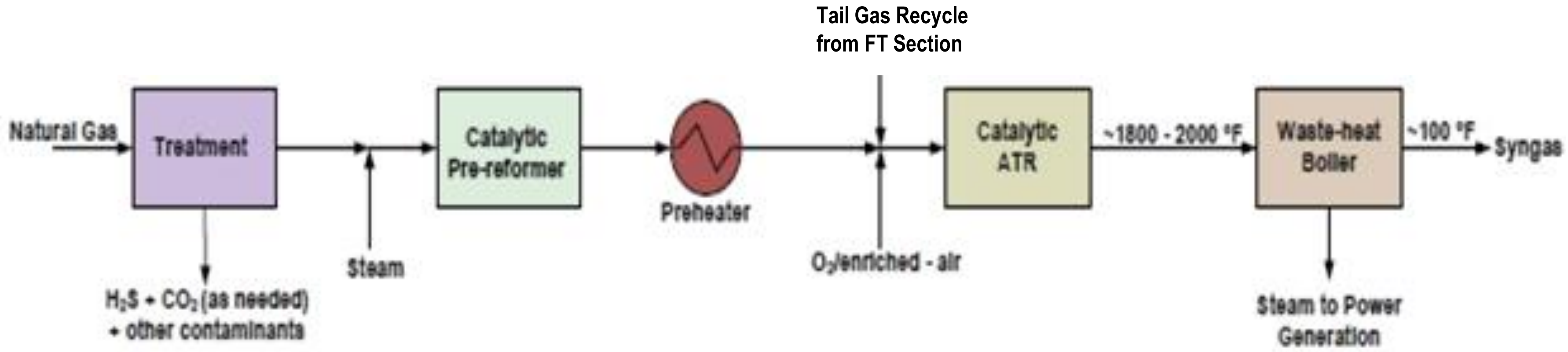
> Typical H_2/CO molar ratio from 3 to 5

- **Key advantage:** no oxygen plant is needed
- **Significant challenges:** Adjusting the H_2/CO ratio for GTL plants (e.g. need to use expensive excess hydrogen as fuel); capturing CO_2 from the reformer flue gas



Conventional Catalytic Autothermal Reformer Process (ATR) for F-T

- Haldor-Topsøe ATR is commercially proven at a Steam/Carbon molar ratio of 0.6
- For a F-T GTL process, the H_2/CO ratio to the F-T reactor needs to be adjusted to ~1.7-2.0 using a relatively large CO_2-rich tail-gas recycle from the F-T step
- Typical tail gas/natural gas feed molar ratio is 0.6-0.8, a very large recycle flow
  - Typical CO_2 level in tail gas is ~45-60 mol%
- The tail-gas recycle increases oxygen requirement and ATR/F-T reactor volumes
- R&D ongoing to reduce S/C ratio



Impact of Reduced Steam/Carbon Ratio on ATR Performance

Case	ATR (Base)	ATR (Advanced) @ Lower S/C
Steam/Carbon Ratio	0.6	0.4
O_2 Usage, tonnes/bbl Produced Index	100	92
Total LHV Efficiency, Index	100	105
Air Separation Unit CAPEX/, $/bbl/day Index	100	83
Syngas Production CAPEX, $/bbl/day Index	100	69
ASU + SGP CAPEX Index	100	76

Ref. : Haldor Topsoe Data (P. K. Bakkerud, Cat. Today, 106 (2005) 30-33)

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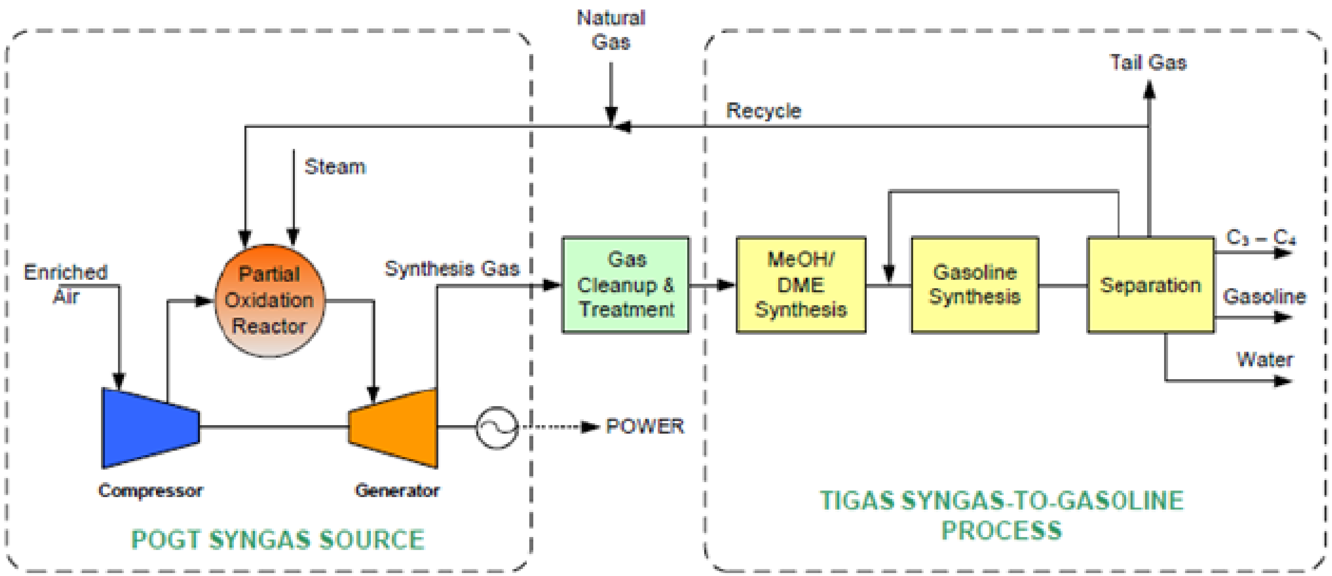
GTI's Process Concept using AR Turbo-POx Technologies for GTL

- Front-end uses AR Turbo-POx technologies for improved overall efficiency and lower liquid production costs
- Multiple backend process capability

GTI Patents

7,421,835-B2
8,268,896-B2

GTI Process **Example Syngas to Liquid Fuels**



Typical Product Mix, Vol%:

Gasoline: 86%
LPG : 14%

Aerojet Rocketdyne (AR) and GTI Collaboration – ARPA-E Program

> Pilot plant testing of AR's non-catalytic POx reactor at GTI
  - ~10 tonnes/day natural gas feed rate
  - A similar reactor was used at GTI for AR's dry-coal feed gasification process R&D using oxygen/steam

> Design studies by AR for Turbo-POx expander

> Techno-economic assessment GTL design cases by GTI
  - ~ 1,000 bbl/day FT products
  - ~ 10,000 bbl/day gasoline plus LPG

AR POx Combustor Testing at GTI

- Full-flow POx combustor & injector testing at 1,000 barrels/day POGT capacity
  - 12 POx combustor cans per expander anticipated
  - GTI testing at 400 psia chamber pressure
- Performance mapping at four discrete temperatures & four discrete steam/methane ratios (16 total tests, with 4 at sooting conditions)
- Correlation of test data with proprietary AR multi-stream kinetics model
  - Predictions of methane slip, free-stream soot formation and effects of injector mixing efficiency

POx Development Combustor at GTI

Ref.: "Partial Oxidation Gas-Turbine Based Turbo-POx Syngas Generation Technology for GTL Applications," S. P. Fusselman and A. Basu, GTL Technology Forum, Gulf Publishing Company, Houston, July 2014

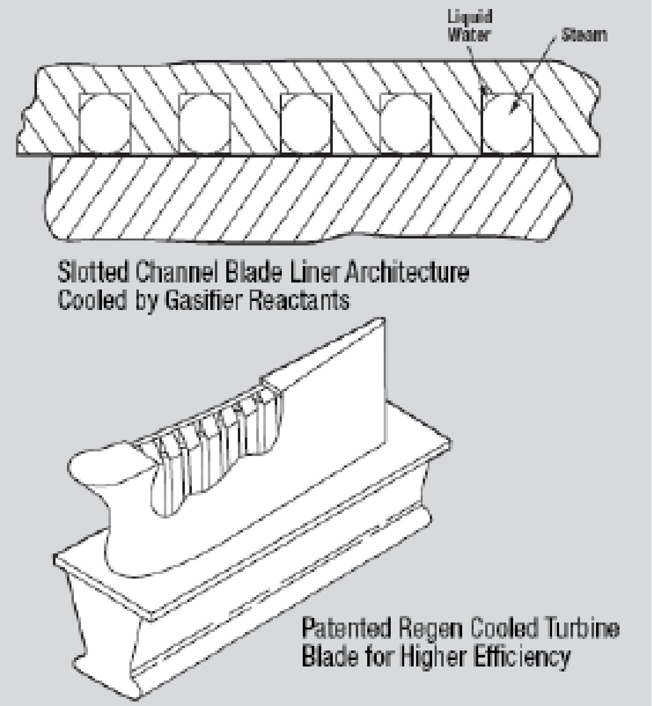
AR Reducing-Gas Turbo-Expander

> Technology expertise from liquid rocket-engine rotating machinery design practices

> Materials compatibility in high-temperature and high-pressure reducing gas (i.e. syngas) environments under high-stress loading
  - Hydrogen embrittlement – generation of detrimental metal hydrides
  - Carbon monoxide (carbon dusting) embrittlement – generation of detrimental metal carbides

> Rapid syngas quench: <6 millisecond (Carbon soot suppression)

> Regenerative (regen) cooling of blades
  - US Patent 6,565,312 (2003)
  - Produces high-pressure (saturated or superheated) steam for use in other process units (e.g. POx combustor; auxiliary power)



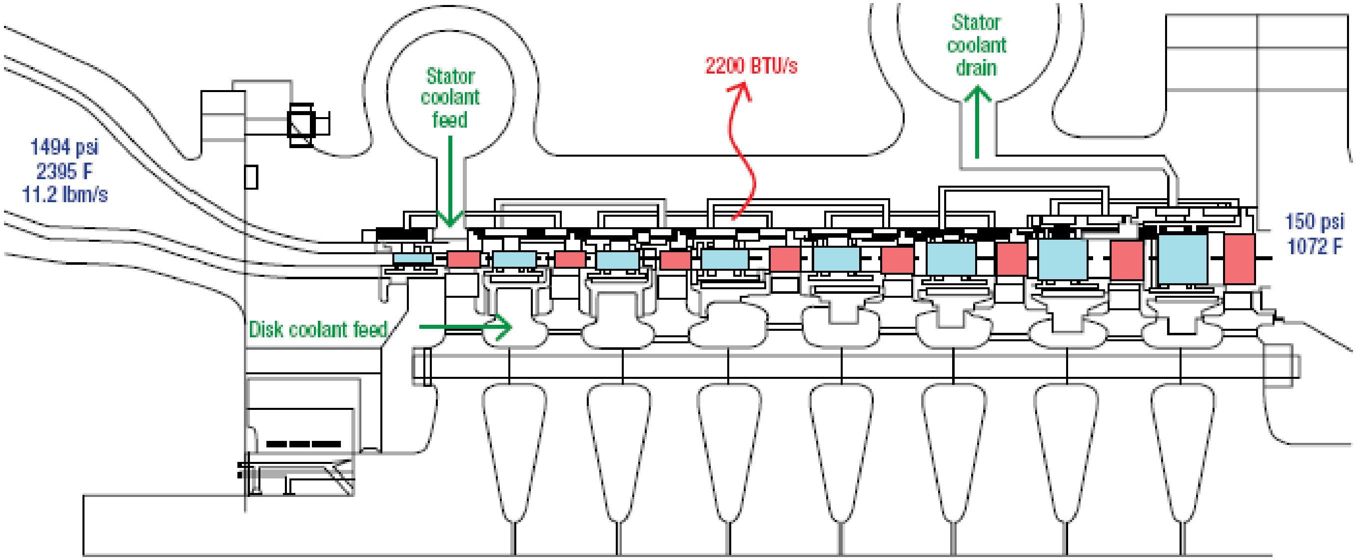
Ref.: "Partial Oxidation Gas-Turbine Based Turbo-POx Syngas Generation Technology for GTL Applications," S. P. Fusselman and A. Basu, GTL Technology Forum, Gulf Publishing Company, Houston, July 2014

AR Expander Development

Current design sized for 1,000 barrels/day of liquids production and 6 MW_e output

> Regen-cooled stator blades provide higher system efficiency than film-cooled blades

> Coolant output is 1,700 psia saturated steam (100% quality)



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Key Potential Advantages for Turbo-POx vs. Catalytic ATR

> Close-coupled compact POx reactor and expander
  - Ideal for shop fabrication and modular small-scale GTL plants

> No catalytic pre-reformer (reduced CAPEX) + no catalyst for POx reactor (reduced OPEX)

> Significantly lower S/C ratio (e.g. **0.2 vs. 0.6** for ATR): this would significantly reduce oxygen requirement + tail-gas recycle in a F-T process
  - Reduced volumes for POx/F-T reactors
  - Reduced compression costs for Tail-gas recycle
  - Reduced O_2 need would lead to less power needed

> Significantly reduced capacities and lower CAPEX/OPEX costs for waste-heat boiler (WHB), steam turbine power-generation unit and steam systems

Comparative Data on Thermodynamic Efficiency
Basis : 13,000 kgmols/hour of Syngas

	Turbo-POx + a Smaller WHB	Conventional AR-POx Reactor + WHB
Gross electric power generation from Expander, MWe[1]	54.8	--
Electricity generated from HP steam from WHB[2]	30.2	52.9
Electricity need for syngas compression (to P : inlet of Methanol Reactor)	(18.1)	
Total, MWe	**66.9**	**52.9**
Total Electricity generated, Relative	126	100

[1] Expander outlet @ 168 psia

[2] Syngas is cooled to 100 F

CAPEX Impact on Steam-Based Systems

(Basis : 16,630 Bbl/day Liquids)

	ATR + WHB	Turbo-POx + WHB
Catalytic-ATR CAPEX	~ $162 MM*	--
Turbo-POx (includes Expander) + WHB CAPEX	--	~ $70 MM
Power-generation Systems + BFW/Steam Systems CAPEX*i:	~ $273* MM	~ $90 MM
Total CAPEX for these Units	~ $435* MM	~ $160 MM
Relative	272	100

i. Total steam-turbine power generation in the ATR-FT Case: 140 MWe (GTI estimate)

* Hatch Inc. Ref. : Alaska Gasoline Development Corp. – Alaska Stand Alone Pipeline/ASAP GTL Economic Feasibility Study (Final Report, 2011)

Expander and System Scale-up Challenges

> Demonstrate close-coupled POx reactor and expander system corresponding to ~1,000 bbl/day liquids (NG at 10 Million SCF/day) and 6 MW_e power output
  - Fabrication of expander system
  - Demonstrate commercially attractive expander-blade life
  - Demonstrate soot-free, metal-dusting free syngas generation at low S/C ratio

Summary and Conclusions

- The AR/GTI Turbo-POx GTL plants offer potential economic advantages compared to conventional POx and ATR GTL processes
- The regen-cooled design needs further maturity to meet expander life requirements in reducing syngas environment
- A 1,000 barrels/day integrated AR POx and expander unit needs to be demonstrated at a brown-field site. Testing should include:
  - Risk mitigation of key expander components
  - Expander performance mapping and long duration test efforts

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