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# PARTIAL OXIDATION GAS-TURBINE BASED TURBO-POx SYNGAS GENERATION TECHNOLOGY FOR GTL APPLICATIONS

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## ABSTRACT

With financial assistance from the Advanced Research Projects Agency – Energy (ARPA-E) - U.S. Department of Energy, Aerojet Rocketdyne Energy Systems Inc. (AR) and Gas Technology Institute (GTI) are collaborating in developing a novel non-catalytic, partial-oxidation based, syngas generation technology called Turbo-POx for Gas-to-Liquids (GTL) and other industrial applications. AR is a leader in high energy density propulsion and power systems with over five decades of combustion and high-pressure turbine development experience. GTI is a not-for-profit R&D organization with over seven decades of experience in energy conversion and monetization of natural resources including natural gas, biomass and coal. The Turbo-POx technology is based on GTI's patented Partial Oxidation Gas Turbine (POGT) concept in which hot synthesis gas from AR's non-catalytic POx gasifier is rapidly cooled in a close-coupled turbo-expander instead of in a conventional waste-heat boiler (WHB). Thus, a considerable portion of the sensible waste heat in the hot synthesis gas is recovered as electrical power and high-pressure steam, thereby resulting in significant capital cost savings compared to a conventional WHB-based synthesis gas cooling process. The AR-POx unit is capable of operating at about 1,500 psia and 2,400 °F outlet conditions using a relatively low steam/carbon molar ratio (typically, ~0.2). The AR turbo-expander would be cooled by the POx gasifier's reactants via a patented regenerative (regen) cooling concept for improved thermal efficiency and for enhanced service life of expander blades. For the integrated AR-POx/expander commercial operation for a nominal 1,000 barrels/day GTL plant, a typical AR turbo-expander system is projected to deliver an electrical power output of about 6 MWe. Key applications of the POGT/Turbo-POx technology would include GTL and polygeneration of electricity and chemicals.

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## INTRODUCTION

With the ongoing shale gas revolution in the U.S., extensive global exploration for shale/conventional natural gas reserves, and concerns with climate change linked to gas flaring, the interest in Gas-to-Liquids (GTL) processes as a way of monetizing low cost natural gas (associated, flared and remote) is growing rapidly. Although key GTL technologies (namely, Sasol/Shell Fischer Tropsch (FT) processes for the production of diesel and ExxonMobil's MTG (Methanol to Gasoline) option for the production of gasoline) have been commercialized, there has been strong ongoing R&D focus on further reductions of total capital cost which is the primary component of the overall production costs for gas-based transportation fuels. Syngas (primarily, a mixture of hydrogen and carbon monoxide) generation from feed gas is a key step in current commercially proven GTL technologies. In this context, the Syngas Generation Process (SGP) step itself accounts for about 40-60% of the total plant investment. The manner in which syngas is produced can be greatly influenced by various aspects of the overall GTL process design, such as:

- Plant capacity and location;
- The need for an oxygen (or enriched air) plant and associated safety issues (e.g., offshore locations);
- Syngas composition (primarily, $H_2$/CO ratio and level of $CO_2$) and how it impacts optimum product yields and selectivities;
- Need for gas recycle and its impact on GTL production costs;
- Configuration and optimization of power/steam generation facilities;
- Potential for modular construction and shop fabrication to reduce plant CAPEX; and
- Economics for $CO_2$ capture, and utilization of low-cost $CO_2$, if available at the plant site.

In this paper, we briefly outline the R&D status and economic potential of GTI's patented POGT (Partial Oxidation Gas Turbine) technology for syngas generation and its integration with the Turbo-POx concept currently being developed by Aerojet-Rocketdyne (AR) under the financial assistance from ARPA-E (Advanced Research Projects Agency- Energy, U.S.-DOE).

## TYPICAL PROCESS CONFIGURATIONS FOR FT AND MTG-TYPE GTL PROCESSES

### *FT GTL Process for the Production of Diesel/Naphtha*

A schematic of a typical FT process is shown in Figure 1. The basic FT process consists of two fundamental steps:

1. The production of syngas from natural gas in the SGP plant. Typically, the $H_2$/CO molar ratio in the syngas feed to the FT section should be about 1.7-2.0. Depending on the type of SGP, a specific amount of $CO_2$-rich tail gas is recycled from the FT section to the SGP unit to control the $H_2$/CO ratio of the syngas feed to the FT section.
2. The production of diesel from the syngas. This involves catalytic (FT) synthesis in special reactors of various designs producing a wide range of paraffinic hydrocarbons (synthetic

crude), specifically those with long-chain molecules (e.g., typically with 100 carbons in the molecule). The syncrude is then refined to specific products (e.g. diesel and naphtha) using catalytic-hydrocracking processes available commercially. A typical product slate could be about 76% diesel and 24% naphtha[1].

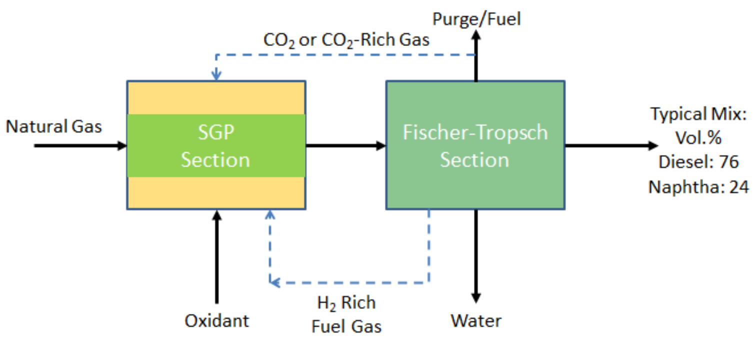


*Figure 1 Typical Process Flow Diagram for a FT GTL Process*

Figure 2 illustrate the selectivity of $C_5$+ liquid components for the FT synthesis as a function of syngas $H_2/CO$ ratio and CO conversion (per pass). As shown in Figure 2a[2], the liquid product selectivity increases with increasing CO conversion up to a specific level based on the reactor operating conditions and then drops off rather sharply with a significant increase in the $CO_2$ selectivity. These changes in selectivities are also dependent on the $H_2/CO$ ratio of feed syngas (Figure 2-b)[2].

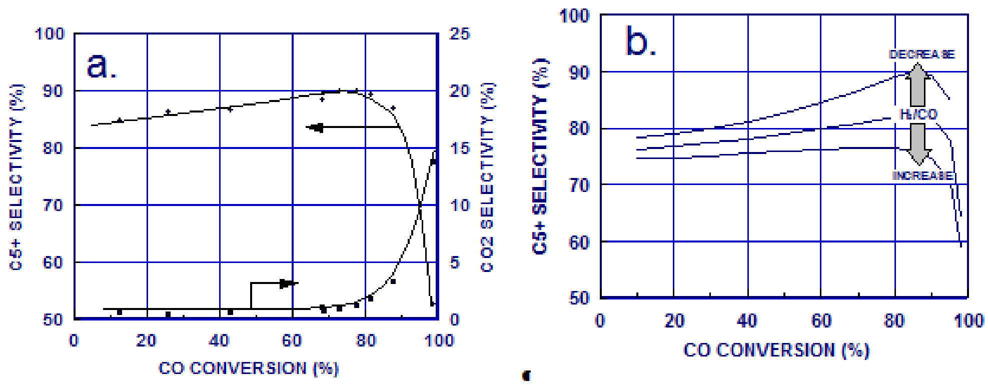


*Figure 2 (a): Experimental data for $C_5$+ and $CO_2$ Selectivity, and (b): Improvements in $C_5$+ selectivity with decreasing $H_2/CO$ molar ratio around 2.0*

### *STG+ GTL Gasoline Production Process*

A schematic of a typical STG+ (Syngas-to-Gasoline technology[3], being developed by Green Energy Inc.) process is shown in

Figure 3. The ExxonMobil gas-based MTG (Methanol to Gasoline) process[4] was commercialized in New Zealand; the coal-based MTG technology has been commercialized recently in China. In the STG+ process, the syngas is converted to methanol, DME, and raw gasoline in three close-coupled fixed-bed catalytic reactors; the gasoline product from reactor R-3 is then further treated in a fourth close-couple reactor (R-4) to produce saleable gasoline. A part of the unconverted

syngas and other gaseous components are recycled to the methanol synthesis reactor (R-1). Haldor Topsoe also has developed a similar technology (known as: TIGAS -- Topsoe Improved Gasoline Synthesis process[5]).

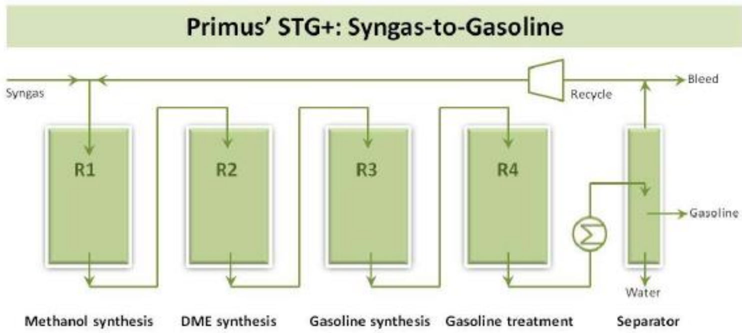


Figure 3 Typical Process Flow Diagram for Primus' Syngas-to-Gasoline (STG+) Process

In STG+/MTG/TIGAS type GTL processes, the syngas feed composition to the methanol reactor is adjusted so that the "Module Factor M" (defined as: $(H_2\text{-}CO_2)/(CO + CO_2)$) is about 2.0-2.5.

## KEY SYNGAS GENERATION PROCESSES

### *Non-catalytic Partial Oxidation (POx)*

In non-catalytic POx type SGP processes, the key reaction is the partial oxidation of methane with oxygen: $CH_4 + 0.5\ O_2 = 2\ H_2 + CO$.

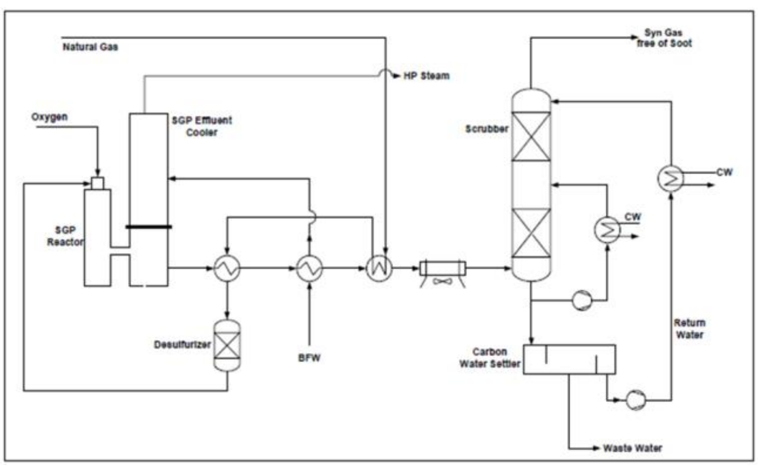


*Figure 4 Schematic of the Shell Non-Catalytic POx Process for FT*

A schematic of the Shell POx technology (SGP: Shell Gasification Process)[6] is shown in Figure 4. The SGP reactor is operated at about 1300 - 1400 °C. Following partial heat recovery to generate high-pressure steam, the syngas is further cooled in a water scrubber to remove soot from the syngas. In the Shell process, the steam/carbon (S/C) molar ratio of the feed gas to the POx reactor is typically less than ~ 0.2 and the $H_2/CO$ molar ratio of the product syngas is about 1.7-2.0

The use of water scrubbing step results in a significant loss of overall thermal efficiency in the process.

### *Conventional Steam Methane Reforming (SMR)*

The SMR process is widely used to generate synthesis gas for various petrochemical processes and for the production of hydrogen used in petroleum refineries.

The key reactions are: $CH_4 + H_2O \rightarrow CO + 3\,H_2$ and $CH_4 + CO_2 \rightarrow 2CO + 2\,H_2$. Figure 5 shows a typical schematic for the production of hydrogen using a SMR process. It is usually carried out in the presence of a catalyst with reactor exit temperatures of 850 - 950 °C, and at pressures of about 300-450 psig.

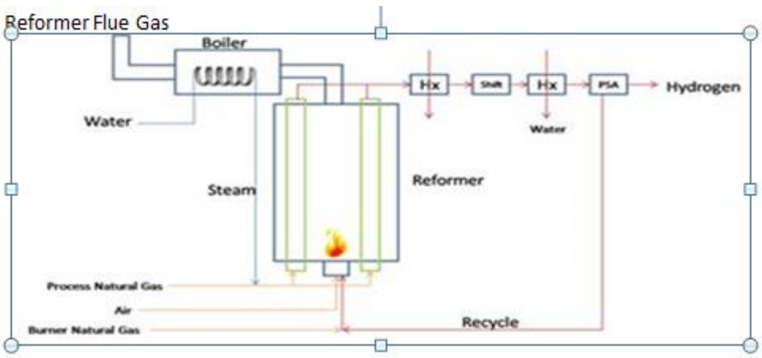


*Figure 5 Typical Process Flow Diagram for Conventional Steam Methane Reforming*

The process is typically conducted in tubular, catalyst-packed reactors with the endothermic heat of reaction supplied in a furnace (using natural gas plus purge gases from downstream operations as fuels). Heat is recovered from flue gases for feed gas preheating and to raise high-pressure steam in waste heat boilers.

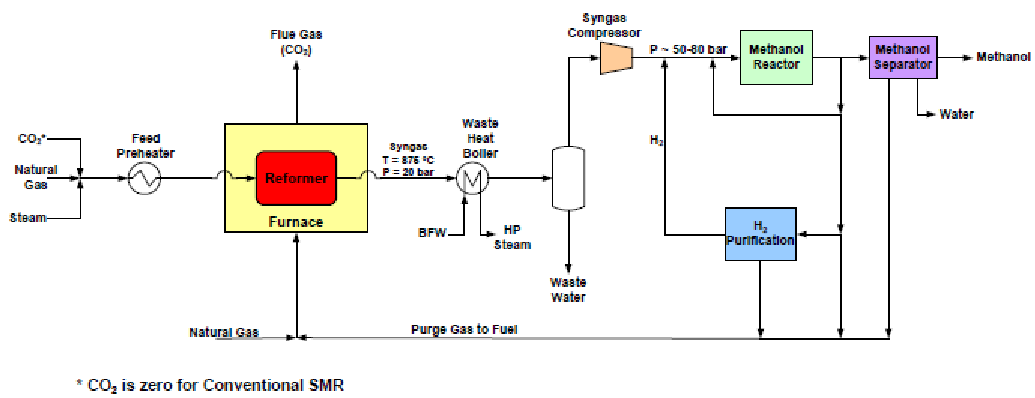


*Figure 6 Potential Use of $CO_2$-rich Feed Gas for Syngas Production in a Methanol Plant*

Key advantages of the SMR technology for GTL applications include: (1) no need for a capital-intensive oxygen unit, and (2) capability for handling $CO_2$-rich natural gas feed or use of $CO_2$-rich streams if available, say as a waste stream at a given plant location (as shown schematically, for methanol production, in Figure 6). The key disadvantages of the SMR technology are: (1) a need for relatively high S/C ratio (~3.0 for conventional SMR catalysts) in the inlet feed, (2) high $H_2$/CO ratio (>3) in product syngas, thereby requiring significant downstream processing for GTL applications, (3) relatively high $CO_2$/CO ratio in syngas and thus, higher $CO_2$ removal costs, (4) limited capability for producing syngas at relatively high pressures due to metallurgical limitations of catalyst-packed tubular reactors, and (5) relatively high costs in capturing $CO_2$from the reformer flue gas.

#### *Conventional Catalytic ATR (Autothermal Reformer)*

Unlike non-catalytic partial oxidation reforming, "autothermal reforming" uses a catalyst to reform the natural gas to syngas in the presence of oxygen plus steam. Due to the use of milder operating conditions (exit temperatures of ~1,000 - 1,100 °C) and the use of relatively high S/C molar ratio, the syngas is soot free. As shown in Figure 7, for a FT-GTL process, Haldor-Topsoe (HTAS) has demonstrated commercially the production of syngas with a $H_2$/CO ratio of ~2.0 by using an S/C ratio of ~0.6 and by recycling a part of the $CO_2$-rich Tail-gas from the FT section[7,8].

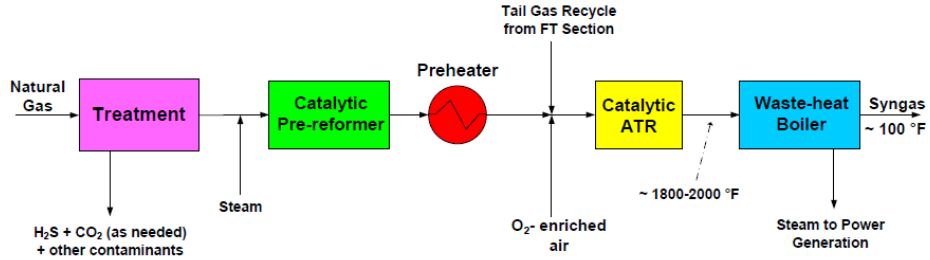


*Figure 7 Typical Process Flow Diagram for a Conventional Catalytic ATR Process for FT*

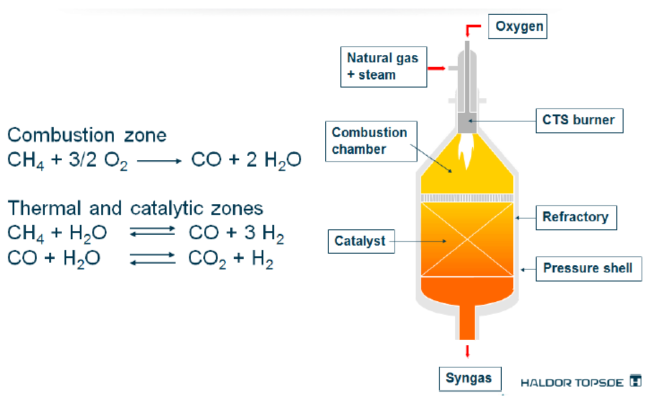


*Figure 8 A Schematic of the HTAS ATR Reactor*

A schematic of the HTAS ATR reactor and key chemical reactions that occur in the reactor are shown in Figure 8[8].

#### *Haldor Topsoe ATR/GHR Integration to Reduce Cost for Syngas Production*

One of the primary cost components in the front-end of a POx or ATR-based GTL plant is the air-separation unit (ASU). Specific engineering improvements in reducing oxygen usage will significantly reduce net costs for a GTL plant. According to HTAS, use of a lower S/C ratio improves the syngas composition and reduces the extent of tail gas recycle[7]. However, the use of a lower S/C ratio also reduces the margin to carbon formation in the pre-reformer and to soot formation in the ATR reactor. HTAS is collaborating with Sasol Inc. in demonstrating novel integrated ATR and HTER (Haldor Topsoe Exchange Reformer; also referred to as GHR : Gas Heated Reformer) process options in reducing overall costs for syngas generation in a FT process[9]. As shown in Figure 9, two different design options (namely, a parallel arrangement and a series arrangement) are being evaluated for an optimum ATR/GHR configuration.

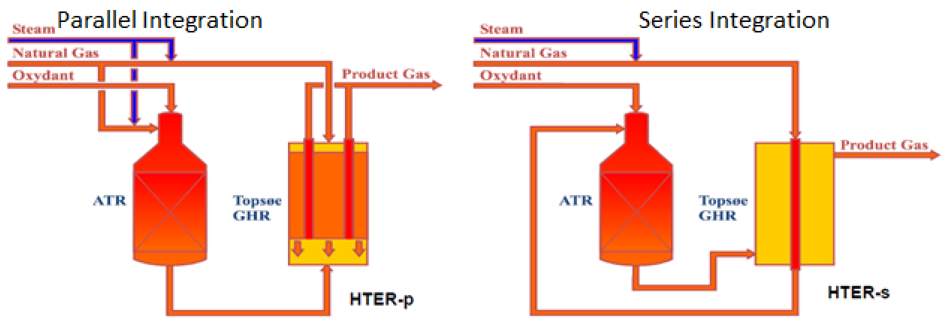


*Figure 9 Typical Flow Diagram for Haldor Topsoe ATR + GHR (Haldor Topsoe Gas Heated Reformer)*

As shown in Table 1, according to HTAS[7], the ATR/GHR options provide substantial cost reductions compared to their stand-alone commercial ATR technology,

*Table 1 Impact of Reduced S/C ratio on ATR and ATR/GHR Performance*

| Design Case | ATR (Base) | ATR (Advanced) @ Lower S/C | ATR with Series GHR |
|---|---|---|---|
| S/C ratio | 0.6 | 0.4 | 0.4/0.55 |
| $O_2$ Usage, Tonnes/bbl Produced Index | 100 | 92 | 81 |
| Total LHV Efficiency Index | 100 | 105 | 109 |
| ASU CAPEX, $/bbl/day Index | 100 | 83 | 74 |
| SGP CAPEX, $/bbl/day Index | 100 | 69 | 76 |
| ASU + SGP CAPEX, $/bbl/day Index | 100 | 76 | 75 |

## GTI's PATENTED POGT CONCEPT FOR CO-PRODUCING SYNGAS PLUS ELECTRICTY FROM NATURAL GAS

With financial assistance from ARPA-E, GTI is currently collaborating with AR to further develop GTI's patented (US # 7,421,835-B2 and 8,268,896-B2) POGT (Partial Oxidation Gas Turbine) concept for low-cost gas-based syngas generation using AR's Turbo-POx[10] technology for various GTL and GTP (Gas-to-Products) processes. In a conventional POx/ATR or a SMR technology, the hot syngas product from the SGP step is cooled to 35 - 40 °C in a typical WHB. In the POGT concept, the hot syngas at ~1,090 - 1,320 °C and at ~500 - 1,500 psia from a partial oxidation reactor would be cooled rapidly in less than ~ 6 milliseconds to about 1,100 °F (~593 °C) and ~150 - 200 psia using a turbo-expander to co-produce electricity and steam. In the AR's Turbo-POx option, where the AR non-catalytic POx technology is integrated with AR's "Reducing Turbo-Expander", a patented (US # 6,565,312) "regenerative" cooling design for the expander blades[10,] would be implemented. The S/C molar ratio in the AR POx reactor would typically be ~0.2 - 0.3.

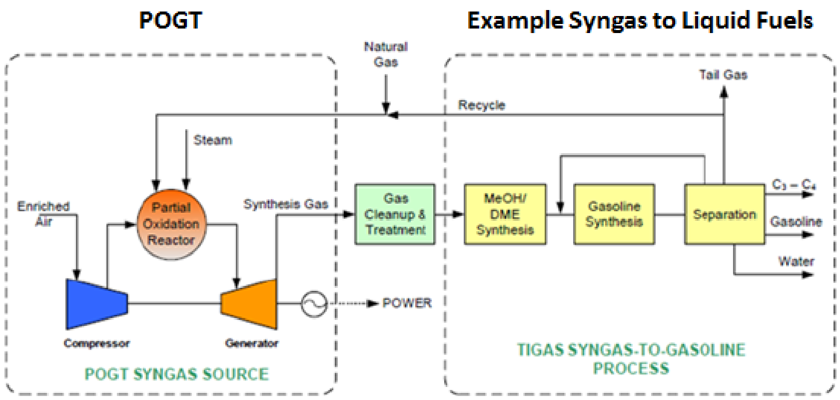


*Figure 10 GTI's Patented POGT Syngas Generation Concept using AR's Turbo-POx for GTL Applications*

As shown in Figure 10, the syngas effluent from the expander will be further cooled to ~ 35 - 40 °C in a relatively small WHB to raise additional HP steam and to remove a major fraction of the water in the syngas. The syngas would then be re-compressed to a higher pressure, depending on the back-end GTL process. In Figure 10, the HTAS TIGAS technology[5] is shown as the back-end GTL option. A typical product slate in the ExxonMobil MTG type GTL process would be ~ 86 volume% zero-sulfur high-octane gasoline and ~14% LPG. The POGT concept can be integrated with a variety of back-end process options including ExxonMobil MTG, Primus STG+, and Velocys micro-channel FT process[11].

### AR Gas-based POx Development Reactor at GTI

POx Development Combustor at GTI

*Figure 11 AR POx Development Combustor at GTI*

As shown in Figure 11, under the ARPA-E program, AR and GTI have been testing an AR POx combustor and the associated injector at ~10 tonnes/day natural gas feed at GTI. A similar AR reactor was used at GTI for AR's dry-coal feed gasification process using oxygen plus steam. It is anticipated that for a commercial 1,000 barrels/day POGT capacity, there would be 12 closely coupled such POx combustor cans per expander. The GTI testing involves a chamber pressure of 400 psia. This ARPA-E project also includes: (1) design studies by AR for their turbo-expander and (2) techno-economic assessment by GTI for two GTL design cases, namely for a 1,000 bbl/day of FT diesel/naphtha case, and the other for a 10,000 bbl/day MTG plant producing gasoline plus LPG.

### AR Expander Development

Under the ARPA-E program, AR is evaluating specific options for the optimum design of a "Reducing Gas Expander" that can be used in a 1,000 barrels/day GTL plant; the schematic of a generic example for such an expander is shown in Figure 12[10]. As shown, this design refers to an inlet syngas pressure of ~1500 psia with a temperature of ~2,395 °F (~1,313 °C); the outlet pressure would be ~150 psia with a temperature of ~ 1,072 °F (~578 °C). For such a plant, the nominal power output from the expander would be ~6 $MW_e$. The stator blades would be "regen-cooled" rather than film cooled to provide higher system efficiency. In this design, 1700 psia saturated-steam (100% quality) would be generated.

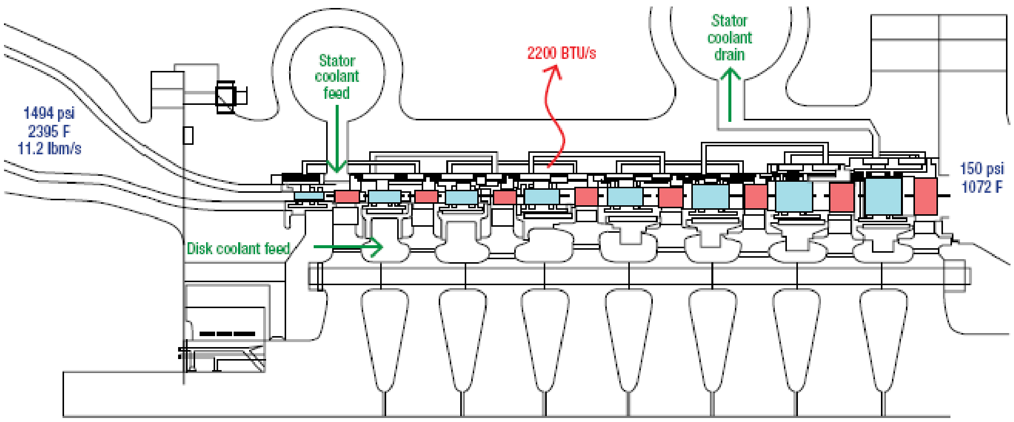


*Figure 12 Schematic of a Specific Design for AR's Reducing Gas Expander*

### *Specific Details on the AR Reducing Gas Expander*

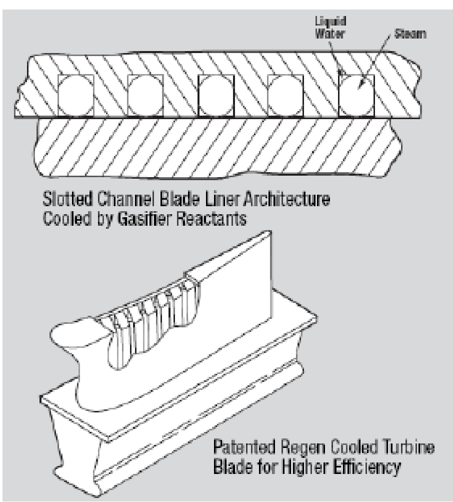


*Figure 13 Specific Details on the AR Reducing Gas Expander*

For the AR "Reducing-Gas Turbo-Expander" technology, the current in-house expertise has evolved from AR's liquid rocket-engine rotating machinery design practices. For the high-temperature and high-pressure reducing gas environment involving syngas, suitable materials would be used to mitigate hydrogen embrittlement (namely, generation of detrimental metal hydrides) as well as carbon monoxide (carbon dusting) embrittlement (primarily, generation of detrimental metal carbides)[10]. The syngas residence time in the expander would be kept at ~6 milliseconds or less to suppress carbon soot. The design of the turbine blades would involve AR's patented (US # 6,565,312; 2003) regenerative cooling methods (Figure 13) to produce high-pressure steam for use in other process units (e.g., in the POx combustor and to generate auxiliary power).

## KEY POTENTIAL ADVANTAGES FOR TURBO-POx vs. CATALYTIC ATR

### *Estimates on Capital Costs (CAPEX) for Steam-based Systems in an ATR-based FT Plant*

The use of a conventional WHB in a catalytic-ATR type SGP for a FT plant leads to significant CAPEX for steam-based power generation and related steam systems. Typical literature data for a 16,630 barrels/day FT are presented in Table 2[1].

*Table 2 Specific Details on the AR Reducing Gas Expander*

| | | Comment |
|---|---|---|
| Gross power generation, $MW_e$ | 140 | Estimate by GTI |
| | | |
| CAPEX, $Million | | |
| Catalytic ATR | 162 | Ref. 1 |
| Steam-based power generation systems | 181 | Ref. 1 |
| Boiler feed water & steam systems | 91 | Ref 1 |

As shown in Table 2 Specific Details on the AR Reducing Gas Expander, the CAPEX for steam-based power generation units plus the steam systems was estimated (by Hatch Inc.) at about $272 Million compared to $162 MM for the ATR itself. In the Turbo-POx case, about 60-70% of the electricity would be generated by the expander itself; in addition, some high-pressure steam would also be generated in the expander.

### *Key Potential Advantages for Turbo-POx over Conventional Catalytic ATR*

For syngas generation in GTL applications, key potential advantages of the Turbo-POx concept over conventional catalytic ATR processes would be:

- The close-coupled compact design of the non-catalytic AR POx reactor and the expander would be very suitable for shop fabrication and for small-scale modular GTL plants.
- Unlike in a catalytic-ATR design, there is no need for a catalytic pre-reformer; this would help reduce overall capital cost as well as operating costs (OPEX) savings related to the pre-reformer catalyst. In addition, there would be significant reduction in OPEX as no catalyst would be required for the AR POx reactor.
- The usage of significantly lower S/C ratio (e.g., 0.2 vs. 0.6 for ATR) in a Turbo-POx design would significantly reduce oxygen requirement as well as the extent of Tail-gas recycle in a FT process which would lead to significant reductions in: (1) total volumes for POx as well as for FT reactor units, (2) compression costs for Tail-gas recycle and (3) total electric power need due to reduction in oxygen usage.
- Significantly reduced capacities and lower CAPEX/OPEX costs for waste-heat boiler, steam turbine power-generation unit and steam systems.

## SUMMARY AND CONCLUSIONS

- The AR/GTI Turbo-POx based GTL plants offer potential economic advantages in relation to conventional POx and ATR GTL processes
- The regen-cooled expander design needs further maturity to meet expander life requirements in reducing syngas environment
  - A 1,000 barrels/day integrated POx reactor/expander system needs to be demonstrated at a brown-field site. Testing should include: (1) soot-free, metal-

dusting free syngas generation at low S/C ratio, (2) risk mitigation of key expander components, including expander-blade life, and (3) expander performance mapping and long duration test efforts.

## ACKNOWLEDEMENT

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