

JET FUEL PRODUCTION AT THE PITTSBURGH AIRPORT: GTL VIA FISCHER-TROPSCH SYNTHESIS

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ACRONYMS AND ABBREVIATIONS

AD	Anaerobic digestion	hr	Hour
Ar	Argon	H ₂	Hydrogen
Aspen	Aspen Plus®	H ₂ /C	Hydrogen to carbon
ASTM	American Society for Testing Materials	H ₂ O	Water
ASU	Air separation unit	H ₂ S	Hydrogen sulfide
ATR	Autothermal reformer	HC	Hydrocracking
B	Billion	HDS	Hydrodesulfurization
bbl	Barrel	HI	Hydroisomerization
BFW	Boiler feed water	HP	High pressure
BP	British Petroleum	HPS	High pressure steam
BPD	Barrel per day	hr	Hour
Btu, BTU	British thermal unit	HS	Hot separator
C _α -C ₁₀₀	Hydrocarbons	HX	Heat exchanger
CCS	Carbon capture and storage	ID	Inner diameter
CH ₄	Methane	in.	inch
Co	Cobalt	kg	Kilogram
CO	Carbon monoxide	kmol	Kilomole
CO ₂	Carbon dioxide	KO	Knockout
CO ₂ e	Carbon dioxide equivalent	kW	Kilowatt
CS	Cold separator	kWh	Kilowatt-hour
CSA	Cross-sectional area	L/D	Length to diameter
CTL	Coal-to-liquids	lb	Pound
CW	Cooling water	lbmol	Pound mole
DOE	Department of Energy	LCA	Life cycle analysis
EFT	Emerging Fuels Technology	LFG	Landfill gas
EOR	Enhanced oil recovery	LHSV	Liquid hourly space velocity
EPC	Engineering, procurement, and construction	LHV	Lower heating value
FEED	Front end engineering and design	LP	Low pressure
FG	Flue gas	LPS	Low pressure steam
ft	Foot, feet	LPG	Liquefied petroleum gas
FT	Fischer-Tropsch	M	Thousand
ft ²	Square feet	m ³	Cubic meter
ft ³	Cubic foot	MFEC	Microfiber-entrapped catalyst
g	Gram	MJ	Megajoule
gal	Gallon	MM	Million
GHG	Greenhouse gas	Mo	Molybdenum
GHSV	Gas hourly space velocity	MP	Medium pressure
REET	Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation Model	MPS	Medium pressure steam
GTL	Gas-to-liquids	MSW	Municipal solid waste
		MTFB	Multi-tubular fixed bed
		MW, MWe	Megawatt electric
		N ₂	Nitrogen

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NETL	National Energy Technology Laboratory	scf	Standard cubic feet
		scfd	Standard cubic feet per day
NG	Natural gas	Sep	Separation
Ni	Nickel	SMR	Steam methane reformer
O&M	Operating and maintenance	syngas	Synthesis gas
O ₂ /C	Oxygen to carbon	SRI	Southern Research Institute
O ₂	Oxygen	SRN	Straight-run naphtha
OD	Outer diameter	STM	Steam
PGM	Platinum group metal	TG	Tail gas
PIT	Pittsburgh international Airport	tonne	Metric ton (1,000 kg)
PRF	Pre-reformer	U.S.	United States
PSA	Pressure swing adsorption	UCO	Unconverted oil
psig	Pound per square inch gauge	USAF	United States Air Force
Q	Quarter (year)	v	Volume
R&D	Research and development	VSA	Vacuum swing adsorption
R/F	Recycle to fresh feed	WGS	Water gas shift
RNG	Renewable natural gas	WHB	Waste heat boiler
ROR	Reduction/oxidation/reduction	WHRU	Waste heat recovery unit
S/C	Steam to carbon	ZnO	Zinc oxide
SBCR	Slurry bubble column reactor	°C	Degrees Celsius
		°F	Degrees Fahrenheit

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EXECUTIVE SUMMARY

The Pittsburgh International Airport (PIT)—with the Allegheny County Airport Authority (which manages PIT)—has established itself as a leader in resiliency by becoming the first major United States (U.S.) airport to have a self-sustaining microgrid, providing electricity, heating, and cooling for airport operations.[1] [2] [3] The microgrid is powered by natural gas and solar power produced on the airport property and was completed in Summer 2021. [4] This study examines the feasibility of producing jet fuel at the airport to provide a secure supply of aviation fuel, furthering PIT’s ability to weather supply disruptions and operate self-sufficiently.

Gas-to-liquids (GTL) is a commercially available technology that converts natural gas to liquid hydrocarbons, including synthetic jet fuel. A GTL facility at PIT could convert natural gas from onsite wells to jet fuel, effectively doubling the onsite fuel stores in the event of a supply disruption.^a [5] Moreover, GTL provides a pathway to renewable jet fuel production and reduced greenhouse gas (GHG) emissions from the aviation sector, particularly if renewable natural gas (RNG) is used as a feedstock or other renewable energy sources are used for energy inputs.

This study has found that it would be technically feasible to construct and operate a GTL facility on PIT’s property. The approximately 6,000-barrel per day (BPD) facility evaluated would produce nearly 70 million (MM) gallons (gal) of synthetic jet fuel per year, which could supplant nearly all (85 percent) current jet fuel consumption at PIT. Given the current blend limitation of 50 percent Fischer-Tropsch fuels by volume, the plant would have excess production capacity available for the United States Air Force (USAF) Pittsburgh Air Reserve Station and the USAF 171st Air Refueling Wing co-located at the airport.

The cost competitiveness of the jet fuel produced—and, therefore, the economic feasibility of the project—is highly dependent on the price of the natural gas fed into the facility. The jet fuel selling price is estimated to be \$1.69–2.37/gal over the \$1–3/MM British thermal unit (Btu) range of natural gas prices evaluated. The sale price includes operating costs and includes the developer’s return on investment. This compares to current jet fuel prices of \$1.88/gal, and a fuel price range of \$0.41/gal (April 2020 during the COVID-19 Pandemic) to over \$4/gal (July 2008). [6] Broadly speaking, the project should be economically viable at natural gas prices of \$1/MMBtu or lower, and in some scenarios a price of \$2/MMBtu may be viable.

The 6,000-BPD facility would cost \$550–740 MM to construct depending on the facility configuration, with higher levels of GHG abatement increasing the facility cost to as much as \$820 MM. The facility could be constructed in four years, including permitting and front-end engineering and design (FEED) phases.

GTL offers an intriguing near-term opportunity for reducing the climate impacts of aviation by generating less emissions than conventional, petroleum-derived fuels and the opportunity also exists to completely decarbonize transportation fuels through the use of carbon-neutral or carbon-negative feedstocks. Nowhere in the transportation sector is this more important than for air

^a While the jet fuel produced at the GTL facility evaluated in this study can be used on its own in a jet engine, it is only certified for use in blends with conventional jet fuel. The American Society for Testing Materials (ASTM) standard regulating synthetic aviation fuels and their certification is ASTM D7566. The synthetic aviation fuel evaluated for this study is produced via Fischer-Tropsch synthesis, which is certified for blends up to 50 percent by volume with conventional jet fuel, meaning existing onsite fuel stores of conventional jet fuel would last twice as long. [151]

transportation where there are limited options for replacing the means of propulsion and doing so safely.

Technologies to reduce or fully decarbonize GTL fuels fall into three broad categories: 1) direct reduction of emissions from the GTL facility, 2) use of alternative carbonaceous feedstocks with reduced upstream GHG emissions, and 3) integration of net-zero or net-negative GHG energy into facility operation. This study examined the direct reduction of emissions by implementing carbon capture and storage (CCS) and found that 58 percent of facility emissions could be eliminated at a very low cost—\$0.16/gal—while a more aggressive approach to CCS could eliminate 95 percent of emissions at a slightly higher cost, an estimated \$0.34/gal increase in selling price of the jet fuel. Both cases assume the use of an autothermal reformer (ATR) for synthesis gas (syngas) production.

Two additional climate impact reduction pathways were examined as sensitivity cases: 1) the use of renewable natural gas as a feedstock and 2) the implementation of dry-reforming to convert a higher percentage of the feedstock carbon into jet fuel. Combined, these pathways have the potential to reduce the demand for onsite natural gas by approximately 17–24 percent depending on the level of carbon dioxide (CO₂) capture pursued. Both are considered near-term opportunities, as the technologies required to implement them are commercially available. Pathways to totally decarbonize jet fuel, such as the direct conversion of CO₂ captured from the atmosphere to synthesis gas, were not evaluated in this study but represent an area for future study.

While GTL is a proven technology, substantial headroom for improved performance exists both in the near term through technologies that are just entering the market and in the longer term with more nascent technologies. These longer-term opportunities are rapidly advancing under Department of Energy-funded research initiatives and—as alluded to in the previous paragraph—provide the opportunity for jet fuel with dramatically reduced or even net-negative GHG emission fuels. This study was limited in scope to commercially available technologies in the interest of evaluating a facility that vendors would be willing to construct immediately. However, areas for future study are identified to more fully explore how different configurational options or technological advancements could improve the performance of a GTL facility.

Lastly, the creation of a GTL facility at PIT has the potential to become a living laboratory and test bed for further technological advances. The proximity to several premier academic, industrial, and governmental research institutions; abundant supplies of domestic natural gas; and a regional commitment to energy innovation all underscore this potential. Such a facility could provide a range of potential opportunities, from the ability to test newly developed catalyst technologies for CO₂ conversion into jet fuel on a slipstream of syngas from the facility to the development of multi-scale models from real process data to inform future GTL plant operation and the next generation of GTL process designs. If successful, this innovation center will have wide ranging impacts, including creating new opportunities for gas that is currently being flared to be monetized, expanding opportunities for RNG utilization, reducing environmental impacts, and broadening the applicability of the GTL technology to feedstocks such as wastes and biomass.

1 INTRODUCTION

1.1 BACKGROUND

In December 2017, a 10-hour power outage at the Hartsfield-Jackson Atlanta International Airport resulted in approximately \$40 million (MM) in losses for Delta Airlines, along with 1,400 cancelled flights, and 30,000 stranded passengers. [7] [8] This outage and similar, lesser magnitude outages at other major airports have brought attention to the potential impacts of power disruptions, and more broadly, energy supply chain disruptions to the airline industry.^b

The Pittsburgh International Airport (PIT) and the Allegheny County Airport Authority (ACAA) (which manages PIT) made a commitment to focus on ensuring resilient and reliable operations, announcing in 2019 plans to construct a microgrid to power the entire airport. [1] The project uses natural gas and solar power produced onsite to make PIT the first major United States (U.S.) airport to have a self-sustaining microgrid, providing electricity, heating, and cooling for airport operations. [2] [3] Construction began on the microgrid in July 2020 and was completed in the Summer of 2021. [4]

This study examines whether further resiliency could be brought to PIT by producing jet fuel at the airport using natural gas produced from wells located on the property. Gas-to-liquids (GTL) is an existing, commercially available technology pathway to produce synthetic jet fuel. While this fuel can be used on its own, standard practice is to use a 50 percent blend with conventional jet fuel, meaning existing onsite fuel stores would last twice as long in the event of a supply disruption.^c [5] Moreover, GTL provides a pathway to renewable jet fuel production and reduced greenhouse gas (GHG) emissions from the aviation sector, particularly if renewable natural gas (RNG) is used as a feedstock or other renewable energy sources are used for energy inputs. Opportunities also exist for the complete decarbonization of jet fuel by leveraging net-zero or net-negative GHG emissions feedstocks.

To assess the feasibility of this concept, the commercial availability of various GTL technologies was analyzed to identify likely candidates, and a techno-economic analysis was performed to determine the projected project cost, fuel price, and environmental performance of such a facility. The GTL designs evaluated would produce nearly 70 MM gallons (gal) of synthetic jet fuel per year, which could supplant up to 85 percent of current jet fuel consumption, leaving the potential for increased levels of fuel consumption at PIT in the future or potential resiliency benefits for the United States Air Force (USAF) Pittsburgh Air Reserve Station co-located at the airport, which includes the USAF 171st Air Refueling Wing.

The study also identifies areas for future study to more fully explore how different configurational options or technological advancements could improve the performance of a GTL facility or otherwise support Pittsburgh becoming a center for energy innovation. While GTL is a proven technology, substantial headroom for improved performance exists and the creation of a GTL

^b Outages have also disrupted operations at Ronald Reagan Washington National Airport; Los Angeles International Airport; [154] New York's LaGuardia Airport; John Wayne Airport in Orange County, California; Philadelphia International Airport; McCarran International Airport in Las Vegas, Nevada; and Louis Armstrong New Orleans International Airport. A separate power outage at the Hartsfield-Jackson Atlanta International Airport in 2016 caused a computer system outage that resulted in an estimated \$150 MM in losses for Delta Airlines. [149]

^c The American Society for Testing Materials (ASTM) standard regulating synthetic aviation fuels (SAF) and their certification is ASTM D7566. The SAF evaluated for this study is produced via Fischer-Tropsch synthesis, which is certified for blends up to 50 percent by volume with conventional jet fuel. [151]

facility at PIT has the potential to become a living laboratory and test bed for further technological advances. These range from the opportunity to test newly developed catalyst technologies for carbon dioxide (CO₂) conversion into jet fuel on a slipstream of synthesis gas (syngas) from the facility to the development of multi-scale models from real process data to inform future GTL plant operation and the next generation of GTL process designs. If successful, this innovation center will have wide ranging impacts, including creating new opportunities for gas that is currently being flared to be monetized, expanded opportunities for RNG utilization, reduced environmental impacts, and broadening the applicability of the GTL technology to feedstocks such as wastes and biomass.

1.2 OBJECTIVES AND SCOPE

The objective of this study is to determine the technical and economic viability of a prospective small-scale GTL facility located at or near PIT to improve the resiliency of PIT operations.^d This work focuses on GTL via Fischer-Tropsch (FT) synthesis, which is a commercially available and widely demonstrated pathway.^e Development of such a facility could be initiated immediately.

The scope of this work includes identification and selection of commercial GTL technologies that could be located at PIT, modeling of the facility performance, assessment of equipment and production costs, and evaluation of the life cycle impacts of the fuels produced. Two potential GTL plant configurations were evaluated in order to more fully inform stakeholders of the range of the costs and performance of the facility. The use of carbon capture and storage (CCS) to reduce the life cycle GHG impacts of the jet fuel produced from the facility was also evaluated. Not covered in this study are a number of new GTL technologies and pathways which are under active development, including several pilot- and demonstration-scale facilities.

Prior Department of Energy (DOE) National Energy Technology Laboratory (NETL) GTL studies were leveraged to provide insights on the broad technical and economic aspects of a domestic GTL facility. [9] [10] This includes the use of equipment and operating cost data, project financing assumptions, and technical performance and design aspects of certain portions of the facility.

Notably, this work identifies future areas of study to better understand the economic and environmental performance of a GTL facility located at the airport. This includes a more in-depth look at natural gas production costs from onsite wells, the selection of two or more cases of more detailed modeling and cost analysis, and a further investigation into the environmental impacts of GTL jet fuel as compared to conventional fuel. Future work should include an assessment of geologic formations capable of CO₂ storage within a 100-mile radius of PIT and a more detailed examination of the cost of CO₂ transport and storage. There are believed to be several formations that meet these criteria based on previous DOE projects; [11] [12] [13] other entities have reportedly characterized formations for other projects in the nearby vicinity.

1.3 HISTORY OF GTL AND PRIOR WORK

GTL is a process that converts natural gas to liquid fuels such as gasoline, diesel, and jet fuel rather than producing these fuels from crude oil. While several GTL pathways exist, this study focuses on the FT synthesis route in which natural gas is first converted to syngas and subsequently into

^d Small-scale GTL is considered to be in the 5,000 barrels per day of production. The world's largest GTL facility produces 260,000 barrels of GTL products and natural gas liquids per day. [150]

^e A detailed discussion of FT GTL projects that are operating or under development can be found in Section B.2.5 in Appendix B: Fischer-Tropsch Technologies.

hydrocarbons (liquid hydrocarbons and aliphatic compounds) via the FT process, typically leveraging iron- or cobalt-based catalysts.^{f,g}

FT technology reaches back to the 1920s and was first applied in areas where conventional fuels were unavailable or in limited supply, or where valuable feedstocks such as natural gas were ‘stranded.’ Stranded refers to the situation when infrastructure (e.g., pipelines) is insufficiently developed and/or the distance to market too long to allow an asset (e.g., natural gas) to be brought to market and capture its full value.

NETL has a long history (dating from the 1940s) in the development and demonstration of FT and other synthetic transportation fuel production processes. This includes the development of pilot projects, new catalysts for improved performance, extensive techno-economic modeling of process performance, and more recently, extensive life cycle analysis. These remain active areas of research as NETL works to unlock the promise of low-cost, low-environmental-impact transportation fuels.

^f A more detailed overview of F-T synthesis can be found on the NETL website:
<https://www.netl.doe.gov/research/coal/energy-systems/gasification/gasifipedia/ftsynthesis>

^g Syngas is a mixture of carbon monoxide by hydrogen, so named because of its utility in synthesizing other compounds such as synthetic fuels, natural gas, ammonia, and methanol.

2 GTL PROCESS OVERVIEW AND DESIGN BASIS

The purpose of this study is to identify a commercially available technology for the production of jet fuel at PIT using natural gas from co-located natural gas wells and to determine the commercial viability of such a facility. Several potential facility designs of the selected technology were screened to understand the relative economic and environmental performance and to inform design criteria and selection.

The designs being evaluated would produce nearly 70 MM gal of synthetic jet fuel and other products per year, which could supplant nearly all (85 percent) of current jet fuel consumption. While synthetic jet fuel can be used on its own, normal practice is to use a 50 percent blend with conventional jet fuel, meaning existing on-site fuel stores would last twice as long in the event of a supply disruption.

2.1 DESIGN BASIS

The production of jet fuel from natural gas at PIT should be done in a manner that improves the resilience of the airport to supply disruptions. The feasibility of such a project is determined by the following criteria:

1. Produces enough synthetic jet fuel to meet a substantial portion of current fuel consumption at PIT
2. Consumes natural gas at a rate understood to be sustainable based on current production from natural gas wells located at the airport
3. Fuel production costs within an acceptable range of historic or projected conventional jet fuel prices
4. Environmental impacts within an acceptable range of or below those of conventional jet fuel

A GTL facility that produces 5,000 barrels per day (BPD) of synthetic jet fuel (and nearly 6,000 BPD of total FT products) was selected for evaluation based upon these design constraints. This facility size would produce synthetic jet fuel up to 85 percent of PIT jet fuel consumption while consuming less natural gas than is currently produced onsite.^h While this facility might be slightly larger than necessary for PIT based on synthetic fuel blending specifications, smaller facility sizes may result in higher fuel prices due to reduced economies of scale. The potential for over-production was, therefore, viewed as an acceptable design trade-off for initial study.ⁱ This topic is revisited in Section 4, along with the potential implications for the USAF 171st Air Refueling Wing, the Air National Guard unit located at PIT.

Several plant configuration options were explored to ascertain their impacts on the environmental impacts and production price of synthetic jet fuel. These include the use of CO₂ capture and storage or utilization to reduce the life cycle GHG impacts of the fuel, a range of natural gas production prices, and the use of pipeline natural gas as opposed to natural gas produced onsite.

^h The synthetic fuels facility will produce a number of liquid products, including synthetic jet fuel. The actual amount of PIT jet fuel needs met by such a facility is dependent on the fraction of jet fuel produced, or the jet fuel yield.

ⁱ Synthetic jet fuel can be used on its own, or "neat", but is only certified for blends of up to 50 percent by volume with conventional fuel per ASTM D7566.

2.2 GTL PROCESS SELECTION

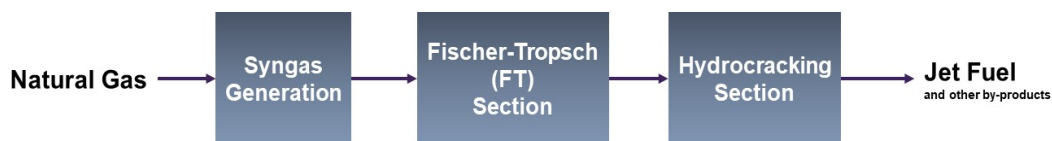
There are several pathways for the production of jet fuel from natural gas, all of which fall under the broad umbrella of GTL. These pathways range in technological maturity. Some pathways, such as FT synthesis, are commercially available from vendors, meaning a facility could be designed and constructed today. Other pathways are less technologically mature, having been tested at the pilot- or demonstration-scale. These less mature pathways carry with them a greater risk of deployment.

GTL via FT synthesis was selected for evaluation in this study based on the key design consideration of selecting a GTL pathway that could be constructed immediately. While FT is a technologically mature pathway, advances are still being made to make these GTL systems more efficient and economically competitive. Some of these advances are sufficiently mature to have been included in this study, such as catalysts that provide improved yields to jet fuel over other products. Others, such as dry- or tri-reforming are still considered to be more novel and still on the horizon. These more nascent technologies were not included in this study but represent additional opportunities to advance the performance of FT GTL.

2.3 GTL PROCESS OVERVIEW AND UNIT OPERATIONS

The FT GTL process consists of three primary plant sections in series, as shown in Exhibit 2-1. This section provides an overview of each plant section and pertinent information on design considerations for that section. Information is also provided on design decisions and ancillary portions of the plant, where pertinent. The main design considerations are the method of syngas generation and whether CCS is leveraged for CO₂ emissions reductions, although several other sensitivity cases were also performed.

Exhibit 2-1. Block flow diagram of the overall process with main sections



Appendix B: Fischer-Tropsch Technologies provides a comprehensive discussion of the technologies and design choices described in this study and also contains an overview of existing FT GTL technology vendors and the commercial maturity and availability of those technologies.

2.3.1 Natural Gas Feedstock Selection

Natural gas is produced on the PIT property from wells operated by CNX resources. This gas is considered “wet gas” as it contains high levels of natural gas liquids such as ethane and propane, which is common for the Marcellus region. PIT also receives natural gas via pipeline from Peoples Gas. The pipeline gas varies in composition and heat content from the wet gas produced on site.

The comparative impacts of using onsite wet gas versus pipeline gas were also evaluated, as described in Section 5.1.

2.3.2 Syngas and Hydrogen Production

The syngas production portion of the plant consists of a syngas generator and ancillary equipment to treat the natural gas coming into the plant, including a pre-reformer.

Two syngas generation pathways were considered: steam methane reforming (SMR) and autothermal reforming (ATR), both commercially available technologies. The GTL process requires syngas with a hydrogen (H_2) to carbon monoxide (CO) ratio of 2 for optimal performance, which both the SMR and ATR can provide.^j The performance of the technologies varies, producing (or consuming) different amounts of water, CO_2 , and natural gas.

In both cases, high-pressure steam is generated from the exothermal reaction of syngas generation. This steam is used to generate electricity for ancillary equipment and, in some cases, for sale into the market.

A H_2 separation unit is also included in this portion of the plant. Hydrogen is removed from the syngas for use in the fuel upgrading portion of the facility, specifically in the hydroisomerization (HI) unit. This is carried out using a commercial pressure swing adsorption (PSA) process. As described in Section 5.3, a sensitivity case was performed on which additional H_2 (beyond the needs of the GTL process) is produced for sale outside the facility.

Lastly, it should be noted that the ATR plant configurations require oxygen (O_2) for syngas production. While this study assumes the O_2 is produced over-the-fence and supplied via pipeline by a partner, O_2 could also be produced onsite at the facility. The different options for O_2 production and the economic tradeoffs of these options are described in Section 4.2.2.3.3.

2.3.3 Fischer-Tropsch Synthesis

This FT synthesis unit is composed of a multi-tubular fixed bed (MTFB) reactor that is fed with syngas.

Cobalt-based FT catalysts were selected as they do not have water gas-shift (WGS) activity, and they produce fewer oxygenates and more saturated products relative to iron-based catalysts.^k This leads to lower H_2 requirements for product upgrading. Additionally, these systems are considered to have superior deactivation resistance and can take advantage of significant, recent commercial FT catalyst research and development (R&D). [14] A syngas ratio (H_2/CO) of approximately 2 was selected to align with the product ratio of the desired transportation fuel products, dictating the technology choice of converting natural gas to syngas. The MFTB is preferred over the slurry bubble column reactors (SBCR) in these scenarios.

The FT process produces a mixture of hydrocarbon liquids and gases ranging from methane (CH_4) to C_{100+} , a large amount of medium-pressure steam, and unreacted syngas. The unreacted syngas and select hydrocarbon gases, along with the select hydrocarbon gases produced from the FT liquid upgrading portion of the facility, are referred to as FT tail gas.

The FT tail gas is used differently depending on the choice of syngas generation. In both the SMR and ATR cases, a portion of the FT tail gas is used for natural gas feed pre-heating and the remaining tail gas is recycled into the SMR or ATR. The recycle levels will be dictated by maintaining a H_2/CO ratio of 2 exiting the SMR or ATR.

^j The H_2/CO ratio of 2 is dictated by the use of cobalt catalysts, common for syngas feedstocks containing more H_2 than carbon. Feedstocks containing larger amounts of carbon (proportionally) could use a different catalyst and require a different H_2/CO ratio.

^k WGS activity would be undesirable for a syngas feedstock that already has a high H_2/CO ratio.

2.3.4 Hydrocracking and Fuel Upgrading

The FT process produces hydrocarbons of carbon chain lengths ranging from 1 carbon atom (CH₄) to more than 100 carbon atoms (C₁₀₀₊). The hydrocracking (HC)/HI unit process converts larger carbon chain products into the appropriate range for jet fuel. The liquid product from the FT unit includes hot wax, intermediate temperature hydrocarbon-rich liquids, and (near) ambient temperature hydrocarbon-rich liquids. The main separation that takes place prior to the HC/HI unit is the removal of C₅–C₇ light naphtha from the C₈₊. The C₈₊ liquids then enter the HC/HI unit along with high-pressure H₂ refined (HC/HI) into jet fuel.

The HC/HI unit operates at relatively high pressures—generally above 600–700 psig using platinum group metal (PGM)-based catalysts and higher (900–1,200 psig) for sulfided base metal catalysts. The final products exiting the unit include C₈–C₁₆ jet fuel, a C₅–C₇ light naphtha, and other lighter products (liquified petroleum gas [LPG]).

2.3.5 Power Generation

Electricity is needed throughout the plant to run auxiliary equipment such as pumps, compressors, and control systems. High-pressure steam (HPS) and medium-pressure steam (MPS) generated in the syngas and FT portions of the plant (respectively) is used in a small steam turbine to generate electricity for this equipment and potentially for sale into the electricity grid.

A variety of design options are available for how to leverage the existing steam to generate electricity. These include superheating the existing pressure steam—typically in the waste heat recovery unit (WHRU) and/or fired heater—for higher performance, use of separate turbines for the HPS and MPS in separate turbine driver gensets, and generating additional steam to correctly match the HPS and MPS flow rates. Such an optimization analysis was beyond the scope of the study and will be undertaken in future work.

In all cases, the turbine exit low-pressure steam (LPS) is condensed and sent to the de-aerators.

2.3.6 CO₂ Capture

CCS provides an opportunity to remove CO₂ from within the GTL facility and reduce the life cycle GHG impacts of the jet fuel. The primary opportunity for CO₂ capture is the removal of CO₂ from the FT tail gas.¹ The FT tail gas contains a high concentration of CO₂ (39–58 percent by volume) and is at fairly high pressure (300–400 psig), both of which reduce the cost of CO₂ removal. In both the SMR and the ATR cases, 95 percent of the CO₂ is removed from the FT tail gas. A sensitivity case was also performed to determine the performance impacts of only treating a portion of the FT tail gas stream in the ATR case—that which is used for pre-heating the natural gas feed—while the portion of the tail gas that is recycled to the ATR is left untreated.

CO₂ can also be removed from the flue gas produced from the syngas generation portion of the plant. This is more difficult than capture from the FT tail gas because of the more dilute CO₂ concentration (5–9 percent by volume) and lower pressure (essentially atmospheric) and, consequently, less economical. There is also a performance penalty associated with CO₂ capture from the flue gas. Assuming an amine-based post-combustion capture unit is leveraged, steam will

¹ "FT tail gas" is the gaseous hydrocarbon product created from the FT process and the FT product upgrading processes. FT tail gas has limited value as a product to be sold and instead is combusted at different areas of the GTL facility to provide heat for the various processes.

be required for solvent regeneration and electricity will be needed for pumps and flue gas fans.^m Nonetheless, this option allows for an additional reduction in the life cycle GHG impacts of the fuel. A sensitivity analysis was performed to evaluate the cost and potential GHG impacts of implementing CO₂ removal from the flue gas.

While the cost of carbon capture and cost of carbon storage was evaluated, a detailed assessment of carbon storage or utilization opportunities within the vicinity of PIT was not included in this study due to limitations in scope. Future work should include an assessment of geologic formations capable of CO₂ storage within a 100-mile radius of PIT and a more detailed assessment of cost of CO₂ transport and storage. There are believed to be several formations that meet these criteria based on previous DOE projects; [11] [12] [13] other entities have reportedly characterized formations for other projects in the nearby vicinity.

2.4 CONCEPTUAL PLANT DESIGNS AND CONFIGURATIONAL OPTIONS

Four main conceptual plant designs were evaluated to determine the impacts of different syngas production methods and the implementation of CCS on plant technical, economic, and environmental performance.

Several sensitivity case analyses were also performed. These examine the impacts of different sources of natural gas for a feedstock—onsite wells versus pipeline gas, H₂ co-product production in the SMR case, and alternative CO₂ removal configurations for the ATR case (Exhibit 2-2). The results of these analyses are summarized in Section 5.

2.4.1 Case SMR-Vent

In this plant configuration, syngas is produced using SMR. CO₂ is captured from high-pressure, high-concentration streams in order to reduce equipment size, but is ultimately vented to the atmosphere.

2.4.2 Case SMR-CCS

In this plant configuration, syngas is produced using SMR. Similar to the SMR-Vent case, CO₂ is captured from high-pressure, high-concentration streams in order to reduce equipment size. This CO₂ is ultimately stored either in a geologic formation (saline aquifer) or as part of an enhanced oil recovery (EOR) process.

2.4.3 Case ATR-Vent

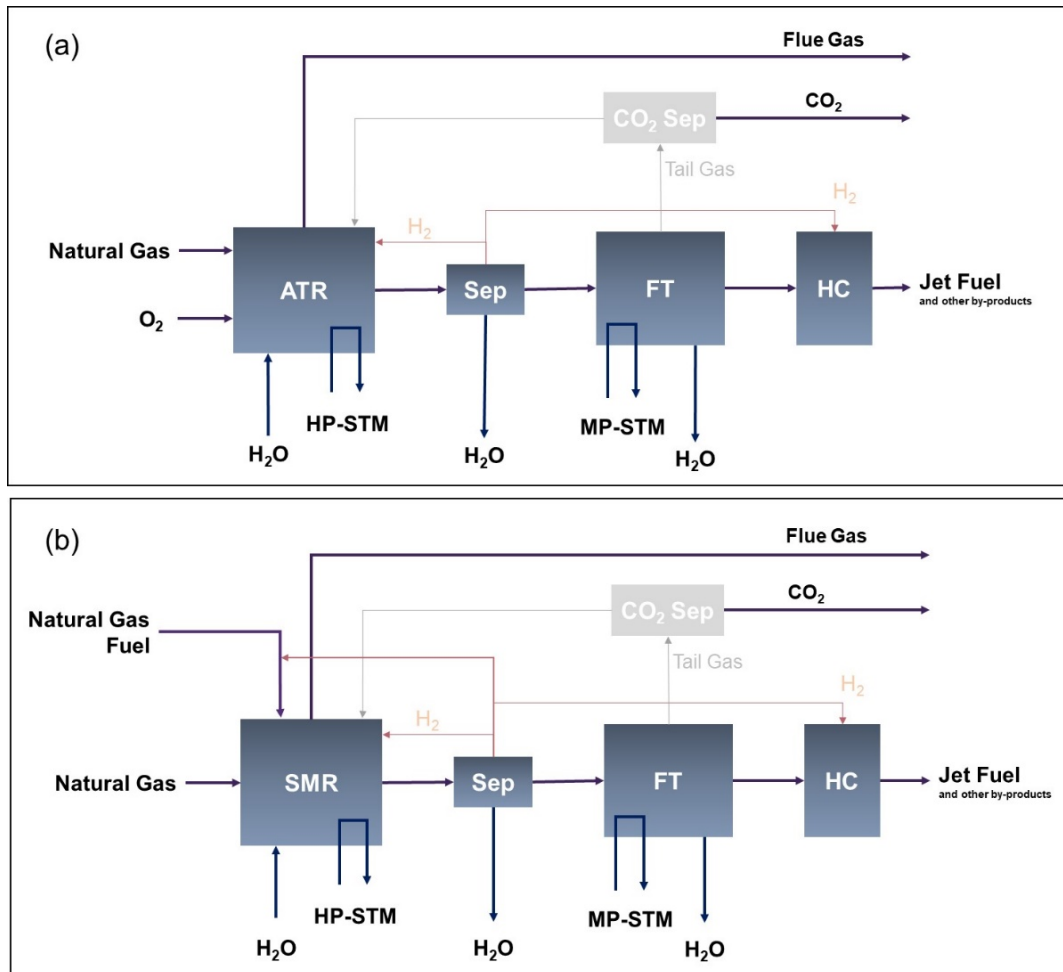
In this plant configuration, syngas is produced using ATR. CO₂ is captured from high-pressure, high-concentration streams in order to reduce equipment size, but is ultimately vented to the atmosphere.

^m The GTL facility produces more process steam and electricity than is required for plant operation. Therefore, while flue gas CO₂ capture will incur a performance penalty, the facility will not have to be redesigned.

2.4.4 Case ATR-CCS

In this plant configuration, syngas is produced using ATR. Similar to the ATR-Vent case, CO₂ is captured from high-pressure, high-concentration streams in order to reduce equipment size. This CO₂ is ultimately stored either in a geologic formation (saline aquifer) or as part of an EOR process.

Exhibit 2-2. Process flow diagrams for different syngas generation configurations: (a) ATR (b) SMR



3 METHODOLOGY

3.1 PROCESS DESIGN AND MODELING

The entire FT GTL process scheme, starting from natural gas and ending with the jet fuel and other auxiliary products, is simulated using the Aspen Plus® (Aspen) V11 process modeling software. Separate models were created for the simulation, analysis, and comparison of the SMR and ATR cases (Exhibit A-1). The model for the FT and hydrocracking sections was kept similar in both cases. A more detailed discussion of the process modeling and simulation methodology leveraged in this study can be found in Appendix A: Process Simulation.

3.2 COST ESTIMATION, PROJECT FINANCING, PRODUCT VALUATION

3.2.1 Cost Estimation

The broad sections contributing to this production cost include 1) fixed capital costs, 2) operating costs, 3) feedstocks (natural gas and O₂), and 4) capital amortization.

This study is similar to a front-end loading 1 study where the project idea is discussed with alternatives and design calculations are preliminary. Consequently, cost estimates for the GTL facility examined in this study are derived from a variety of sources, including values estimated using historical data, known unit costs, literature and other public references, and direct price quotes obtained from vendors. When possible, cost estimates were compared across multiple sources for validation. With this ballpark estimate, the accuracy is ± 30 percent.

The cost of the natural gas feedstock has a substantial impact on the project economics. To understand the impacts of natural gas pricing, three scenarios are used for the feed natural gas price: \$1, \$2, and \$3 per MM British thermal unit (Btu). Examining the production costs of natural gas from onsite wells will provide an important point of comparison for this study and is an area of future research.

3.2.2 Project Financing and Required Fuel Production Costs

The total project and fuel production costs were calculated using project financing assumptions from previous NETL studies on alternative liquid transportation fuel production systems, with several notable changes due to current lending and market conditions:

- 14% internal rate of return on equity (the rate used as a sensitivity case in prior work, instead of a 20% internal rate of return on equity)
- 10% interest rate for debt (compared to 8% for prior work)
- 20-year debt repayment term (compared to 15 years in prior GTL studies)

3.2.3 Product Valuation

As the primary goal of this study was to evaluate several different potential GTL process configurations—to screen different GTL system options—there is considerable uncertainty and variability regarding what co-products will be produced, and the potential market value of those products. Consequently, a simplified approach of only valuing primary products (jet fuel and naphtha) was adopted to provide a better means of comparing cases. Not placing a value on

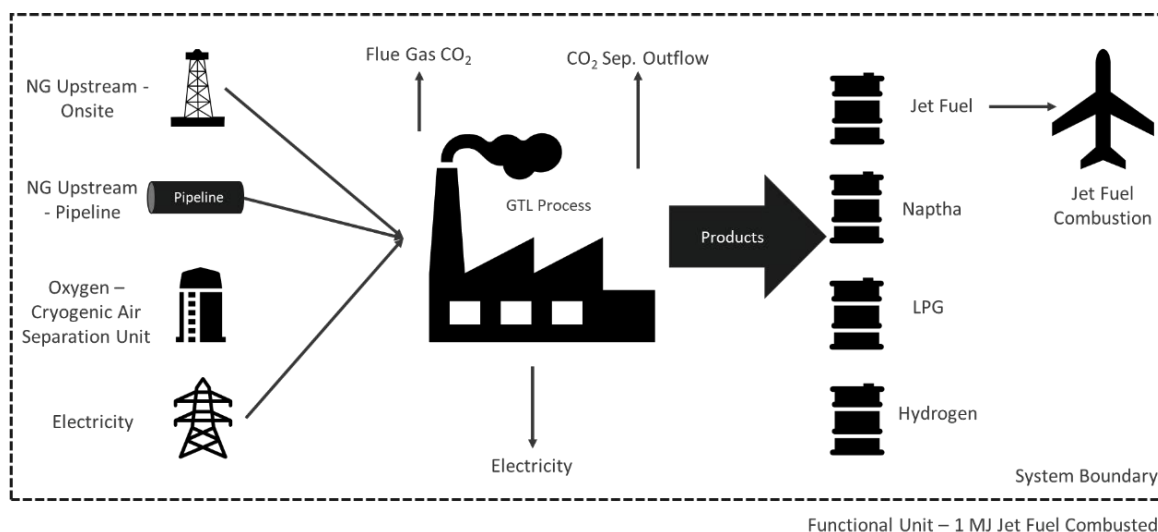
secondary products or ones with which there is uncertainty regarding market value or total product produced means that the project economics are likely to improve over the results presented within this study. LPG, electricity, and CO₂ fall into this category of secondary products which are—for the purposes of this study—essentially given away.

3.3 LIFE CYCLE ANALYSIS

Life cycle analysis (LCA) is a common means of comparing the environmental impact of liquid transportation fuels produced from non-petroleum feedstocks. LCA has the advantage of accounting for environmental impacts across the entire lifecycle of the product, from cradle-to-combustion. In this case, emissions starting at the “cradle” (natural gas production) through the combustion or use of the jet fuel. This provides a more comprehensive means of accounting for GHG emissions than just examining combustion emissions at the point of use or emissions at the fuel production facility. Typically, the LCA GHG emissions from the alternative fuel, in this case GTL jet fuel, are then compared to conventional jet fuel as a means of illustrating relative impacts.

Exhibit 3-1 provides a visualization of the cradle-to-combustion flow diagram and the system boundary, i.e., the limit beyond which emissions are not accounted for. The system boundary for this study includes emissions from upstream natural gas and electricity production, the GTL process, and jet fuel combustion. Because the GTL facility produces other products in addition to jet fuel, a portion of the emissions would typically be assigned to those products using the system expansion with displacement method. This uses emissions profiles for the existing market items these products will be displacing through their production as a means of accounting for impact of the new products: in this case naphtha, LPG, electricity, and potentially H₂.

Exhibit 3-1. GTL jet fuel flow diagram and system boundary for the base case



The scope of this study was focused on screening the technical and economic performance of a number of different GTL plant configurations and sensitivity scenarios. The substantial amount of uncertainty around the GTL facility choice of feedstock, products and co-products, facility emissions, and characteristics of the jet fuel produced make performing a detailed and quantitative LCA challenging. Therefore, a number of qualitative observations are provided on how select configuration or facility design choices impact the LCA GHG emissions of the jet fuel produced. A more detailed LCA is expected to be performed as part of future work.

4 RESULTS

4.1 PLANT PERFORMANCE

The entire FT GTL process scheme, starting from natural gas and ending with the jet fuel and other auxiliary products is simulated using the Aspen process modeling software. Separate models were created for the simulation, analysis, and comparison of the SMR and ATR cases (shown in Appendix A, Exhibit A-1). The models for the FT and HC sections were kept similar across both the SMR and ATR cases, and this results in the production of equal amounts of jet fuel and other liquid products and provides an equal basis for comparison between those two scenarios. The key results of the simulation are listed in Exhibit 4-1, which reports the feedstocks and inputs into the facility, the FT product slate, and the facility outputs, including water produced from different processes (FT water, knockout [KO] water, etc.). The facility requires natural gas as a jet fuel feedstock and for integrated heating, water for the FT process (FT water), and H₂ for upgrading the FT products during HC and hydrodesulfurization (HDS).

Exhibit 4-1. Key process output variables from the simulation (using both ATR and SMR)

Parameters	Unit	ATR	SMR
Natural gas for syngas production	MMscfd	52.6	43.3
Natural gas fuel for fired heater	MMscfd	0	20.7
Total natural gas feed	MMscfd	52.6	64.0
KO water produced	tonne/hr	46.7	138.0
FT water produced	tonne/hr	49.5	51.1
MPS generated	tonne/hr	150.5	146.7
Wax (211°C, 50 psig)	bbl/day	5100	4685
HS hydrocarbons (114°C, 40 psig)	bbl/day	1280	1171.5
CS hydrocarbons (53°C, 30 psig)	bbl/day	1160	1355.4
FT liquids (C₅₊)	bbl/day	5,920	
FT gases (C₁–C₄) – liquid basis	bbl/day	659	

The FT process produces waxes, liquid hydrocarbons, and gases, which are further processed into jet fuel, LPG, and straight-run naphtha (SRN) (Exhibit 4-2). FT tail gas—a mixture of hydrocarbon gases that are a byproduct of the FT process—is also produced and used throughout the facility for process heating. Other products include a substantial amount of water (KO water), H₂ for sale (in the SMR case), and process steam. The process steam was assumed to be converted into electricity for export from the plant but could easily be exported or leveraged for other industrial processes.

Exhibit 4-2. Saleable products and key outputs

Parameters	Unit	CO ₂ Vent		CCS		Aggressive CCS	
		ATR	SMR	ATR	SMR	ATR	SMR
CO ₂ Stored	tonne/hr	-	-	27.8	13.2	46.2	107.6
CO ₂ Emitted	tonne/hr	48.2	118.0	20.4	104.8	2.0	2.1
Power Generation (Potential)	MWe	20	20	20	20	20	20
Jet fuel	bbl/day	5,000					
C ₅ –C ₇ and SRN	bbl/day	920					
LPG	bbl/day	659					

The facility also produces CO₂ in the syngas production and FT processes, as well as through the combustion of FT tail gas for processing heating. Three CO₂ capture scenarios were evaluated for both the ATR and SMR process configurations. In the “Vent” and “CCS” scenarios, a portion of the CO₂ is captured, in part to reduce equipment sizes in the facility but also to provide an opportunity to reduce the GHG footprint of the plant. In the “Vent” case, this CO₂ is ultimately vented to the atmosphere and has no ultimate impact on the CO₂ emissions from the GTL facility or the GHG intensity of the jet fuel produced. In the “CCS” cases, CO₂ captured from high-pressure, high-concentration streams is stored either in a geologic formation (saline aquifer) or as part of an EOR process. This abates 50–60 percent of the emissions in the ATR case and 11–16 percent of the emissions in the SMR case, and has the impact of reducing total CO₂ emissions from the process and, therefore, the GHG footprint of the GTL facility.

A third scenario in which a more aggressive approach to CCS is undertaken was also explored. In this scenario, CO₂ is captured and stored from both high-concentration streams (as in the ATR-CCS and SMR-CCS cases above) and also from low-concentration flue gas streams. This abates approximately 95 percent and 91 percent of the CO₂ emissions in the ATR and SMR cases, respectively.

The amount of CO₂ stored or emitted varies significantly between the ATR and SMR syngas generation cases, as the substantially more CO₂ is produced in the SMR cases, and less of it is in high-purity streams. Consequently, the CCS case has a lesser impact for the SMR cases, with only the aggressive CCS scenario having a significant impact on reducing facility CO₂ emissions.

In the ATR cases, less CO₂ is produced overall, and a larger portion of that CO₂ exists in high-concentration, high-purity streams and is, therefore, addressed in the less aggressive CCS case. Therefore, implementing CCS for the ATR cases results in a relatively low-cost abatement pathway. The cost impacts of the aggressive CCS cases are discussed in more detail in Section 5.

A more detailed examination of the natural gas, FT tail gas, and electricity requirements of the different sections of the GTL facility is provided in Exhibit A-11.

4.1.1 Product Steam and Electricity

As noted above, steam is generated at several points within the GTL facility, and this steam can be converted into electricity for use within the facility as well as for export to the electric grid.

Numerous options exist for how the electricity will be produced, ranging from higher cost and efficiency options to more simple process configurations.

In a larger GTL facility, the steam would generally be superheated—typically in the WHRU and/or fired heater—to improve the efficiency of the power generation cycle. However, the steam could also be used directly in a standalone turbine, particularly for this project scale. At this scale, it is possible to use HPS (from the WHB for main compressor duties with turbine drivers) and FT MPS in separate turbine driver gensets. Regardless of the electricity generating system, in all cases, the turbine exit LPS is condensed and sent to the de-aerators, requiring onsite condensing equipment.

4.1.2 Liquefied Petroleum Gas

The smallest of the FT product streams is LPG. Several options exist for the LPG product, ranging from sale into the market as a consumer good to the recycling of the LPG to the pre-reforming unit to reduce the natural gas consumption requirements of the facility. Recycling the LPG could reduce the natural gas inputs to the facility by an estimated 4–5 percent, but the economic and environmental impacts of doing so will be dependent on the price of producing natural gas from onsite wells and local market conditions for LPG.

As the ultimate decision on the fate of LPG will be driven by the project developer, this study assumes that LPG is sold into the market at the cost of packaging the product.

4.1.3 Captured CO₂ Product

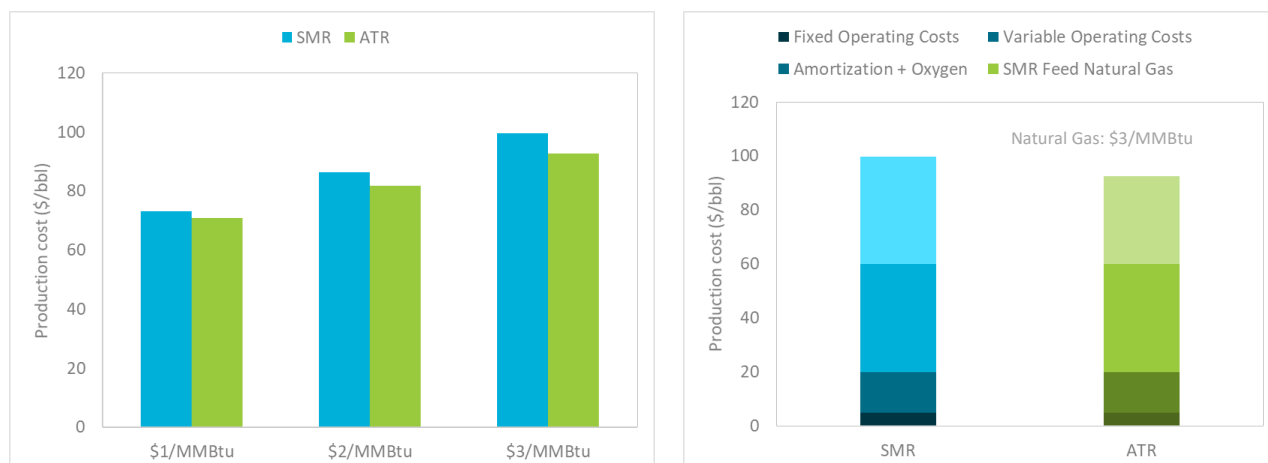
CO₂ captured at the facility is dried, compressed, and shipped via pipeline for geologic storage, either as part of an EOR operation or for permanent storage in a geologic reservoir. No tax credits or other value is assumed to be derived from the CO₂.

4.2 COST ESTIMATES

The total capital cost of the facility is estimated to be \$550–740 MM depending on the choice of plant configuration and accounting for uncertainty associated with equipment cost estimates. Such a facility would produce jet fuel that could be sold at \$1.69–2.37/gal after operating costs and the developer's return on investment is accounted for. This compares to current jet fuel prices of \$1.88/gal, and a price range of \$0.41/gal (April 2020 during the COVID-19 Pandemic) to over \$4/gal (July 2008) over the last 20 years (as reported by the Energy Information Administration). [6] The facility could be constructed in four years, including permitting and front end engineering and design (FEED) design phases.

Exhibit 4-3 explores the jet fuel production costs for both the ATR and SMR cases at 1) different natural gas feedstock prices and 2) broken down by cost contribution type. The sensitivity of cost for the three natural gas prices evaluated is shown on the right side of the chart. Note that in all cases, the production prices for the SMR case are higher due to an increased level of natural gas consumption per unit of jet fuel produced.

Exhibit 4-3. Comparison of liquid fuel (\$/bbl) production cost between SMR and ATR



The production cost breakdown by cost type is shown on the left side of the chart, examining the cost contributions of 1) fixed capital costs, 2) operating costs, 3) feedstocks (natural gas and O₂), and 4) capital amortization. These are explained in more detail in the following sections.

4.2.1 Plant Capital Costs

As noted in Section 3.2.1, this study is similar to a front-end loading 1 study where the project idea is discussed with various alternative configurations or scenarios. Current industry capital cost estimates for a conventional GTL facility ranges \$110,000–120,000/BPD of FT products produced (\$110,000–120,000/BPD) for a facility that uses an ATR for syngas generation and includes the equipment required to upgrade FT products into a “drop-in” jet fuel.ⁿ This cost estimate includes the cost of an air separation unit (ASU) for O₂ production—required when an ATR is used for syngas generation—and limited CO₂ capture equipment.

Industry experts reported that a similar GTL facility equipped with an SMR for syngas generation would have a similar capital cost to the ATR facility, with the \$110,000–120,000/BPD cost range representing a minimum cost, rather than an average cost range (for the ATR with ASU). Similar to the ATR case, a minimum amount of CO₂ capture equipment is included in the facility cost, although no ASU is needed.

The HC/HI process included in this facility represents a recent process advance that enables a greater percentage of the FT liquids to be converted to jet fuel (e.g., higher yields). A vendor quote was obtained from Topsoe for this portion of the facility, and the installed inside battery limits estimate of \$61 MM (~\$10,000/BPD) is in line with previous estimates for the older HC/HI upgrading process.^o Consequently, no update to the overall industry cost estimate for the facility is necessary.

These cost estimates provide a total capital cost range of \$660–720 MM for both the ATR (with ASU) and SMR cases based on the a ~6,000 BPD facility considered in this study (Exhibit 4-4). In

ⁿ The FT process produces a synthetic crude oil (“syncrude”), which must be further refined into transportation fuels that can be directly used in aircraft and vehicles. Some GTL systems don’t include the equipment to refine (or “upgrade”) the syncrude to finished transportation fuels, which reduces the capital cost of those facilities.

^o The Topsoe HC/HI unit modeled in this study performs at a higher level than previously modeled HC/HI processes and, therefore, has more uncertainty associated with the cost. The vendor quote provides greater cost certainty.

both of these cases, CO₂ is captured as part of normal operations (to reduce equipment sizes) but vented to the atmosphere. As noted above, it is anticipated that the SMR facility will have a higher capital cost than the ATR facility; therefore, while the capital cost ranges listed are the same for both cases, this is a reflection of the granularity of the capital cost estimate and something that will be resolved by additional analysis and equipment price quotes from vendors.

Both the ATR and SMR cases leverage CO₂ capture equipment to remove CO₂ from syngas streams and reduce equipment sizes. The main difference between the cases in which CO₂ is vented to the atmosphere versus stored is the existence of CO₂ compression and drying equipment to prepare the CO₂ for pipeline transport. Because the ATR and SMR syngas production systems produce different amounts of CO₂, the capital costs for the compression and drying systems between these cases are different: costing approximately \$15 MM for the ATR-CCS case and \$10 MM for the SMR-CCS case. While the capital cost increase for the ATR case is higher than the SMR case based on the increased amount—over double—of CO₂ being stored, this cost differential is not expected to be statistically relevant based on the expectation of the SMR cases being slightly more costly than the ATR cases. This cost differential is represented in Exhibit 4-4. A scenario in which a more aggressive approach is taken to reducing CO₂ emissions from the facility was also investigated. This scenario is described in Section 5.2.

Exhibit 4-4. Capital costs of different plant configurations

Plant Configuration	Capital Cost Range (\$MM)
ATR-Vent (with ASU)	\$660–720
SMR-Vent	\$660–720
ATR-CCS (with ASU)	\$675–735
SMR-CCS	\$670–730
ATR-Vent (no ASU)	\$530–690
ATR-CCS (no ASU)	\$545–705

One option to reduce the capital cost of a GTL facility with an ATR would be to purchase O₂ from an offsite vendor instead of producing it onsite. This option would have the benefit of reducing the capital and operating expenses associated with the ASU. It could also result in overall cost savings if locally sourced O₂ was available at prices below that of onsite production prices. The ASU cost is estimated to be 20 percent of the plant cost, or \$130 MM, which establishes \$520 MM as a lower bound for the total plant cost of a 6,000 BPD facility. While the lower capital cost will save on amortization, it does not necessarily translate into a lower jet fuel production cost, as is discussed in Section 4.2.2.3.3.

4.2.1.1 Additional Capital Costs

The study assumes that excess steam produced by the GTL process is converted to electricity for use in the facility and for export to the grid, which would require equipment in excess of what is described above. The capital cost of a small-scale power plant to convert the process steam into electricity would fall in the range of \$1,000 per kilowatt (kW) of electricity generating capacity

(\$1000/kW).^p The addition of this equipment would, therefore, add up to \$20 MM to the GTL facility cost based on the estimated 20 megawatts (MW) of electricity that will be produced using excess process steam (Exhibit 4-5). This would not result in a major cost considering the total cost of roughly \$700 MM for the entire GTL plant.

Exhibit 4-5. Capital costs of selected equipment/plant sections

Plant Configuration	Capital Cost (\$MM)
Power Generation Block	\$20
ASU (ATR case only)	\$130

4.2.2 Plant Operating Costs

Plant operating costs are broken down into four categories: natural gas feedstock, fixed operating costs, variable operating costs, and oxygen cost. Typically, the cost of the natural gas feed is the largest contributor to operating costs, with the possible exception of capital amortization exceeding it at low natural gas prices or high interest rates. This is not necessarily the case at low natural gas prices, including in locations such as the Southwestern Pennsylvania region and specifically for natural gas produced at PTT.

It should be noted that the total fixed and variable operating and maintenance (O&M) cost for the facility was determined to be just under \$20/barrel (bbl) based on the references and citations used as the study basis. This seemed high based on the previous experience of the industry experts consulted for the study, with a value of \$10–15 being more common. Absent a more defined/refined estimate, however, the value of \$20/bbl was used.

4.2.2.1 Natural Gas Feedstock

The required natural gas feed rates of the various configurations were determined by simulations of both the ATR and SMR (H₂ as fuel) cases in this study. Rich natural gas produced onsite with 1,221 Btu/standard cubic feet (scf) heating value is the basis for the cost calculations, with natural gas costs of \$1, \$2, and \$3/MMBtu (Exhibit 4-6). Therefore, the flow times the heat content gives MMBtu/day, times the cost gives daily expense, and divided by production rate gives natural gas cost in \$/bbl. As will be illustrated in more detail below, natural gas prices at or below \$2/MMBtu will likely be required for the project to be economically competitive at current crude oil (and therefore jet fuel) prices.

Exhibit 4-6. Cost of feed natural gas, \$/bbl product, at different natural gas prices

Unit	Flow, MMscfd	Natural Gas Price		
		\$1/MMscf	\$2/MMscf	\$3/MMscf
ATR	52.6	\$10.85/bbl	\$21.70/bbl	\$32.55/bbl
SMR	64.0	\$13.20/bbl	\$26.40/bbl	\$39.60/bbl

^p Generating electricity would only require the addition of a steam turbine and genset as other ancillary equipment, notably condensers, will already be present at the GTL facility for handling process steam.

4.2.2.2 Fixed Operating Costs

This encompasses the O&M labor costs and is based on Exhibit 5-4, p. 33, of the DOE study. [10] The 2013 DOE study came up with \$5/bbl for this category. [10] There is currently no better basis, and even if it is different, it won't significantly impact the result.

4.2.2.3 Variable Operating Costs

Variable operating costs consist of materials that are consumed during normal operation of the facility, either as consumables or parts and materials required to keep the facility operational. They fall into three broad categories: maintenance materials for equipment and parts, consumables such as chemicals and catalysts, and O₂, which is required for syngas production in the ATR configuration. Variable operating costs of \$15/bbl were used in this study based on a maintenance material costs of \$5/bbl, non-FT catalyst costs of \$5/bbl, and FT catalyst costs of \$5/bbl.

The following sections discuss what is included in the various cost estimates, the provenance of the estimate, cost comparisons, and configurational options that might impact those costs.

4.2.2.3.1 Maintenance Materials

The 2013 DOE study used ~4 percent of the total equipment cost per year for maintenance and material cost. [10] This is reasonable as the usual range is 3–5 percent. The plant in this study is considerably simpler, so 3 percent/year is a reasonable number. Equipment cost should be approximately half of the total cost, which is assumed to be ~\$650 MM.

Next, 340 operating days per year (93 percent service factor) were assumed, which should be pretty typical, although a number as low as 90 percent for the first year or two could be supported. That means annual production is somewhat more than 2 MMbbl. Taking all of this together, maintenance materials cost of \$4.41/bbl is estimated. While this seems slightly high, there is no basis to challenge any of the numbers used. Past experience says \$2–3/bbl could be more realistic.

4.2.2.3.2 Catalysts and Chemicals

There are some significant differences between catalyst and chemical estimates for this study and the 2013 DOE study. [10] The items included in this category are as follows:

- Make-up water (a lot for the SMR, potentially none for the ATR)
- Boiler feed water (BFW) treatment chemicals
- FT process water treatment chemicals (if they aren't injected into the reformer)
- Dimethyl sulfide used to keep the HC/HI sulfided; amounts are very low
- HDS catalyst
- Zinc oxide (ZnO) adsorbents
- Pre-reformer catalyst
- Reformer catalyst – ATR or SMR
- FT catalyst
- HC/HI catalyst

The 2013 DOE study catalyst cost is low based on prior experience, coming up with a total of less than \$1.10/bbl. [10] From past experience, the sum of all of the catalysts and chemicals other than the FT (e.g., non-FT catalysts) is expected to be less than \$5/bbl—possibly as low as \$3/bbl—but \$5/bbl will be used for this study.

For the FT catalyst, this varies tremendously with vendor/technology. Values can vary from below \$2/bbl to as high as \$8/bbl. For simplicity, \$5/bbl was used.

4.2.2.3.3 Oxygen Cost

The ATR plant configuration requires O₂ for syngas production. This O₂ can either be purchased from an outside vendor, produced over-the-fence by a partner, or produced onsite. These options and the associated costs are described below.

This study assumes the O₂ is produced over-the-fence and supplied via pipeline by a partner. The cost for this O₂ is anticipated to be approximately \$30/ton. This production cost could be reduced if excess steam and electricity produced at the GTL facility were leveraged and provided as utilities to the partner as the largest operating expenses in an ASU are the operation of compressor drives, which can be steam or electricity driven. This study assumes enough steam/power could be supplied to drive at least the study portion of the plant (it would likely be built larger than needed) and settles at an O₂ price of \$15/ton in this minimum cost scenario.

The most expensive O₂ option for the facility would be to truck it in from an outside vendor. This would cost \$50/ton and might impact the desired resiliency of the facility.

Another alternative would be for the project developers to build, own, and operate an O₂ plant (i.e., an ASU) at the facility. The result would be no charge for O₂ purchasing but a significantly higher amount of amortized capital cost.

Evaluating the full range of these options based on the ATR case operational requirement of 66,346 kilogram (kg)/hour (hr) of O₂ (or 1,751 ton/day), equates to variable operating costs of \$14.80/bbl, \$8.90/bbl, and \$4.45/bbl at O₂ prices of \$50/ton, \$30/ton, and \$15/ton, respectively. Owning and operating an O₂ plant would constitute a \$10/bbl cost, as is described in Section 4.2.3.

4.2.3 Capital Amortization

There are many possible assumptions for financing options. In this study, the plant capital is treated like a loan at 10 percent interest that needs to be paid back in 20 years. For the ASU-containing plant (\$650 MM), the cost is ~\$40/bbl. For the buy-O₂ plant (\$520 MM), the result is \$30/bbl. So, building the ASU in this extremely simplistic case would cost \$10/bbl, while it could be less than that depending on the O₂ vendor relationship.

Note that the facility capital costs include the cost of CO₂ removal costs from the higher CO₂ concentration FT tail gas, as well as the cost of CO₂ transport and storage. In a scenario where more aggressive CO₂ capture schemes were employed and CO₂ is removed from flue gas streams in the facility using post-combustion capture units, an additional cost is incurred as discussed in Section 5.2.

4.2.4 Total Jet Fuel Production Costs

The total jet fuel production costs, shown in Exhibit 4-7, range \$71–100/bbl of jet fuel produced depending on the syngas production pathway (ATR or SMR) and natural gas feedstock price. These

are the minimum product selling prices required to satisfy the financial assumptions in the 2013 DOE study (Exhibit 5-5, pages 34-35), inclusive of all project costs and an internal return on revenue for the project developer of 14 percent. [10]

Exhibit 4-7. Cost estimate for the ATR-Vent and SMR-Vent cases (\$/bbl product)

Natural Gas Cost	\$1/MMBtu	\$2/MMBtu	\$3/MMBtu
Fixed Operating Costs	5.00		
Variable Operating Costs	15.00		
Amortization + Oxygen	40.00		
ATR Feed Natural Gas	10.85	21.70	32.55
SMR Feed Natural Gas	13.20	26.40	39.60
ATR-Vent Total	70.85	81.70	92.55
SMR-Vent Total	73.20	86.40	99.60

Fixed and non-feedstock variable operating costs are \$5/bbl and \$15/bbl respectively, for a total of \$20/bbl. This excludes the cost of the natural gas and, in the ATR case, O₂ consumed by the facility. These costs constitute between 20 percent (high natural gas price case) and 28 percent (low natural gas price case) of the total fuel production costs. As mentioned in Section 4.2.2, the total fixed and variable O&M cost of \$20/bbl used for the facility seemed high based on the previous experience of the industry experts consulted for the study, with a value of \$10–15 being more common. Absent a more defined/refined estimate, however, the value of \$20/bbl was used.

The amortization of the capital and project costs was estimated to range from \$30/bbl (ATR case without O₂ plant) to \$40/bbl (SMR case and ATR case with O₂ plant). These are based on a total plant cost of \$110,000–120,000/BPD of production, the full project cost estimate for either the SMR case or the ATR case with an O₂ plant, with the O₂ plant representing \$10/bbl of the amortized capital cost in the ATR case. In an ATR case scenario where O₂ is purchased from an external vendor, either via an over-the-fence facility connected via pipeline or trucked in, this could lower or raise O₂ costs, down to \$4.5/bbl or as high as \$15/bbl.

The amortized capital cost portion of the jet fuel production price ranges from 40 percent of the total production cost (high natural gas price scenario) to 56 percent of the total cost (low natural gas price scenario), with the ATR case without an O₂ plant representing a middle case (42 percent at the low natural gas price). In the latter case, the cost of purchasing O₂ would represent a separate charge in the range of 6–21 percent of the total jet fuel price (integrated O₂ plant connected by pipeline and trucked in O₂ price, respectively).

Note that the capital cost estimate does not include the cost of the turbine genset required to produce electricity from excess steam available at the facility, as a number of scenarios exist where the steam would be used for other purposes. The inclusion of a genset would increase the amortized capital cost portion of the jet fuel production price by approximately \$1.50/bbl.

Natural gas fed into the GTL facility has the largest range in impact on the jet fuel production price. In the low natural gas price cases (\$1 MMBtu/scf), natural gas constitutes approximately 15 percent of the fuel production price, while in the high gas price case it constitutes up to 40 percent, over 2.5 times more. This illustrates the outsized impact gas prices can have on project economics and

underscores how the long-term stability of gas produced from onsite wells could benefit at GTL project at PIT.

Exhibit 4-8 describes the breakdown of incremental CCS costs for the ATR-CCS case, as compared to the ATR-Vent case. Note that as the pure stream of CO₂ is being separated in both cases, there is no incremental cost for CO₂ capture. The cost of CO₂ drying and compression is relatively low, under \$1/bbl of product, due to the CO₂ stream being of relatively high pressure to start. The incremental cost of transporting and storing the CO₂ is just under \$6/bbl of product. The incremental costs are lower for the SMR-CCS case as less CO₂ is removed in that case, as shown in Exhibit 4-9.

Exhibit 4-8. Cost estimate for the ATR-CCS case (\$/bbl product)

Natural Gas Cost	\$1/MMBtu	\$2/MMBtu	\$3/MMBtu
ATR-Vent Total	70.85	81.7	92.55
Amortized CO ₂ Compression and Drying Costs	0.76		
CO ₂ Transport and Storage Costs	5.75		
ATR-CCS Total	77.37	88.22	99.07

Exhibit 4-9. Cost estimate for the SMR-CCS case (\$/bbl product)

Natural Gas Cost	\$1/MMBtu	\$2/MMBtu	\$3/MMBtu
SMR-Vent Total	73.20	86.4	99.6
Amortized CO ₂ Compression and Drying Costs	0.48		
CO ₂ Transport and Storage Costs	2.74		
SMR-CCS Total	76.42	89.62	102.82

4.2.5 Market Competitiveness of GTL Jet Fuel Production

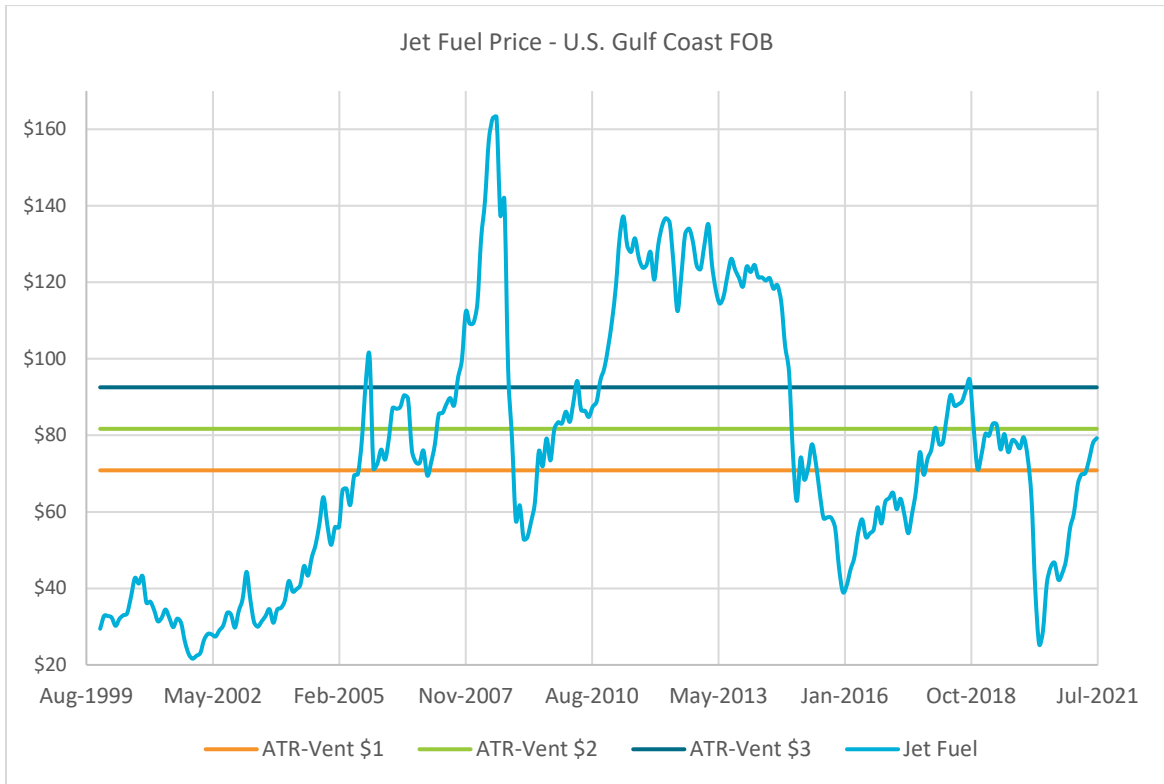
Exhibit 4-10 provides the historical price of crude oil over the last 20 years, with the shaded gray areas representing times of economic contraction: the time immediately following the “dot com bubble” and 9/11, the Great Recession, and the COVID-19 Pandemic. These historic crude oil prices directly relate to jet fuel prices, which are compared to the ATR calculated prices (Exhibit 4-11 and Exhibit 4-12) and SMR calculated prices (Exhibit 4-13 and Exhibit 4-14) at the 3 different natural gas prices evaluated: \$1, \$2, and \$3/MMBtu.

JET FUEL PRODUCTION AT THE PITTSBURGH AIRPORT: GTL VIA FISCHER-TROPSCH SYNTHESIS

Exhibit 4-10. WTI/NYMEX for the last 20 years, historical crude data (\$/bbl)

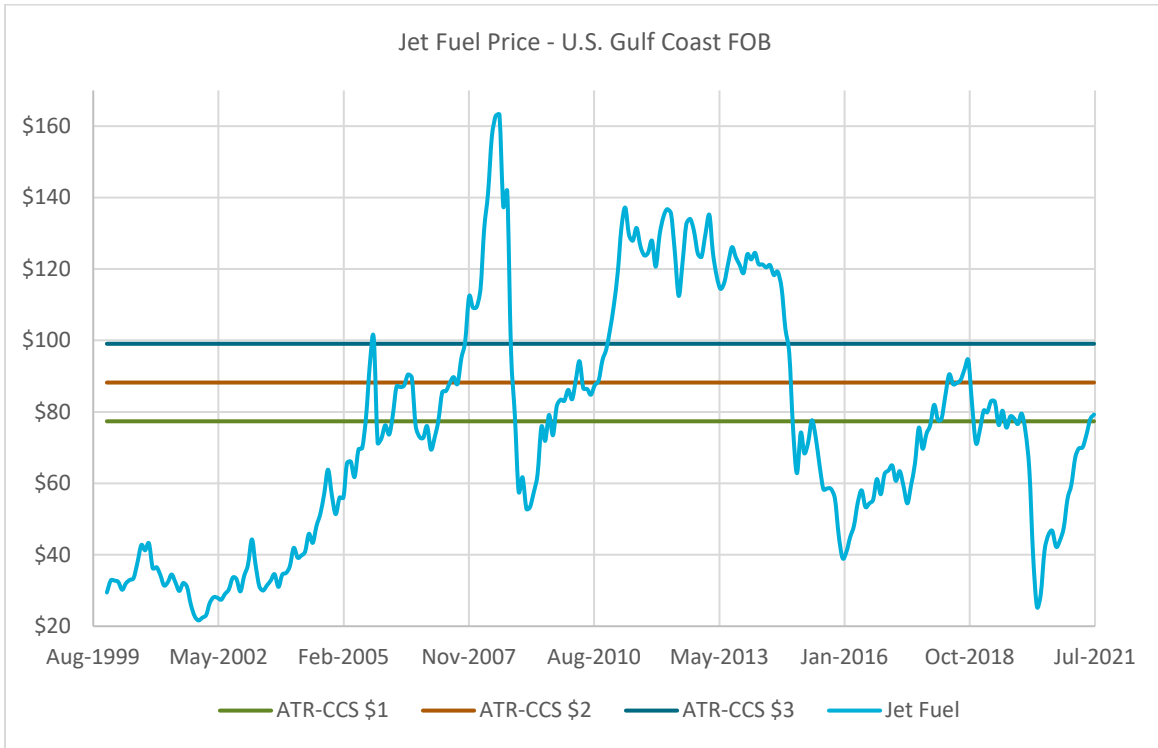


Exhibit 4-11. Comparing the jet fuel prices with the ATR-Vent based values



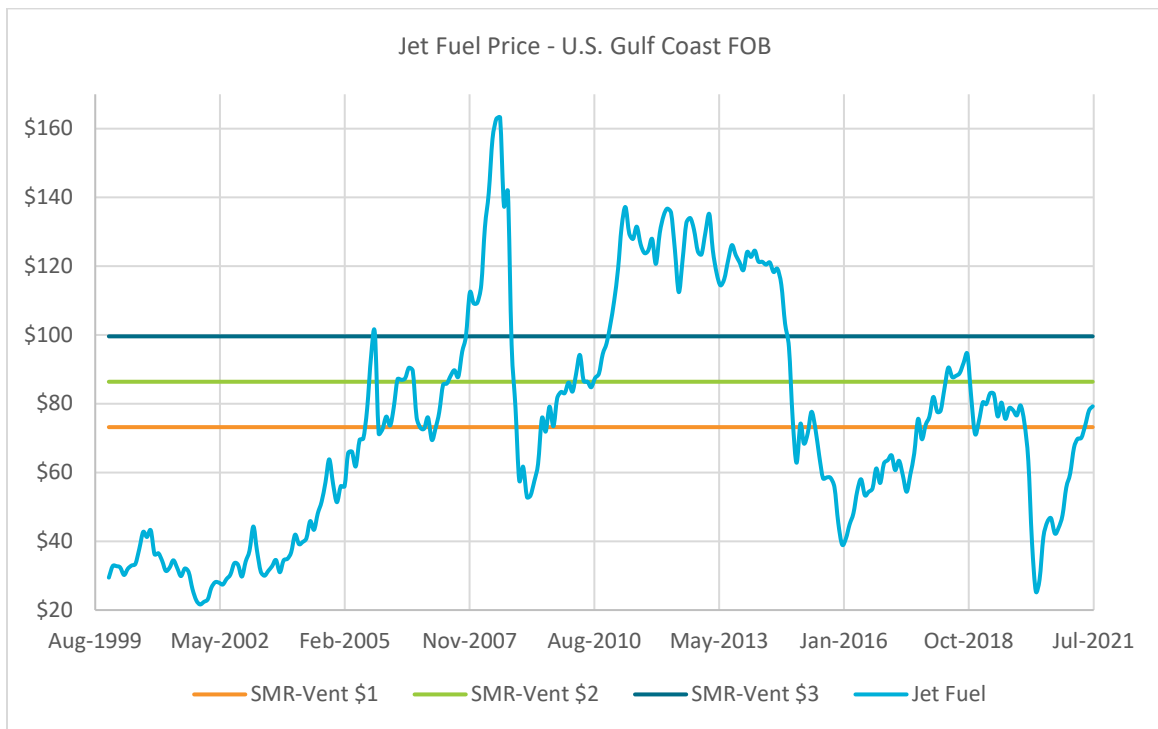
Note: ATR-based values given in Exhibit 4-6

Exhibit 4-12. Comparing the jet fuel prices with the ATR-CCS based values



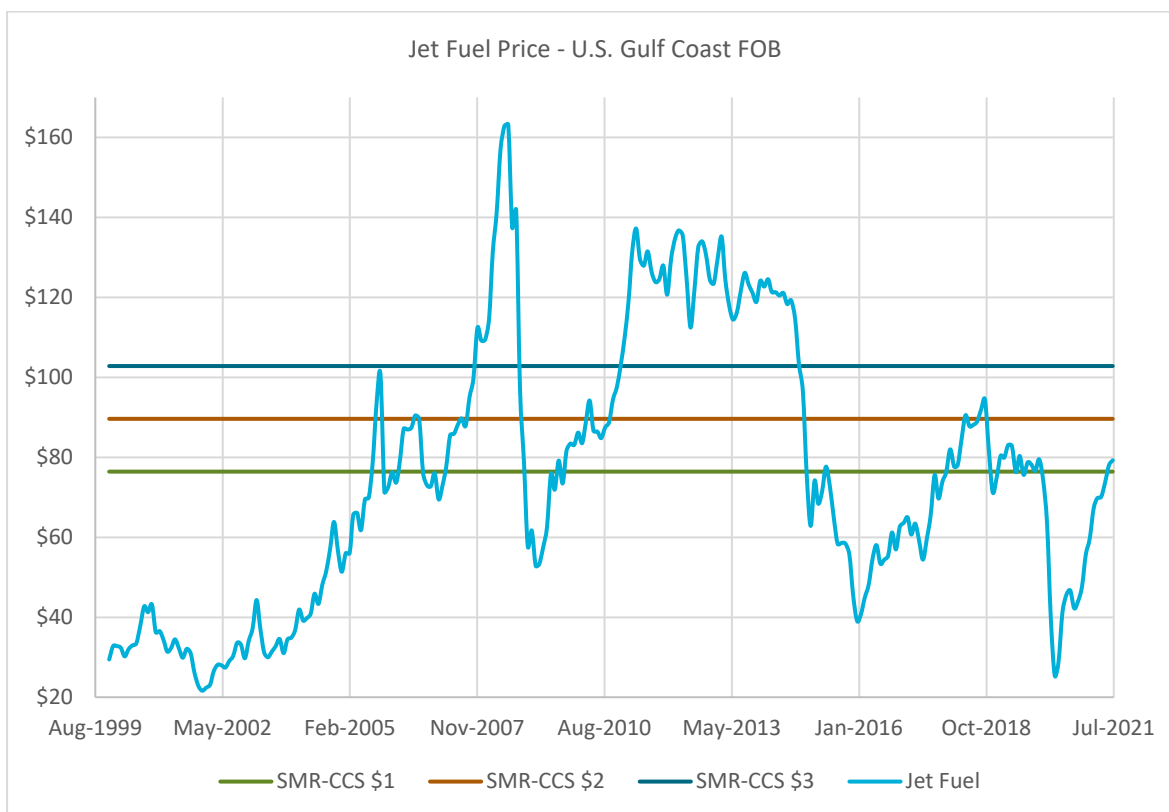
Note: ATR-based values given in Exhibit 4-6

Exhibit 4-13. Comparing the jet fuel prices with the SMR-Vent based values



Note: SMR-based values given in Exhibit 4-6

Exhibit 4-14. Comparing the jet fuel prices with the SMR-CCS based values



Note: SMR-based values given in Exhibit 4-6

As illustrated, the \$70–100/bbl GTL jet fuel sales price would have been economically viable at several points during several periods over the last 20 years, particularly after the year 2005. At the time of this study, Argus Media Limited (“Argus”) reported an average jet fuel spot price of \$1.88/gal, or \$79/bbl.⁹ At this jet fuel price, the ATR and SMR cases would be competitive with conventional jet fuel if onsite natural gas production prices were less than \$1.75/MMBtu or \$1.4/MMBtu, respectively.

More research needs to be done on both the cost of natural gas production onsite and how jet fuel spot prices at PIT compare to the average reported by Argus for the major hubs. It is conceivable that spot jet fuel prices at PIT are higher than the major hubs, particularly as Atlantic Airlines, which sells fuel to independent airlines at PIT, reports much higher prices (above \$5/gal). It is also likely that natural gas production prices at the airport are below \$1/MMBtu.

Given the very conservative capital and operating cost basis for this plant, these cost estimates are expected to have an accuracy of ±25–30 percent. This is a reduced level of uncertainty compared to what would normally be expected for a scoping study of this nature, in which the accuracy of the cost estimate would be in the ±50 percent range.

⁹ Airlines for America, which handles jet fuel sales to the airlines at PIT, links to Argus Media Limited’s website for reporting on the average jet fuel spot prices at the major airport hubs of Chicago, Houston, Los Angeles, and New York.

4.2.6 Cost Estimates in Context of Prior Work

Exhibit 4-15 summarizes the different studies on GTL systems for context on how the cost estimate in this study compares to previous work. Note that smaller production capacity systems (in terms of BPD) will generally have higher specific capital costs (\$/BPD) than larger systems. This is due to the larger systems benefitting from economies of scale.^f

Exhibit 4-15. Summary of the existing techno-economic analysis on GTL plants and comparison with this study

Study	Production Capacity	Plant Cost	Cost per BPD	Comments
2010 DOE Study [15]	2,500 BPD	~\$500 MM (N th -of-a-kind)	\$200,000	Combined biomass and natural gas to liquids plant Includes an O ₂ blown gasifier, FT and HC/HI
Green Chemistry Study [16]	3,500 BPD	~\$570 MM	\$163,000	Similar to Baliban et al. [15] Assumed gasifier cost is extremely low No product upgrading
2013 DOE Study [10]	50,000 BPD	~\$5 B	\$100,000	ATR + 2-stage slurry FT reactor + complicated upgrading
This Study	6,000 BPD	\$550–720 MM	\$92,000–120,000	Includes upgrading FT liquids to jet fuel

A more detailed cost comparison was performed by examining the summary breakdown of costs from NETL's most recent GTL study (which includes all assumptions about debt, equity, taxation, construction period, etc.). The capital recovery cost in the 2013 study is \$37/bbl, very similar to results of this study, which is to be expected given the similar total plant cost: ~\$100,000/BPD for the 2013 study versus the \$110,000–120,000/DB used in this study. [10]

For \$2/MMBtu natural gas and 14 percent internal return on revenue, the 2013 DOE study calculated a crude price of ~\$75–80/bbl, or a diesel price of ~\$90/bbl (the target was diesel fuel, not jet). [10] Given all the various assumptions and uncertainties, this study is well within 15 percent of the previous numbers. The major difference is that the DOE base case was for \$4/MMBtu natural gas.

4.3 LIFE CYCLE GREENHOUSE GAS ESTIMATES

The scope of this study was focused on screening the technical and economic performance of a number of different GTL plant configurations and sensitivity scenarios. The substantial amount of uncertainty around the GTL facility choice of feedstock, products and co-products, facility emissions, and characteristics of the jet fuel produced make performing a detailed and quantitative LCA challenging. Therefore, a number of qualitative observations are provided on how select configuration or facility design choices affect the LCA impacts of the jet fuel produced with a focus placed on the GHG emissions intensity of the fuel.

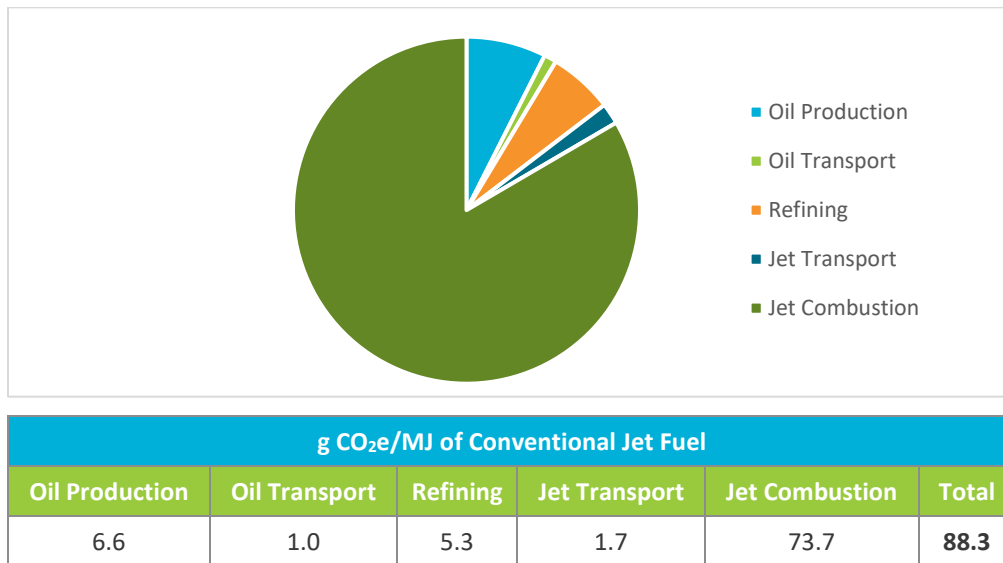
^f Many GTL developers have sought to commercialize modular GTL systems for the purpose of monetizing stranded natural gas. These systems also have the potential to reduce the capital intensity (\$/daily bbl of production) through mass production, standardization, and automation, all of which would minimize the positive impacts of scale economies. The authors are not aware of any commercial offerings that have fully recognized these benefits.

Note that while the benefits of blending FT jet fuel with conventional jet fuel on reducing criteria pollutants during combustion are widely reported in the literature, quantifying those benefits was beyond the scope of this study. [17] [18]

4.3.1 LCA Emissions of Conventional Jet Fuel

The “well-to-wake” LCA GHG emissions associated conventional jet fuel usage are dominated by the CO₂ emissions produced when the fuel is combusted. These emissions constitute 73.7 grams (g) CO₂ equivalent (CO₂e)/megajoule (MJ) of jet fuel, or 83 percent of the 88.3 g CO₂e/MJ of jet fuel GHG intensity of conventional jet fuel estimated in the literature. [19] Exhibit 4-16 describes the breakdown of GHG emissions across the different life cycle stages.

Exhibit 4-16. Well-to-wake GHG emissions of conventional jet fuel



4.3.2 Impact of Natural Gas Choice

The GTL facilities modeled in the study were evaluated using both natural gas produced on the PIT property from wells operated by CNX resources and using natural gas via pipeline from Peoples Gas. Despite differences in gas composition and heat content, the technical performance of the GTL facility is essentially the same for the different natural gas feedstocks. However, a substantial difference exists in the life cycle GHG emissions associated with producing natural gas from the two different sources.

The LCA GHG footprint of using pipeline natural gas was estimated to be over four times larger than using gas produced onsite at PIT. This compares the combined footprint of pipeline natural gas extraction and transportation via pipeline to the site to the emissions produced from the onsite wells. Using gas produced onsite has the additional advantage that more aggressive emissions abatement schemes and/or monitoring systems can be leveraged to reduce and monitor emissions. Utilizing air-instrumented pneumatic devices onsite at PIT’s natural gas extraction and processing along with other methane emissions reductions strategies will further improve the environmental GHG performance of the GTL-derived jet fuel.

The LCA GHG footprint of using onsite natural gas was found to be comparable to the emissions produced during oil extraction and transportation during the production of conventional jet fuel and

could potentially offer an opportunity for emissions reductions. A more precise understanding of how the emissions compare will require a more thorough analysis of FT jet fuel characteristics.

4.3.3 Impact of Product Slate

When evaluating a facility such as the GTL systems described in this study, the system expansion with displacement method is used to account for the co-products. This methodology examines the LCA GHG emissions of the products already being sold in the market that the products produced by the facility would be “displacing” and assigns the emissions of the displaced product as an LCA GHG “credit” for the facility. Therefore, the naphtha and LPG produced at the GTL facility would provide an emissions offset, as would any electricity, steam, H₂, or other products that are sold into the market.

Performing a life cycle GHG evaluation of emissions offsets is premature for this study given that a plant configuration selection and the resultant co-product slate has yet to be determined. Of the potential co-products, naphtha is the only co-product that will be produced, although even this co-product could be upgraded into gasoline if there was sufficient interest, changing the LCA.

Regarding the other potential co-products:

- LPG may be a co-product or may be recycled into the natural gas feed stream, a decision that will be based on market conditions for LPG, among other factors.
- Electricity production levels will depend on factors such as the level of CO₂ capture (and associated electricity requirements), local market conditions for electricity and steam, and a determination of whether O₂ should be produced onsite.
- Steam may be a co-product depending on local market conditions for both steam and electricity.
- H₂ could be a valuable co-product, depending on the interests of GTL facility operators in diversifying the product slate.

In addition to these uncertainties, it is noted that the emissions offset provided by certain products can potentially have a disproportionate impact on the associated emissions of the main product being evaluated—in this case jet fuel—if the products being displaced in the market have a substantial enough GHG footprint. Special care must, therefore, be taken in comparing the LCA GHG profiles of GTL configurations with disparate product slates, as the comparison is not an equivalent comparison and may misguide interpretation of co-product impacts.

While a detailed examination of how different co-products can impact the LCA GHG profile of GTL jet fuel is beyond the scope of this study, it is expected to be explored in future work when one or more process configurations are selected for additional modeling. An example of different methods of evaluating the impacts of co-products can be found in the Tarka, et al. study. [20]

4.3.4 Impacts of O₂ Production – ATR Cases Only

A GTL facility that leverages an ATR for syngas generation will require O₂ as an input to the process, as described in Section 2.3.2 and Section 4.2.2.3.3. This study assumes that O₂ will be purchased from an offsite vendor and transported to the GTL facility via pipeline. In this scenario, the upstream emissions associated with O₂ production would be determined and accounted for in the GHG emissions profile of the jet fuel, similar to how the emissions of the oil production and transport are accounted for in the conventional jet fuel scenario. Another option is for O₂ to be

produced onsite at the GTL facility, in which case the emissions associated with O₂ production will be explicitly captured in the modeling of the system.

A future analysis on the relative benefits of producing O₂ onsite to the GHG should be performed to identify the cost and emissions impact trade-offs.

4.3.5 Impacts of CO₂ Capture

Capturing and permanently storing CO₂ produced by the GTL process can directly impact the GHG emissions intensity of the jet fuel product. Three CO₂ capture scenarios were evaluated for both the ATR and SMR process configurations:

1. CO₂ is captured from high-pressure, high-concentration streams to reduce equipment size, but is ultimately vented
2. CO₂ is captured from high-pressure, high-concentration streams to reduce equipment size and is ultimately stored either in a geologic formation (saline aquifer) or as part of an EOR process
3. CO₂ is captured from both high-concentration streams (as in #1 and #2 above) and from low-concentration flue gas streams, then stored

The amount of CO₂ stored or emitted varies significantly between the ATR and SMR syngas generation cases, as substantially more CO₂ is produced in the SMR cases, and also varies based on the process configuration selected. Consequently, the impact of implementing CCS will be different for different cases, both in terms of cost and impact on the GHG intensity of the jet fuel produced. These relative impacts are described below, but the overarching take-away is that implementing CCS will be lower cost for the ATR cases, and that the failure to implement CCS for the SMR cases has a more dramatic effect on the GHG intensity of the jet fuel produced. Similarly, implementing an aggressive CCS strategy for the SMR cases will result in higher jet fuel costs than for an equivalent ATR case, as more CO₂ will be captured. A more detailed examination of the impacts of the different CCS strategies on the GHG emissions of the fuels follows.

Scenario #1—the Vent case—has no ultimate impact on the CO₂ emissions from the GTL facility or the GHG intensity of the jet fuel produced. In these scenarios, the GHG emissions of the synthetic jet fuel will almost certainly be higher than those of conventional jet fuel barring other considerations not evaluated here (e.g., the integration of RNG as a feedstock). Jet fuel produced in the SMR cases will have higher GHG profiles than the ATR cases based on the lower carbon conversion efficiency (less carbon from the feedstock ends up in the finished product).

Scenario #2—the CCS case—abates 58 percent of the GTL facility emissions in the ATR case and 11 percent of the emissions in the SMR case. This is the result of 1) less CO₂ being produced in the ATR case, and 2) a greater portion of the CO₂ being available in a higher pressure and relatively high purity form. Therefore, this low incremental cost CCS pathway will have a greater impact on the GHG intensity of the ATR case jet fuel. The GHG emissions intensity of the jet fuel produced in these scenarios will be close to that of conventional jet fuel, with factors such as the co-product slate and the characteristics of the FT jet fuel playing a larger role in determining whether the fuel has a lower or higher GHG intensity than conventional jet fuel. In general, the ATR-produced fuel will have a lower GHG intensity than the SMR fuel, although the co-production of H₂ in the SMR case can play a role in this determination.

Scenario #3—the most aggressive CCS scheme—abates approximately 95 percent and 91 percent of the CO₂ emissions in the ATR and SMR cases, respectively. In this scenario, the CO₂ emissions from the facility contribute very little to the GHG intensity of the jet fuel, although the energy requirements of the CCS equipment have the potential to reduce the export of co-products like electricity and steam, which will result in emissions offsets for the fuel (as described in Section 4.3.3). Similar to Scenario #2 above, the GHG emissions intensity of the jet fuel produced in these scenarios will be close to that of conventional jet fuel, although here it is more likely to be equivalent or lower than conventional jet fuel, depending again on factors such as the co-product slate and the characteristics of the FT jet fuel. It should be noted that while the CO₂ emissions abatement levels for the ATR and SMR cases are similar, the cost of implementing this aggressive CCS scheme is significantly higher for the SMR case based on the increased levels of CO₂ produced.

The decision to implement CCS can have a substantial impact on CO₂ emissions at the GTL facility and, in some cases, a meaningful impact on the GHG intensity of the jet fuel produced. More study is certainly warranted on this topic to identify the impacts and tradeoffs of implementing different CCS systems on different GTL process configurations. Additional information on the cost and performance impacts of implementing CCS at the facility is detailed in Section 5.2.

4.3.6 FT Product Quality and Upgrading

The LCA GHG emissions of jet fuel are dominated by emissions during combustion when the hydrocarbon chains in the jet fuel are converted to CO₂. The literature reports the combustion emissions for FT and conventional jet fuels to be 71.7 g CO_{2e}/MJ and 73.7 g CO_{2e}/MJ, respectively. Hence, the FT jet produces 2.7 percent fewer GHG emissions when combusted.

However, the FT upgrading section of this facility leverages a different catalyst than in previous work as has been mentioned above. This produces a higher jet fuel yield but also may change the characteristics of the jet fuel produced, notably the amount of carbon per MJ of energy and the energy density (MJ/gal of fuel). Both of these factors directly impact the combustion emissions of the jet fuel, which generally dominate the LCA GHG impacts of jet fuel usage.

More research will be required to reduce the uncertainty surrounding the combustion emissions from the jet fuel produced via the new FT upgrading schema and catalysts. The findings of said research must then be weighed against other operational and market considerations, such as acceptable energy and other fuel characteristics required by fuel purchasers.

4.3.7 LCA Conclusions

There is considerable uncertainty associated in evaluating the LCA GHG impacts of a jet fuel produced by a GTL facility located at PIT because of the variety of options for how a facility would be configured and uncertainty regarding process outputs, particularly the characteristics of the jet fuel produced using new upgrading processes and catalysts.

A number of options exist to reduce the GHG profile of the fuels produced at the GTL facility if that is deemed to be a strategic priority. Some of these options are likely to have both a GHG and an economic benefit, such as the use of natural gas produced onsite as a feedstock. Other options, such as the use of aggressive CO₂ capture schemes to minimize all CO₂ emissions, will come at a cost to economic and plant performance. The authors are confident that the facility can be designed such that the GTL jet fuel will have LCA GHG impacts that are equivalent to or below those of conventional jet fuel based on the preliminary investigation of GHG mitigation options available.

Further emissions reductions over conventional fuels may also be realized with diligent designs, although it will ultimately come to a trade-off between economic and environmental performance. Advances in the technologies used within the GTL facility or the integration of renewable energy inputs into the facility can also result in a reduction in the GHG impacts of the fuel. Section 8 catalogs a number of these potential improvements, and it is easy to imagine several early mover opportunities for renewable energy integration, such as using RNG as a feedstock or leveraging O₂ and H₂ produced from renewable energy (e.g., solar or wind power) to offset plant utility needs for these feeds.

Conversely, if no attempts are made to mitigate GHG emissions across the life cycle of the GTL jet fuel production, the LCA GHG impacts are expected to be greater than those of conventional jet fuel. Argonne National Laboratory's Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation Model (GREET) estimates the GHG intensity of GTL jet fuel without carbon capture to be 115 g CO_{2e}/MJ of jet fuel [21], a 30 percent increase in GHG intensity over the estimated GHG intensity of conventional jet fuel of 88.3 g CO_{2e}/MJ from the literature. [19] This value will vary based on the considerations described above, inclusive of feedstock choice, syngas generation technology, and co-products produced, but the GREET value provides valuable data point for consideration if GHG mitigation is not a priority in the design of the facility.

5 SENSITIVITY CASES

Several alternative case scenarios were evaluated to understand how changes to variables such as feedstock quality, process configuration, and additional process equipment could impact GTL plant performance. While several of these scenarios were modeled in Aspen to provide a detailed performance assessment, others were limited in scope to screening assessments performed with the goal of determining if further assessment is warranted. All scenario analyses performed are detailed below.

5.1 PIPELINE NATURAL GAS SCENARIO

The GTL facilities modeled for this study include a “pre-reformer” that reforms the natural gas coming into the facility in preparation for conversion into syngas. The presence of the pre-reformer negates any significant differences between using pipeline gas and using wet gas produced onsite. Consequently, the GTL facility performance is not impacted by the choice of natural gas feedstock and operation is essentially the same regardless of the source of the natural gas used.

The remaining differences between the two sources of natural gas are the price of the gas and the life cycle emissions footprint associated with gas production and transportation. Gas produced onsite is superior to pipeline natural gas in both of these categories, having a lower production price, a lower emissions footprint associated with production, and no emissions footprint associated with natural gas transportation to the facility. The production of gas onsite also provides an opportunity for other abatement actions to be implemented and emissions to be closely monitored.

Consequently, onsite natural gas was found to be the clear choice of natural gas feedstocks for the facility.

5.2 AGGRESSIVE CO₂ CAPTURE SCENARIO

The opportunity also exists to further reduce CO₂ generated by facility operation by employing a more aggressive CO₂ capture scheme. This would involve the installation of amine-based, post-combustion CO₂ capture units, which would be used to remove CO₂ from flue gas streams in the facility. This aggressive CO₂ capture strategy would result in approximately 95 percent and 91 percent of the CO₂ emissions from the ATR and SMR facilities being abated. This compares favorably to the ATR-CCS case, where 58 percent of the emissions are abated, and the SMR-CCS case where 11 percent of the emissions are abated.

The estimated cost of deploying these systems on the ATR- and SMR-based GTL systems are \$80 MM and \$200 MM, respectively. The cost increase is much higher in the SMR scenario due to the significantly larger amounts of flue gas being processed and CO₂ being stored in that case, over five times the amount being addressed in the ATR case. This is expected to raise the price of the jet fuel by approximately \$14/bbl and \$34/bbl in the ATR and SMR cases, respectively. This cost increase is relative to the ATR-Vent and SMR-Vent scenarios, as described in Exhibit 5-1 and Exhibit 5-2.

Exhibit 5-1. Cost estimate for the ATR with aggressive CCS case (\$/bbl product)

Natural Gas Cost	\$1/MMBtu	\$2/MMBtu	\$3/MMBtu
ATR-Vent Total	70.85	81.7	92.55
Amortized CO ₂ Capture, Compression and Drying Costs	4.76		
CO ₂ Transport and Storage Costs	9.55		
ATR w/ Aggressive CCS Total	85.16	96.01	106.86

Exhibit 5-2. Cost estimate for the SMR with aggressive CCS case (\$/bbl product)

Natural Gas Cost	\$1/MMBtu	\$2/MMBtu	\$3/MMBtu
SMR-Vent Total	73.20	86.4	99.6
Amortized CO ₂ Capture, Compression and Drying Costs	12.02		
CO ₂ Transport and Storage Costs	22.25		
SMR w/ Aggressive CCS Total	107.47	120.67	133.87

5.3 ADDITIONAL PRODUCT SCENARIO: HYDROGEN – SMR ONLY

The cobalt catalyst-based FT synthesis process used in this study requires syngas with a H₂-to-CO ratio of 2 for optimal operation, as described in Section 2.3.2. The syngas produced using a SMR has a H₂/CO ratio of 3.06, meaning that excess H₂ exists in the syngas that must be removed prior to conversion to FT liquids. A portion of this H₂ is used in the HC unit and the remainder is combusted in a fired heater for process heat.

H₂, however, is a valuable commodity that can be sold into local markets. A sensitivity analysis was performed to determine the plant performance impact of combusting FT tail gas for process heat such that excess H₂ could be sold into the market. It was determined that using the FT tail gas for process heat raised the flue gas CO₂ emissions for the facility. These emissions could be abated in the scenario where a more aggressive CCS scheme was leveraged, as described in Section 5.2, but otherwise would result in more direct CO₂ emissions from the facility. It is possible that the life cycle impact of these emissions would be offset by the reduced environmental impact of the H₂ being produced, which could be determined by a more detailed LCA.

The benefit of selling the H₂ to the overall economics of the GTL facility was not evaluated due to uncertainty regarding the market for H₂ in the proximity of PIT and scope limitations.

5.4 PROCESS OPTIMIZATION SCENARIO: FT RECYCLE CARBON ABATEMENT IMPACT ON ATR PERFORMANCE

The FT tail gas in the ATR cases is primarily used for fired heaters throughout the GTL facility, with the remainder recycled to the ATR as a feedstock (supplanting a portion of the natural gas feed). Two scenarios were modeled to explore the impact of different carbon abatement strategies on the CO₂ emissions from the facility: 1) only the FT tail gas being used in process heaters goes through a CO₂ capture process, 2) the full FT tail gas stream—inclusive of what is recycled to the ATR—is processed for CO₂ removal.

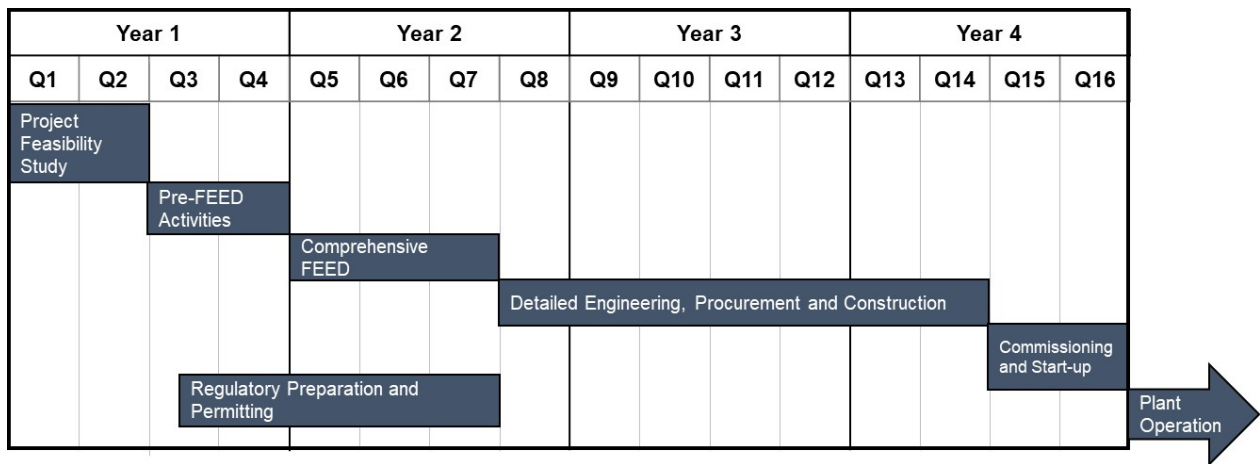
It was found that since most of the FT tail gas is to be used for process heat—and, consequently, is processed for CO₂ capture—there is not much difference between the two scenarios, although the case in which the whole stream is processed does have slightly lower CO₂ emissions. It was determined that significant changes in the ATR feed and operating conditions need to be made to observe differences in the two ATR cases, which is beyond the scope of this study.

6 PRELIMINARY PROJECT SCHEDULE

The construction of a GTL facility can be completed within 4 years, inclusive of design, engineering, and permitting. Design and engineering (and fundraising) can be time consuming, but can reasonably be expected to require 12–18 months from initiation.

Exhibit 6-1 shows the anticipated 4-year implementation effort for a typical project schedule for a GTL facility. The first couple of quarters involve the feasibility study, which will be followed by the FEED activities for over a year. The detailed engineering, procurement, and construction (EPC) effort is estimated to take close to 2 years, starting in Year 2 until Year 4. The EPC contract would be initiated once the regulatory check and permitting is completed in Year 2. After a successful commissioning and start-up, the plant operation would start at the end of Year 4.

Exhibit 6-1. Estimated project schedule



7 DECARBONIZATION PATHWAYS

GTL and other synthetic transportation fuel production pathways present an opportunity to reduce GHG emissions from the transportation sector by generating less emissions than conventional, petroleum-derived fuels. The opportunity also exists to completely decarbonize transportation fuels through the use of carbon-neutral or carbon-negative feedstocks. Nowhere in the transportation sector is this more important than for air transportation where there are limited options for replacing the means of propulsion and doing so safely. This is in contrast to the ground transport sector where electric and fuel cell vehicles already exist as viable decarbonization pathways.

Technologies to reduce or fully decarbonize GTL fuels fall into three broad categories: 1) direct reduction of emissions from the GTL facility, 2) the use of alternative carbonaceous feedstocks with reduced upstream GHG emissions, and 3) the integration of net-zero or net-negative GHG energy into facility operation. Decarbonization pathways within these categories range from near-term opportunities that could be immediately integrated into the plant design to lower technology readiness level (TRL) technologies that would benefit from additional R&D. These categories and the pathways within them are described in more detail below.

It is worth noting that absent a price on GHG emissions, all the technologies would result in a higher price of jet fuel and some would add deployment risk due to uncertainty regarding technology performance or lack of technology maturity. Uncertainty regarding technology maturity could also negatively impact project financing terms (due to the higher risk), which would also increase jet fuel selling price.

7.1 DIRECT REDUCTION OF EMISSIONS

The most straightforward method of reducing the GHG impact of GTL fuels is the direct reduction of GHG emissions from either the GTL facility or the feedstock (e.g., natural gas) production and transportation infrastructure. The primary contributor to GHG emissions from the GTL facility is emissions of CO₂—either high purity CO₂ or low concentration CO₂ within the flue gas—abating these emissions is discussed in depth above, particularly in Section 4.3.5 and Section 5.2. While this study focuses on the storage of captured CO₂, there is also the opportunity to leverage the CO₂ as a feedstock to the facility.

Another opportunity for direct emissions reductions from the GTL facility is the prevention of fugitive emissions, both during normal operation and startup/shutdown of the plant. These emissions are harder to quantify but warrant attention and can be minimized with a combination of proper facility design and mitigation strategies.

Direct reduction of emissions from natural gas production and transportation can primarily be achieved by CH₄ emissions mitigation strategies, which is touched on in Section 4.3.2. The impact of these strategies can be meaningful as evidenced by the difference between the use of natural gas produced onsite versus pipeline gas.

7.2 ALTERNATIVE CARBONACEOUS FEEDSTOCKS

Supplanting natural gas with alternative carbonaceous feedstocks into the GTL process presents the best option for total decarbonization of the jet fuel. This can range from using a feedstock that has lower GHG emissions associated with its creation than natural gas to feedstocks that have net-zero or net-negative GHG emissions associated with their use. A number of options exists for

supplanting some or all of the natural gas feed into the GTL plant, including recycling CO₂ generated by the process, the use of RNG, alternate sources of syngas (e.g., biomass or waste gasification), or even the direct conversion of CO₂ to syngas. Several of these options are described below, including a preliminary assessment of their potential impact on reducing the raw natural gas feed into the facility, and thereby reducing the GHG impact of the jet fuel.

7.2.1 Dry Reforming for CO₂ and CH₄ Co-conversion to Syngas

Dry reforming, or the conversion of CH₄ (the primary component of natural gas) and CO₂ into syngas, is an alternative means of syngas production that could supplant the ATR or SMR in a GTL facility. The use of dry reforming would allow some or all of the CO₂ produced by the facility to be converted into syngas, removing the need for the CO₂ to be otherwise stored.

A screening analysis was performed to determine the impact of use of dry reforming instead of an ATR to produce syngas, using dry reforming performance data provided by NETL researchers. [22] It was found that if the relatively pure stream of CO₂ produced within the facility was reformed with natural gas instead of being vented or stored (i.e., the ATR-Vent or ATR-CCS case) that the total feed of natural gas into the facility could be reduced by approximately 8 percent. In this scenario, enough CO₂ would be available for 50 percent of the syngas into the facility to be produced via dry reforming and an ATR would be required to meet the remainder of the syngas demand.

In the scenario where a more aggressive CO₂ capture scheme is used, as described in Section 5.2, sufficient CO₂ would be available for dry reforming to provide nearly 90 percent of the syngas demand of the facility. This would reduce the raw natural gas feed into the facility by approximately 15 percent. Both of these cases warrant additional study to better understand the performance and cost impacts of leveraging dry reforming as a syngas production pathway for the GTL facility.

Perhaps as important as the reduction in natural gas feed into the facility is the removal of a need for CO₂ storage or disposal. Dry reforming essentially recycles the carbon (as CO₂) that was not initially converted into jet fuel, resulting in a higher overall carbon conversion and simultaneously eliminating CO₂ emissions.

Dry reforming is a commercially available technology that could be leveraged in a new GTL facility. It was not evaluated as part of this study because of the relative newness of the commercial offerings and a lack of verifiable performance data, as is discussed in more detail in Section 8.1.2. This is an area that warrants additional evaluation.

7.2.2 Renewable Natural Gas

RNG, natural gas/CH₄ equivalents produced from non-fossil fuel sources, is an alternative feedstock that could be fed directly into the GTL facility, either as a standalone feedstock if sufficient RNG was available or blended with natural gas produced onsite. A recent study by researchers at Penn State University found that over 2,000,000 MMBtu of RNG could be produced a year in Allegheny County, the location of PIT. [23] This could provide approximately 10 percent of the natural gas feedstock required by the GTL facility, in jet fuel that is both partially generated from a renewable source and that has reduced GHG impacts. The dry reforming syngas pathway described in Section 7.2.1 is also pursued, this pathway has the potential to reduce the demand for onsite natural gas by approximately 17 percent (pure CO₂ stream case) or 24 percent (aggressive CO₂ capture case).

RNG represents a near-term and low-risk opportunity to reduce the GHG impact of jet fuel produced at PIT because of the ease of integration and the relatively short timeframe required to develop local RNG resources. Additional details on the use of RNG can be found in Section 8.2.

7.2.3 Alternative Syngas Sources

Another option for integrating alternative carbonaceous feedstocks into the GTL facility is the production of syngas from other source materials that either have a lower GHG impact than the onsite produced natural gas or that come from renewable sources. This syngas would then be blended with the natural gas-derived syngas, offsetting a portion of the natural gas demand for the facility.

The gasification of solid biomass materials into syngas offers one opportunity to integrate renewable energy into the facility. Biomass gasification technologies are commercially available, including air-blown gasifiers that produce a low-nitrogen syngas that would be amenable for blending into the natural gas-derived syngas feed and others that produce biomethane. [24] [25] [26] This pathway is amendable to a wide variety of feedstocks, including trees, forest trimmings, energy crops such as miscanthus, or agricultural byproducts such as corn stover. Some of these feedstocks have even shown promise as energy crops that can be cultivated on reclaimed mine sites or degraded agricultural lands. [27] [28] [29] [30]

Gasification can also be used to produce syngas from waste materials such as municipal solid waste (MSW) as alternative to using natural gas. Other syngas production technologies also exist, including pyrolysis, but are beyond the scope of this study.

The integration of non-natural-gas-derived syngas can be considered a near-term opportunity for integration into a GTL facility with certain caveats. The size and output of the alternative syngas feed should be well understood during the design phase of the facility so that the ATR or SMR can be sized appropriately and other design considerations can be made. The production of biomethane (via gasification) may present a better opportunity for integration as it is fungible with natural gas produced onsite, but a comparative analysis of the performance, cost, and relative technology readiness should be performed to identify the benefits of each pathway.

7.2.4 Direct Conversion of CO₂ to Syngas

An intriguing opportunity for the production of net-zero or net-negative GHG jet fuel is to use CO₂ captured from the ambient air as a carbon source for the GTL process. This would essentially recycle CO₂ from the atmosphere: CO₂ is captured from the atmosphere and converted into jet fuel, which, when combusted, becomes CO₂ in the atmosphere. While this is not technically a GTL technology, the facility envisioned here could be converted to leverage CO₂-derived syngas (instead of natural gas-derived syngas) at a point when sufficient CO₂ syngas was available. Or CO₂-derived syngas could be blended into the natural gas syngas stream in a scenario similar to the one described above in Section 7.2.3.

The underlying technology exists to convert CO₂ directly into syngas, but has not been demonstrated at an industrial scale. [31] Demonstration- and commercial-scale direct air capture (DAC) facilities that capture CO₂ from the atmosphere are currently under construction and should prove viable in a number of years. However, additional development will be required to bring down costs and technology risk.

For this concept to have a substantial GHG emissions impact on the jet fuel, sufficient low GHG-intensive energy (e.g., renewable, nuclear, or CCS-enabled fossil) will be required to run both the DAC facility and the electrochemical CO₂ conversion process.

This technology pathway will necessarily increase the production cost of the jet fuel (at present DAC and CO₂ conversion costs) and should be considered to be viable in the medium- to long-term based on technology readiness. The requirement for substantial amounts of low GHG-intensive energy may also be a barrier to near-term deployment.

7.3 NET-ZERO OR NET-NEGATIVE ENERGY INTEGRATION

A final pathway means to reduce the GHG emissions impact of the GTL facility and jet fuel is the use of net-zero or net-negative energy to run portions of the facility or to produce feedstocks for use in the facility. Of particular interest is whether low GHG-intensive electricity (e.g., renewable, nuclear, or CCS-enabled fossil) could be leveraged to either run the ASU or to generate H₂ and O₂ for the facility via electrolysis. These options warrant more study but will necessitate the availability of large amounts of low GHG-intensive energy and will substantially increase the jet fuel sale price at current electrolyzer costs. It is, therefore, considered a mid- to long-term option for decarbonization.

8 FUTURE TECHNOLOGY IMPROVEMENTS

GTL, inclusive of syngas generation and jet fuel production via FT synthesis, is a commercially demonstrated technology that has been deployed around the world. Yet, there remains headroom for technology improvements in the underlying technologies within GTL systems, and consequently a large amount of global R&D is ongoing, particularly in the areas of syngas generation and conversion. Some of these may already be in commercial use. A significant number of projects are in the pilot and/or demonstration plant scale-up stages, while others are currently limited to laboratory-scale and/or other small-scale proof-of-principle type operations.

This section of the study aims to cover the main areas that could have significant impact on an existing or near-term GTL plant, as well as others that could be implemented as they became sufficiently demonstrated. This section will, by definition, not cover all of the possible technologies in various R&D stages at present but will provide sufficient detail to allow others to identify and track at least some of these as this project may be developed.

8.1 SYNGAS GENERATION TECHNOLOGIES

8.1.1 Autothermal Reforming Improvements

Current ATRs are compact and highly efficient. Other than obvious continuing improvements in catalyst performance (mainly reforming activity, operating lifetime, and cost), there do not appear to be many obvious improvements to be made to the ATR itself.

However, provision of high purity O₂ for an ATR, although fully developed and commercialized, requires both high capital and operating/energy costs. Reducing the cost and energy requirements of O₂ generation has consequently been a long-term focus in industrial- and government-sponsored R&D.

One area which has received a great deal of time, effort, and funding has been invested in the concept of O₂ transport membranes, as well as ion transport membranes. These are generally solid ceramic materials that exhibit high O₂ transport through them, although usually only at high temperatures. Two major DOE-supported industrial joint ventures, one led by Praxair, the other by Air Products, were initiated in the 1990s. Both Praxair and Air Products have continued their development to the present. To date, some significant progress has been made in both projects, but fully achieving the original concept has been slow. Sealing the necessary connections between ceramic membranes and metal-based piping has been especially challenging. Coke formation at the interface between the O₂-containing membrane surface and the CH₄-containing process gas to be oxidized has also been problematic. Air Products stopped the work on the O₂ transport membrane technology.

A smaller effort in the area of polymeric O₂ membrane development was also evident in the past. These were more like the classic H₂, or newer CO₂, porous membranes. Significant breakthroughs in this area are not known, although such an event cannot be ruled out in the future.

An alternative technology would be water electrolysis, which, to date, has largely been focused on H₂ production, with the co-produced O₂ more of an afterthought. While this is certainly technically possible today, supplying the O₂ needed for this GTL plant would require a very large electrolysis plant consuming an enormous quantity of electricity.

This GTL plant would consume $\sim 67,000$ kg/hr of O_2 . With 1 mole of O_2 produced for every 2 moles of H_2 , this would be an electrolysis plant capable of producing 8,375 kg/hr of H_2 . At 55 kilowatt-hour (kWh)/kg H_2 , this would require 460 MW of power; in general, the large H_2 electrolysis plants under consideration today would (primarily) use renewable (solar, wind, or hydro) power. Conventional cryogenic air separation at this scale would generally require a power input of only ~ 9 – 10 MW (based on 250 kWh/ton O_2). It would, therefore, appear more practical to use renewable electricity to power a conventional ASU unless the (byproduct) electrolysis O_2 was available from an existing electrolysis plant based/justified on H_2 production.

It might be desirable to produce H_2 for HDS and HC/HI from an alternative source, rather than harvesting it from the ATR syngas, in order to allow easier HDS start-up and the possibility of HC/HI operations when the ATR and FT units are shutdown. One alternative would be a small, standalone SMR. Another option could be a H_2 electrolysis unit. The base ATR plant has an estimated total H_2 demand of ~ 460 kg/hr. With the same efficiency used above this would require ~ 25 MW of power and co-produce $\sim 3,700$ kg/hr of O_2 , or 5.5 percent of the plant O_2 demand.

8.1.2 Steam Methane Reformer Improvements

SMRs were originally developed for H_2 production and are more suitable for this purpose than for low H_2/CO ratio syngas production. The economics of an SMR feeding a GTL plant are hampered by its large size, lack of economies of scale, large heat transfer requirements at high temperatures and pressures, and very large heat loads. Because of these challenges for conventional SMR technologies, there appears to be significant room for improvements compared to the more efficient ATRs.

Several potential pathways for improving SMR efficiency and reducing SMR costs exist, including the following:

- Reforming vendors offer a large variety of SMR type technologies, with difference in orientation, flow direction, tube geometries, and inlet and outlet connections, etc. “Bayonet tube” design can be attractive for GTL plants because it uses the hot syngas product to heat the process gas in the reformer tubes, decreasing required firebox fuel demand and, hence, reducing the amount of excess steam produced in the WHRU.
- Combustion air preheat is also a well-known method of improving fuel combustion and decreasing fuel demand, although this can come at a price of increased combustion air compression requirements. There are a number of efforts underway to improve SMR heat transfer rates and potentially catalyst utilization as well by employing new catalyst types that can generally be described as structured materials. Johnson Matthey, through their subsidiary Catacel, has developed the “SSR” technology, which reported “substantial trims fuel savings and lower tube wall temperature at normal operating conditions and removal of pressure drop limitations.” [32] ZoneFlow Reactor Technologies also makes a structured SMR catalyst with similar claims for performance improvement. [33] There are almost certainly others.
- A novel approach referenced in a recent publication by Danish researchers demonstrates a single SMR tube driven by direct electric resistance heating. [34] The authors calculated a potential SMR size reduction of ~ 100 times compared to conventional a SMR, with a much lower amount of catalysts required. In a limiting case, a collection/bundle of such tubes could lie inside a refractory lined pressure containment shell, allowing for the use of lower delta P tubes and making such an SMR closely resemble an ATR in that respect. A pilot

plant demonstration of this technology is reportedly underway. [35] Use of such an electrically driven SMR should provide significant capital cost and plot plan savings regardless of the source of the electrical power employed. If the power came from fossil fuel-based plants with carbon capture and utilization/storage or from renewable power plants, SMR carbon emissions would be significantly reduced as well.

Another potential pathway for improved efficiency would be tuning the H_2/CO ratio of the syngas produced by the SMR. Excess H_2 , and therefore CO_2 , production is also a disadvantage to using SMR syngas in a GTL plant. Current SMR catalysts are limited in their ability to operate at lower steam/carbon and/or higher CO_2/CH_4 feed ratios, both of which would lower the syngas product H_2/CO ratio. The limiting case of feeding only CO_2 and CH_4 is referred to as “dry reforming,” [36] [37] [38] while the combination of higher CO_2/C and lower S/C is commonly referred to as “tri-reforming.” These are also very active areas for both government and industrial R&D. [39] [40] Several technology vendors have recently announced that they are licensing such technologies with the capability of producing H_2/CO ratios as low as 1.0, and as high as 3.0. These include BASF/Linde and Haldor Topsoe. [41] [42] [43] Besides potential catalyst deactivation issues with producing low H_2/CO ratios, an SMR also suffers from significantly higher inert (CO_2 and CH_4) concentrations compared to an ATR due to high inert concentrations in the FT recycle loop. Incomplete water (steam) consumption is not an issue as this is readily condensed and removed from the product syngas. Details of these new low H_2/CO ratio reforming technologies are not readily available today, and the resulting syngas compositions are unknown. It is, therefore, possible that these might be even more inferior than an SMR in terms of FT unit syngas inert levels, as neither CH_4 nor CO_2 conversion would be especially high.

A variation of dry reforming was recently developed by Texas A&M Qatar researchers, and involves reaction of CH_4 /natural gas with captured CO_2 (such as from a GTL plant tail gas purge) to produce syngas and carbon nanotubes. [44] [45] [46] Such a process would produce extra syngas (allowing less natural gas feed), and a potentially valuable co-product as well as directly employing the captured CO_2 in the plant rather than relying on another method of disposal. This technology is currently in the scale-up/demonstration stage.

Because it is always going to be necessary to purge some FT tail gas from the process side of a GTL plant, the use of this purge in providing fuel to preheat an ATR as described earlier or an electrically heated SMR as described above would be a good use for this stream. Therefore, other preheat options are not a focus, except for the possibility of allowing for easier CO_2 flue gas capture by employing oxy-combustion in a fired heater. However, if another suitable use for the purge FT tail gas was identified, it would certainly be possible to use (low carbon) electrical heating in all plant preheat services.

8.1.3 Alternative Syngas Production Technologies

Besides conventional ATR and/or SMR units, there is a very large amount of work going on in the area of alternative syngas production technologies, particularly from solids (e.g., biomass or MSW gasification) although pathways also exist for liquids and gases. Several studies have evaluated the potential of integrating alternative syngas production pathways with natural gas syngas. [47] [48] [16] Evaluation of these pathways was beyond the scope of this study but provides an intriguing opportunity for decarbonization of jet fuel, which should be investigated in future work.

An R&D area of interest today involves what is referred to as “chemical looping” combustion/oxidation/reforming. [49] [50] [51] The basis for these technologies is the use of a

multi-valent solid material (often on a support). The solid is oxidized in air after which it is exposed to/mixed with the hydrocarbon in question, in this case natural gas. The “excess” O₂ in the solid reacts with the hydrocarbon based on the ratio of O/C; hence, anything from partial to complete combustion. A typical configuration involves two fluidized bed reactors, one fed with air, the other with hydrocarbon, with the redox solid circulating between the two beds. Alternative designs with cyclic flow between two or more fixed bed reactors are also known.

The main challenges involve the long-term performance of the solids. These may be subject to mechanical breakage and erosion, leading to losses, and/or active component sintering (particle growth) or fracturing due to constant redox cycling. Long(er) term and larger scale developments are currently in progress and, if successful, could solve the major problems/limitations/costs involved with conventional reformers—high heat input requirements for SMRs and pure O₂ requirements for ATRs.

8.2 ALTERNATIVE GAS-TO-LIQUIDS PLANT FEEDSTOCKS

There is also current R&D in the area of alternative feedstocks for GTL plants, including the use of renewable or non-traditional sources of natural gas/methane, syngas generation from solids such as biomass, and other feedstocks such as CO₂. Processes that start with CO₂, for example, may involve co-feeding CO₂ with electrolytic H₂ or with water to a co-electrolysis unit to produce a syngas feed for the facility. Syngas produced from alternative feedstocks or CO₂ are not considered in any detail in this study because they would significantly change the design of GTL facility, by either 1) ruling out the use of natural gas in the first place (which is the basis of this study), 2) completely replacing the front-end ATR or SMR in an existing plant, or 3) requiring design optimizations to blend syngas streams with different characteristics, including different H₂/CO ratios.

RNG, a natural gas/CH₄ equivalent produced from non-fossil fuel sources, is an alternative feedstock that would be viable for an existing reformer-based GTL plant. The most promising sources of RNG, and those potentially available in relatively large quantities, could be landfill gas and biogas (CH₄ and CO₂) produced by anaerobic digestion (AD) of various bio-based feedstocks. These could be gradually added to an existing GTL plant, slowly decreasing the amount of natural gas feed at the same time. As more RNG feed became available, the CO₂ emissions profile of the plant would continually improve. Bio-based feedstocks from AD is a trending area, with new projects announced all the time, including at least one project to demonstrate the conversion of AD biogas to FT liquids [52] [53] and one to demonstrate conversion of the same to methanol and/or dimethyl ether. [54] The near-term opportunity for RNG integration into a GTL facility located at PIT is described in Section 7.2.2.

8.3 FISCHER-TROPSCH SYNTHESIS TECHNOLOGY IMPROVEMENTS

Like syngas generation, FT is a very active R&D area. Heat transfer limitations are a significant issue with fixed bed FT reactors. There are a number of different developments that show promise to improve heat transfer significantly, which would potentially lead to large decreases in fixed bed reactor sizes and/or costs. Most conventional fixed bed FT technologies employ ~1-in. diameter tubes and are, consequently, limited to ~300–400 volume (v)/v/hr CO productivities. Shell operates at a somewhat higher value, ~400–500 v/v/hr, and may be using liquid co-feed to achieve this, which would be complicated/expensive if so.

The Russian technology development company Infra Technology claimed a productivity of ~ 600 v/v/hr in 1 in. tubes through the use of metallic aluminum-containing catalyst particles, which is said to greatly improve internal tube heat transfer. [55]

In an SRI-operated field test, relatively short 2 in. and 4 in. diameter reactors employing a Chevron-developed hybrid FT/HC catalyst system using IntraMicron's microfiber-entrapped catalyst (MFEC) packing system were used. [56] These reactors were claimed to operate at productivities as high as 1,000 v/v/hr. Unfortunately, sufficient details regarding the packing were not included in the project report so it was impossible to verify the claims.

Ceramatec/Oxeon reported similar-type results using a metallic tube insert designed to maximize heat transfer and minimize radial heat transfer distances. [57] [58] They reported producing 0.25 BPD in a 4 in. diameter by 5 ft long FT reactor, which corresponds to a productivity of ~ 150 v/v/hr. This is extremely high for a 4 in. diameter tube, although lower than what is practiced in 1 in. tubes.

As discussed previously, Johnson Matthey/BP/Davy developed an innovative radial flow FT catalyst system that also appears to operate in 3-4 in. diameter tubes. Actual catalyst productivities achieved are not generally included in their public reports, but according to patents assigned to BP, it appears to be in the general range reported by Oxeon—100–150 v/v/hr.

Based on the FT tube requirement discussed during reactor sizing, if the catalyst productivity is 400 v/v/hr the tube number drops to 34,400. Alternatively, with a productivity of 300 v/v/hr, and 2 in. ID by 40 ft tubes, the tube number drops to $\sim 8,800$. With 3 in. ID tubes the tube number drops to $\sim 4,000$.

While tube size and count will largely determine FT reactor capital cost, the actual operating productivity will have a direct effect on required catalyst loading and, hence, catalyst cost. Taking the base case of 300 v/v/hr productivity and 46,000 1 in. OD tubes, the catalyst loading would be $\sim 7,700$ ft³. Then, assuming a packed bed density of 1.2 g/cubic centimeter, the weight of catalyst is $\sim 580,000$ lb. Next, assuming a very conservative catalyst cost of \$30/lb, a single charge of catalyst is \sim \$17 MM. Expected catalyst lifetime is typically three years. For the hypothetical reactors, assume the 46,000 tubes can be accommodated in 5 vessels, each containing somewhat more than 9,000 tubes. Even with the tubes taking up only 35 percent of the shell cross-sectional area (CSA) the required shell ID is somewhat less than 12 ft. At 45 percent of the CSA, the shell ID is ~ 10.5 ft. Assuming the 9,000-tube reactor capital cost is as much as \$5 MM, which is likely a large over-estimate of actual cost, the total reactor capital cost would be \$25 MM. Given that reactor capital cost is a one-time expenditure, the catalyst cost will clearly dwarf reactor cost on a total project basis. It is typical to include the first charge of catalyst as a plant capital cost.

Catalyst cost is a function of a number of different variables. The catalyst support would typically be purchased by weight or volume, and there may be any number of additives/promoters added to it. The support cost will, therefore, largely be a function of required catalyst loaded and will vary inversely with catalyst operating productivity. For a GTL plant, the active catalyst metal is cobalt. Like most metals, its price varies over time, but cobalt has typically been \sim \$20/lb, and typical catalyst cobalt loading would be ~ 20 –50 percent. There are also usually more expensive promoters, typically PGMs that are added to improve activation and/or activity, although the amounts employed are typically very small, much less than 1 percent. Activity, in turn, is related to cobalt loading, but not necessarily directly (doubling loading will generally not double activity, for example). A significant fraction of total catalyst manufacturing cost is related to the number of metal impregnation and subsequent drying and calcining steps required after each, and the number of

steps is usually strongly related to the total metal loading. The net result of these considerations is that if catalyst productivity is lower in a reactor with larger diameter tubes—for example going from 300 v/v/hr in 1 in. outer diameter (OD) tubes to 100–150 v/v/hr in 2–3 in. diameter tubes—the reactor capital cost savings in using larger tube diameters are likely to be smaller than the increased catalyst cost in operating at lower catalyst productivity. The ideal situation would be to maintain the 300 v/v/hr catalyst productivity (or higher) from 1 in. diameter tubes while actually using larger ones.

It is clearly possible to manufacture high activity/productivity FT catalysts. Both Velocys [59] and Ineratec [60] have shown operating results with catalyst productivities of ~2,000–4,000 v/v/hr, while typical slurry bubble column reactor productivities are normally ~1,000–1,500 v/v/hr. Velocys and Ineratec have also demonstrated that it is possible to design a type of fixed bed reactor (in these cases, microchannel reactors) that are capable of operating with catalyst productivities in this range. What they have not demonstrated publicly, at least to date, is that the combination of catalyst and reactor cost is actually lower than the equivalent conventional fixed bed values. And while these microchannel reactors are much smaller than conventional fixed bed reactors, the rest of the FT unit is more-or-less unchanged, so total unit size is not reduced nearly as much as the reduction in reactor size.

In the end, it is possible to use a combination of reasonably high activity catalysts, ~500–1,000 v/v/hr in conventional multi-tubular fixed bed reactors with tube diameters of ~1–2 in. through a combination of appropriate catalyst formulation (such as Infra's aluminum-containing particles) and enhanced heat transfer inserts (such as Oxeon's).

There is also a great deal of R&D going on in the area of catalyst selectivity, especially in attempting to produce a limited range of products directly in the FT reactor rather than making a wide distribution of products, including wax, and processing that further to generate the desired products. Unfortunately, achieving wax-free results appears to be accompanied by a large increase in light gas (C₁–C₄) make. The products of these systems include a large fraction of diesel fuel, although, in general, the low-temperature properties are rather poor (high cloud and pour points), although the Chevron catalyst, which includes a zeolite HC/HI function, are relatively good. The SRI report on the Chevron catalyst demonstrated an approximate 70 percent selectivity to jet fuel at 70–75 percent liquid selectivity (25–30 percent gas selectivity), or a jet fuel yield of ~50 percent. This is quite a bit lower than the 75 percent jet fuel selectivity at 88 percent liquid selectivity (~65 percent jet fuel yield) calculated in this study but is still relatively high and would be attractive in a small plant.

More promising results have been published in various scientific journals, although these are far from commercial at this time. These include maximizing selectivity/yield to various products [61] [62] [63] including light olefins, [64] [65] [66] high octane gasoline, [67] [68] [69] jet fuel, [70] [71] [72] and various oxygenates, including alcohols [73] [74] and aldehydes. [75] [76]

Another trending R&D area involves photo- and/or electro-catalysis. [77] [78] [79] [80] These systems typically operate at far milder conditions (lower temperatures and/or pressures) and have demonstrated extremely high specific catalyst activities but are similarly far from being commercialized.

Cobalt catalyzed FT reactors operate at fairly low temperatures, typically ~400–420°F. The Chevron and Infra catalysts operate above the high end of this temperature range, up to ~480°F max. With at least 10°F temperature difference between the catalyst and BFW/steam coolant, coolant side temperatures are typically ~390–410°F, with an upper limit of ~470°F. These are equivalent to ~210–265 psig, with an upper limit of ~500 psig. A GTL plant produces a great deal of steam from

the FT reactors, little of which is of use directly in the process. As discussed earlier, this steam is often used for driving turbines, either on compressors or power generators. While 500 psig is a reasonable pressure for turbine drivers, it has long been recognized that the more common 210–265 psig steam available results in low turbine efficiency. There has long been a strong push to consider alternative vapor/liquid systems for FT reactor cooling. Often this has resulted in the desire to employ a hydrocarbon liquid such as pentane or hexane. While the latent heat of vaporization of these liquids is much lower than that of water, the corresponding saturated pressures are much higher. This would clearly facilitate the use of the FT reactor coolant vapor in turbines, but it is unknown whether any technology developer has attempted to use one of these materials, almost always on hazard/safety grounds. Perhaps alternatives to steam production are worth revisiting, at least for catalysts operating in the typical temperature range.

The possibility of disposing oxygenate-containing FT process water by adding back to the reformer as steam, as opposed to treating it in a more conventional wastewater treatment facility, was discussed previously. Additional options in this area should also be investigated.

8.4 HYDROCRACKING/HYDROISOMERIZATION TECHNOLOGY IMPROVEMENTS

The major expenses in the HC/HI unit are catalyst and reactor costs, the same as in FT. Catalysts are typically either PGM or sulfided metal based. Operating pressures are higher than those employed in FT, and sulfided base metals usually require higher pressure than PGMs. Many different vendors are active in HC/HI technology development, and improvements are announced on a continuing basis. Clearly selectivity to the desired product, in this case jet fuel, is a very important parameter. As noted earlier, in previous studies, only the FT was sent to the HC/HI unit. Straight-run diesel (with typically very poor low-temperature characteristics) was either left as is or required a separate (HI) upgrading unit to convert it to more valuable products. Haldor Topsoe's recent demonstration of the ability to convert wax plus straight-run diesel and heavy naphtha is a huge improvement in overall plant jet fuel yield. It's expected that other vendors will achieve similar results and continue to optimize their HC/HI technologies to any number of desired products.

Catalyst productivity, including reactor design, is another area with some promise. Although the details vary with technology vendor, the typical FT wax HC/HI reactor operates at a liquid hourly space velocity of 0.5 to ~ 2.0 hr⁻¹. About 10–12 years ago, Velocys published data from a small-scale microchannel hydrocracker (similar to their microchannel FT reactor) demonstrating good conversion and yield at liquid hourly space velocities (LHSV) of ~ 10 –40 hr⁻¹. [81] They appear to have dropped this development at some point in the mid-2010s. Assuming a typical conventional HC/HI unit operating at an LHSV of 1 hr⁻¹ to a microchannel system operating at 20 hr⁻¹ indicates a 20-fold decrease in catalyst loading and, hence, a significant reduction in reactor size. As mentioned above in relation to microchannel FT reactors and high activity FT catalysts, it is not currently known whether these much smaller reactors and higher activity catalysts will actually result in a reduction in HC/HI system costs or improve the overall process economics, but at least the potential to do so appears worth investigating.

8.5 SUMMARY OF TECHNOLOGY IMPROVEMENT POSSIBILITIES

At a $\sim 6,000$ BPD GTL plant envisioned for this study, costs can be summarized as syngas generation that are greater than FT synthesis costs, which, in turn, are greater than the cost of the FT product upgrading (e.g., HC/HI) portion of the facility. Clearly the largest potential for

improved economics lies in the syngas generation process. Large possibilities are apparent in lower O_2 generation cost for ATRs (although O_2 generation has been studied extensively for the past 30 years) and/or in significant redesign of SMR catalyst capabilities and reactor configurations. FT improvements will typically be more modest, although the FT catalyst cost is generally the highest plant operating cost after feed natural gas costs. HC/HI improvements will still be more modest and will largely consist of improvements in the selectivity and/or yield of desired products.

Larger cost reductions and/or improvements in overall economics could be realized with the development of a combined FT-HC/HI system that does not suffer from as large of an increase in light gas selectivity as those developed by Greyrock, Infra, and Chevron. These systems appear very suitable/applicable to small GTL plants, at least smaller than ~ 800 – $1,000$ BPD, but appear to be less economic at larger scales today due to the high gas make.

Since at least the mid-1980s, the concept of direct conversion of CH_4 to products, explicitly not through a syngas intermediate, has been the holy grail of GTL process development. To date some improvements have been made, but commercialization remains a long way off. Because CH_4 is much more inert than the various products that are produced from it, such systems have been strongly limited by the fact that high selectivities to products are only possible at low CH_4 conversions, while at high CH_4 conversions, selectivity to desired products is very low. A large number of different routes have been explored, including the use of a halogen (generally chlorine or bromine) compound to activate the CH_4 followed by further reactions, ideally leaving the halogen unchanged to repeat the cycle (i.e., functioning much like a catalyst). More recently the company Siluria (now part of Lummus) published very promising small-scale results of the use of designer catalysts for direct and selective reaction between CH_4 and O_2 , referred to as oxidative coupling of CH_4 . They appear to have had difficulty scaling their system up, and their present status is not well known. [82] The GTL process developer Gas Technologies has also claimed success with related technology, but despite reportedly excellent overall economics has not yet succeeded in large-scale commercialization. [83] Reasons why this should be are not apparent.

9 CONCLUSIONS AND FUTURE WORK

This study found that it would be technically feasible to construct and operate a GTL facility on PIT's property. The approximately 6,000-BPD facility evaluated would produce nearly 70 MM gal of synthetic jet fuel per year, which could supplant nearly all (85 percent) current jet fuel consumption at PIT. Given the current blend limitation of 50 percent FT fuels by volume, the plant would have excess production capacity available for the USAF Pittsburgh Air Reserve Station and the USAF 171st Air Refueling Wing co-located at the airport.

The cost competitiveness of the jet fuel produced—and, therefore, the economic feasibility of the project—is highly dependent on the price of the natural gas fed into the facility. The jet fuel selling price is estimated to be \$1.69–2.37/gal over the \$1–3/MMBtu range of natural gas prices evaluated. The sale price includes operating costs and includes the developer's return on investment. This compares to current jet fuel prices of \$1.88/gal, and a fuel price range of \$0.41/gal (April 2020 during the COVID-19 Pandemic) to over \$4/gal (July 2008). [6] Broadly speaking, the project should be economically viable at natural gas prices of \$1/MMBtu or lower, and in some scenarios a price of \$2/MMBtu may be viable.

The 6,000-BPD facility would cost \$550–740 MM to construct depending on the facility configuration, with higher levels of GHG abatement increasing the facility cost to as much as \$820 MM. The facility could be constructed in four years, including permitting and FEED design phases.

There is considerable uncertainty associated in evaluating the LCA GHG impacts of the jet fuel produced by a GTL facility located at PIT because of the variety of options for how a facility would be configured and uncertainty regarding what products would be produced. Nonetheless, GTL offers an intriguing near-term opportunity for reducing the climate impacts of aviation by generating less emissions than conventional, petroleum-derived fuels and the opportunity also exists to completely decarbonize transportation fuels through the use of carbon-neutral or carbon-negative feedstocks. Nowhere in the transportation sector is this more important than for air transportation where there are limited options for replacing the means of propulsion and doing so safely.

Technologies to reduce or fully decarbonize GTL fuels fall into three broad categories: 1) direct reduction of emissions from the GTL facility, 2) use of alternative carbonaceous feedstocks with reduced upstream GHG emissions, and 3) integration of net-zero or net-negative GHG energy into facility operation. This study examined the direct reduction of emissions by implementing CCS and found that 58 percent of facility emissions in the ATR case could be eliminated at a very low cost—\$0.16/gal—while a more aggressive approach to CCS could eliminate 95 percent of emissions at a slightly higher cost, an estimated \$0.34/gal increase in selling price of the jet fuel.

Two additional climate impact reduction pathways were examined as sensitivity cases: the use of renewable natural gas as a feedstock and the implementation of dry-reforming to convert a higher percentage of the feedstock carbon into jet fuel. Combined, these pathways have the potential to reduce the demand for onsite natural gas by approximately 17–24 percent depending on the level of CO₂ capture pursued. Both are considered near-term opportunities, as the technologies required to implement them are commercially available. Pathways to totally decarbonize jet fuel, such as the direct conversion of CO₂ captured from the atmosphere to syngas, were not evaluated in this study but represent an area for future study.

Several topics for future study have been identified to better understand the opportunity associated with locating a GTL facility at the airport. The authors recommend the consideration of the following highest-priority analysis topics:

- Selection and modeling of two to three final plant configurations and product slates for detailed economic performance analysis, inclusive of one with CO₂ recycling via dry reforming
- Detailed analysis of FT jet fuel characteristics based on new refining catalysts to inform LCA of global warming potential impacts of jet fuel
- In-depth look at natural gas production costs from onsite wells
- Evaluation of whether the construction of a smaller GTL facility that produces 3,500 BPD of FT liquids—equivalent to 50% of PIT demand by volume—would be negatively impacted by economies of scale, making the required jet fuel sale price higher
- Assessment of geologic formations capable of CO₂ storage within a 100-mile radius of PIT to inform a more detailed examination of the cost of CO₂ transport and storage
- Full characterization of the non-global warming potential impacts of the jet fuel, particularly in the reduction of non-GHG emissions during combustion of FT jet blends

A number of other topics are also of interest, with the screening of configurational options that further reduce the GHG impacts or completely decarbonize the jet fuel being at the top of the list. These options include increased levels of renewable energy integration for oxygen or hydrogen production, the capture and conversion to syngas of CO₂ captured from the ambient air, and the economic impacts of integrating renewable energy feedstocks such as RNG or biomass-derived syngas or methane. Section 7 and Section 8 provide more detail on these potential options.

A final area of interest is the evaluation of a GTL facility in the context of the regional chemical and industrial sectors and a proposed regional hydrogen economy or corridor; the following questions are of particular interest:

- Which alternative GTL product slates would most effectively serve other regional industries?
- What is the role of a GTL facility in a regional hydrogen corridor?
 - Is it a net producer or consumer of hydrogen and how does that impact the facility?

The wide variety of potential topics for future analysis speaks to the robustness and flexibility of the GTL platform. A nearly infinite number of configurational possibilities exist depending on the goals and regional market opportunities. Notably, new modeling techniques such as those recently proposed in the literature and being developed within DOE present an opportunity to rapidly explore a “solution space” to screen how a given technology may be integrated with other energy systems, feedstock types, and product slates for optimal economic and environmental performance.⁵ [84] GTL systems seem to be a natural fit for evaluation using these modeling techniques based on

⁵ Computer models designed to evaluate “Multiple Input, Multiple Output” or MIMO systems could potentially be leveraged very effectively in this area. A MIMO system is one in which multiple feedstocks (e.g. natural gas, electricity, biomass, etc.) are fed into an energy conversion system (e.g. a GTL facility) with the potential of producing multiple products (e.g. jet fuel, electricity, hydrogen, etc.). Given the flexibility of GTL facilities, both in terms of inputs and outputs, a well-designed MIMO model could be very effective in screening potential facility configurations to determine what might be optimal for the PIT region. Such a model could be used to select individual configurations for additional study based on existing and projected market conditions for different products in the region.

their ability to down-select plant configurations of integrated energy systems for more detailed study, thereby allowing optimized solutions to be identified in a reduced amount of time and at a reduced cost.

10 REFERENCES

- [1] H. Baskas, "More airports consider going off the grid as power outages ground flights," 3 November 2019. [Online]. Available: <https://www.cnbc.com/2019/11/03/more-airports-consider-going-off-the-grid-to-avoid-power-outages.html>. [Accessed 16 February 2021].
- [2] M. Adams, "Resilient Airport Microgrids," 28 June 2019. [Online]. Available: <https://www.districtenergy.org/idea2019/viewdocument/resilient-airport-microgrids>. [Accessed 16 February 2021].
- [3] Peoples, "Powering the Future: Pittsburgh International Airport Microgrid," 18 October 2019. [Online]. Available: <https://www.peoples-gas.com/news/airport-microgrid>. [Accessed 6 February 2021].
- [4] A. Walls, "Construction Begins on First-of-its-Kind Airport Microgrid," 20 July 2020. [Online]. Available: <https://blueskypit.com/2020/07/20/construction-begins-on-first-of-its-kind-airport-microgrid/>. [Accessed 16 February 2021].
- [5] International Air Transport Association, "Fact Sheet 2: Sustainable Aviation Fuel: Technical Certification," undated. [Online]. Available: <https://www.iata.org/contentassets/d13875e9ed784f75bac90f000760e998/saf-technical-certifications.pdf>. [Accessed August 2021].
- [6] Energy Information Administration, "PETROLEUM & OTHER LIQUIDS: U.S. Gulf Coast Kerosene-Type Jet Fuel Spot Price FOB," 2 June 2021. [Online]. Available: https://www.eia.gov/dnav/pet/hist/eer_epjk_pf4_rgc_dpgD.htm. [Accessed 3 June 2021].
- [7] Reuters Staff, "Atlanta airport power outage cost Delta Air Lines up to \$50 million," 20 December 2017. [Online]. Available: <https://www.reuters.com/article/us-atlanta-airport-delta-air/atlanta-airport-power-outage-cost-delta-air-lines-up-to-50-million-idUSKBN1EE2LC>. [Accessed 16 February 2021].
- [8] The Atlanta Journal-Constitution, "Delta says airport power outage caused around \$40 million loss," 11 January 2018. [Online]. Available: <https://www.ajc.com/news/local/delta-says-airport-power-outage-caused-60-million-loss/682118589/>. [Accessed 16 February 2021].
- [9] Federal Energy Technology Center, Morgantown, WV and Pittsburgh, PA, Baseline design/economics for advanced Fischer-Tropsch technology, DE-AC22-91PC90027-01, DOE, April 1998.
- [10] E. Shuster and J. Goellner, Analysis of Natural Gas-to-Liquid Transportation Fuels via Fischer-Tropsch, NETL/DOE-2013/1597, NETL, September 2013.
- [11] D. Gilliland and M. Usher, "Mountaineer Commercial Scale Carbon Capture and Storage (CCS) Project," DOE, 31 December 2011. [Online]. Available: <https://www.osti.gov/biblio/1031460>. [Accessed 16 February 2021].

- [12] POWER Engineering, "Mountaineer CCS project deemed a success," 5 May 2011. [Online]. Available: <https://www.power-eng.com/emissions/air-pollution-control-equipment-services/mountaineer-ccs-project-deemed-a-success/#grefhttps://www.battelle.org/newsroom/press-releases/press-releases-detail/battelle-completes-15-year-co2-storage-project-at-mountaineer>. [Accessed 16 February 2021].
- [13] IEA Greenhouse Gas R&D Programme, "CO₂ Storage in Depleted Oilfields: Global Application Criteria for Carbon Dioxide Enhanced Oil Recovery," December 2009. [Online]. Available: https://ieaghg.org/docs/General_Docs/Reports/2009-12.pdf. [Accessed 16 February 2021].
- [14] C. H. Bartholomew and R. J. Farrauto, *Fundamentals of Industrial Catalytic Processes*, 2nd Edition, Wiley, August 2010.
- [15] R. Baliban, J. Elia and C. Floudas, "Toward novel hybrid biomass, coal, and natural gas processes for satisfying current transportation fuel demands, 1: Process alternatives, gasification modeling, process simulation, and economic analysis," *Industrial & Engineering Chemistry Research*, vol. 49, no. 16, pp. 7343-70, August 18, 2010.
- [16] Y. Zhang, A. H. Sahir, E. C. D. Tan, M. S. Talmadge, R. Davis, M. J. Bidy and L. Tao, "Economic and environmental potentials for natural gas to enhance biomass-to-liquid fuels technologies," *Green Chem*, vol. 20, no. 23, p. 5358–5373, November 2018.
- [17] A. E. Thomas, N. T. Saxena, D. T. Shouse, C. Neuroth, A. Lynch, C. W. Frayne, J. S. Stutrud, E. Corporan, T. Hankins and R. C. Hendricks, "Heating and Efficiency Comparison of a Fischer-Tropsch (FT) Fuel, JP-8+100, and Blends in a Three-Cup Combustor Sector," *International Scholarly Research Notices*, vol. 2012.
- [18] D. Shouse, C. Neuroth, R. Hendricks, A. Lynch, C. Frayne, J. Stutrud, E. Corporan and Capt. T. Hankins, "Alternate-Fueled Combustor-Sector Performance: Part A: Combustor Performance, Part B: Combustor Emissions," NASA Technical Reports Server, 2010. [Online]. Available: <https://ntrs.nasa.gov/api/citations/20100017413/downloads/20100017413.pdf>. [Accessed August 2021].
- [19] G. Cooney, M. Jamieson, J. Marriott, J. Bergerson, A. Brandt and T. J. Skone, "Updating the U.S. Life Cycle GHG Petroleum Baseline to 2014 with Projections to 2040 Using Open-Source Engineering-Based Models," vol. 51, no. 2, pp. 977-987, 22 November 2016.
- [20] T. J. Tarka, J. G. Wimer, P. C. Balash, T. J. Skone, K. C. Kern, M. C. Vargas, B. D. Morreale, C. W. White III and D. Gray, "Affordable Low Carbon Diesel from Domestic Coal and Biomass," DOE/NETL, 14 January 2009. [Online]. Available: <https://www.netl.doe.gov/sites/default/files/netl-file/CBTL-Final-Report.pdf>. [Accessed 2021].

- [21] A. Elgowainy, J. Han, M. Wang, N. Carter, R. Stratton, J. Hileman, A. Malwitz and S. Balasubramanian, "Life-Cycle Analysis of Alternative Aviation Fuels in GREET, ANL/ESD/12-8," Argonne National Laboratory, June 2012.
- [22] T. Tarka, Discussion with Douglas Kauffman of NETL's Functional Materials Team, RIC Materials Engineering & Manufacturing Directorate, 2021.
- [23] T. Tarka, Discussions with Tom Richard, Professor of Agricultural and Biological Engineering, Director, Institutes of Energy and the Environment, Penn State University, trichard@psu.edu, 1 (814) 863-0291, <https://abe.psu.edu/directory/tlr20>, 2021.
- [24] West Biofuels, "Gasification for Biochemicals & Biofuels," undated. [Online]. Available: https://uploads-ssl.webflow.com/5bd88ea13bd618e35be5f155/5eced74e8f0af8b02070b9a5_FICFB%20Brochure.pdf. [Accessed August 2021].
- [25] A. Alamia, A. Larsson, C. Breitholtz and H. Thunman, "Performance of large-scale biomass gasifiers in a biorefinery, a state-of-the-art reference," *International Journal of Energy Research*, 29 May 2017.
- [26] A. Larsson, I. Gunnarsson and F. Tengberg, "The GoBiGas Project: Demonstration of the Production of Biomethane from Biomass via Gasification," Göteborg Energi AB, undated. [Online]. Available: https://www.goteborgenergi.se/Files/Webb20/Kategoriserad%20information/Forskningsprojekt/The%20GoBiGas%20Project%20-%20Demonstration%20of%20the%20Production%20of%20Biomethane%20from%20Biomass%20v%20230507_6_0.pdf?TS=636807191662780982. [Accessed August 2021].
- [27] A. S. Warr, "The Impacts of Energy Development on Agricultural Land Values in North-Central West Virginia," WVU: Graduate Theses, Dissertations, and Problem Reports, 2018. [Online]. Available: <https://researchrepository.wvu.edu/cgi/viewcontent.cgi?article=7957&context=etd>. [Accessed August 2021].
- [28] Marshall University, "Marshall University to lead renewable energy project for surface-mined properties," 19 February 2010. [Online]. Available: <https://www.marshall.edu/murc/marshall-university-to-lead-renewable-energy-project-for-surface-mined-properties/>. [Accessed August 2021].
- [29] J. Frederick, "Evaluating Reforestation Options for Surface Mines in Appalachia," UK: Theses and Dissertations--Forestry and Natural Resources, 2019. [Online]. Available: https://uknowledge.uky.edu/forestry_etds/49/. [Accessed August 2021].
- [30] Z. Qin, Q. Zhuang and X. Cai, "Bioenergy crop productivity and potential climate change mitigation from marginal lands in the United States: An ecosystem modeling perspective," 2014. [Online]. Available: <https://www.osti.gov/pages/biblio/1435596>. [Accessed August 2021].

- [31] D. R. Kauffman, J. Thakkar, R. Siva, C. Matranga, P. R. Ohodnicki, C. Zeng and R. Jin, "Efficient Electrochemical CO₂ Conversion Powered by Renewable Energy," *ACS Appl. Mater. Interfaces*, vol. 7, no. 28, p. 15626–15632, 2015.
- [32] Johnson Matthey, "CATACEL SSR catalyst," 2020. [Online]. Available: <https://matthey.com/en/products-and-services/chemical-processes/chemical-catalysts/catacel-ssr-catalyst>. [Accessed January 2021].
- [33] ZoneFlow™ Reactor Technologies, LLC, "Catalyst for Steam Methane Reforming," undated. [Online]. Available: <https://zoneflowtech.com/>. [Accessed January 2021].
- [34] S. T. Wismann, J. S. Engbæk, S. B. Vendelbo, F. B. Bendixen, W. L. Eriksen, K. Aasberg-Petersen, C. Frandsen, I. Chorkendorff and P. M. Mortensen, "Electrified methane reforming: A compact approach to greener industrial hydrogen production," *Science*, vol. 364, pp. 756-759, May 2019.
- [35] Svend Ravn, "Topsoe to build demonstration plant to produce cost-competitive CO₂-neutral methanol from biogas and green electricity," Haldor Topsoe, 16 July 2019. [Online]. Available: <https://blog.topsoe.com/topsoe-to-build-demonstration-plant-to-produce-cost-competitive-co2-neutral-methanol-from-biogas-and-green-electricity>. [Accessed January 2021].
- [36] K. Wittich, M. Krämer, N. Bottke and S. A. Schunk, "Catalytic Dry Reforming of Methane: Insights from Model Systems," *ChemCatChem*, vol. 12, no. 8, p. 2130–2147, 2020.
- [37] C. Wang, Y. Wang, M. Chen, D. Liang, Z. Yang, W. Cheng, Z. Tang, J. Wang and H. Zhang, "Recent advances during CH₄ dry reforming for syngas production: A mini review," *Int. J. Hydrog. Energy*, November 2020.
- [38] Z. Lia, Q. Lin, M. Li, J. Cao, F. Liu, H. Pan, Z. Wang and S. Kawi, "Recent advances in process and catalyst for CO₂ reforming of methane," *Renew. Sustain. Energy Rev.*, vol. 134, p. 110312, December 2020.
- [39] X. Zhao, J. Kuhn, B. Joseph and S. Ozcan, "Biogas Reforming to Syngas: A Review," *iScience*, vol. 23.5, May 2020.
- [40] L. Chen, P. Gangadharan and H. H. Lou, "Sustainability assessment of combined steam and dry reforming versus tri-reforming of methane for syngas production," *Asia-Pac. J. Chem. Eng.*, vol. 13, no. 2, p. e2168, March 2018.
- [41] M. Burgess, "BASF and Linde win award," *gasworld*, [Online]. Available: <https://www.gasworld.com/basf-and-linde-win-award/2018241.article>. [Accessed January 2021].
- [42] BASF Catalysts, "Syngas Catalysts," BASF Catalysts, 2021. [Online]. Available: <https://catalysts.basf.com/products-and-industries/process-catalysts/chemical-catalysts/syngas-process-pre-reforming-catalysts>. [Accessed January 2021].
- [43] S. Winter-Madsen, "Turning waste CO₂ into feedstock," Haldor Topsoe, 11 June 2020. [Online]. Available: <https://blog.topsoe.com/turning-waste-co2-into-feedstock>. [Accessed January 2021].

- [44] M. S. Challiwala, H. Afzal, D. Choudhury, M. M. E.-H. M. Sengupta and N. Elbashir, "Alternative Pathways for CO₂ Utilization via Dry Reforming of Methane," 2020.
- [45] Texas A&M, "Researchers develop natural gas processing technology that could reduce Qatar's carbon footprint," Texas A&M University at Qatar, 9 October 2019. [Online]. Available: <https://www.qatar.tamu.edu/news-and-events/news/2019/10/08/researchers-develop-gas-processing-technology-to-reduce-carbon-footprint/>.
- [46] Qatar Foundation, "A Miracle Material from Trapped Carbon - Scientific American," Qatar Foundation, 2021. [Online]. Available: <https://www.scientificamerican.com/custom-media/a-new-dawn-for-innovation-in-qatar/a-miracle-material-from-trapped-carbon/>.
- [47] M. M. Wright, N. Seifkar, W. H. Green and Y. Román-Leshkov, "Natural Gas and Cellulosic Biomass: A Clean Fuel Combination? Determining the Natural Gas Blending Wall in Biofuel Production," *Environ Sci Technol*, vol. 49, no. 13, pp. 8183-92, 7 July 2015.
- [48] E. C. Tan, "Biomass-Derived Liquid Fuels Via Fischer-Tropsch Process As a Potential Replacement for Marine Fuels," in *2019 AIChE Annual Meeting*, Orlando, FL, November 12, 2019.
- [49] L. Qin, Z. Cheng, D. Baser, T. Goldenbaum, J. A. Fan and L.-S. Fan, "Cyclic redox scheme towards shale gas reforming: a review and perspectives," *React. Chem. Eng.*, vol. 5, no. 12, p. 2204–2220, November 2020.
- [50] D. Li, R. Xu, X. Li, Z. Li, X. Zhu and K. Li, "Chemical Looping Conversion of Gaseous and Liquid Fuels for Chemical Production: A Review," *Energy Fuels*, vol. 34, no. 5, p. 5381–5413, May 2020.
- [51] V. Shah, Z. Cheng, D. S. Baser, J. A. Fan and L.-S. Fan, "Highly Selective Production of Syngas from Chemical Looping Reforming of Methane with CO₂ Utilization on MgO-supported Calcium Ferrite Redox Materials," *Appl. Energy*, vol. 282, no. 116111, January 2021.
- [52] J. Underwood, "Southern Research licenses technology to Agra for 'waste-to-energy' project," *Southern Research*, September 18, 2019.
- [53] News Bureau, "UW Oshkosh and Agra Energy bring renewable fuel technology to dairy farms," October 15, 2020. [Online]. Available: <https://uwosh.edu/today/90757/uw-oshkosh-and-agra-energy-bring-renewable-fuel-technology-to-dairy-farms/>. [Accessed January 2021].
- [54] Oberon Fuels, "Oberon Fuels, SHV Energy partner to accelerate use of rDME," *Biomassmagazine.com*, 12 February 2020. [Online]. Available: <http://biomassmagazine.com/articles/16807/oberon-fuels-shv-energy-partner-to-accelerate-use-of-rdme>. [Accessed January 2021].
- [55] INFRA XTL Technology, "Technology," 2021. [Online]. Available: <https://en.infratechnology.com/technology/>. [Accessed January 2021].

- [56] S. K. Gangwal and K. McCabe, "Indirect Liquefaction of Coal-Biomass Mixture for Production of Jet Fuel with High Productivity and Selectivity, DOE-Southern Research-FE0024083," Southern Research Institute, Durham, NC, April 2018.
- [57] L. Frost, J. Hartvigsen and S. Elangovan, "Development of a Compact Fischer Tropsch Reactor," in *Conference: 2011 AIChE Annual Meeting*, October 2011.
- [58] J. J. Hartvigsen, "Fixed bed reactor heat transfer structure". United States Patent US20140134067A1, 15 May 2014.
- [59] S. LeViness, S. R. Deshmukh, L. A. Richard and H. J. Robota, "Velocys Fischer-Tropsch Synthesis Technology—New Advances on State-of-the-Art," *Top. Catal.*, vol. 57, no. 6, p. 518–525, April 2014.
- [60] M. Loewert, J. Hoffmann, P. Piermartini, M. Selinsek, R. Dittmeyer and P. Pfeifer, "Microstructured Fischer-Tropsch Reactor Scale-up and Opportunities for Decentralized Application," *Chem. Eng. Technol.*, vol. 42, July 2019.
- [61] B. Eisenberg, R. A. Fiato, C. H. Mauldin, G. R. Say and S. L. Soled, "Exxon's advanced gas-to-liquids technology," in *international natural gas conversion symposium*, December 1998.
- [62] D. Ce, P. Lu and N. Tsubaki, "Efficient and New Production Methods of Chemicals and Liquid Fuels by Carbon Monoxide Hydrogenation," *ACS omega*, vol. 5, no. 1, p. 49–56, December 2019.
- [63] J. Li, Y. He, L. Tan, P. Zhang, X. Peng, A. Oruganti, G. Yang, H. Abe, Y. Wang and N. Tsubaki, "Integrated tuneable synthesis of liquid fuels via Fischer-Tropsch technology," *Nature Catalysis*, vol. 1, no. 10, p. 787–793, October 2019.
- [64] K. Gong, T. Lin, Y. An, X. Wang, F. Yu, B. Wu, X. Li, S. Li, Y. Lu, L. Zhong and Y. Sun, "Fischer-Tropsch to olefins over CoMn-based catalysts: Effect of preparation methods," *Appl. Catal. Gen.*, vol. 592, p. 117414, February 2020.
- [65] T. Lin, K. Gong, C. Wang, Y. An, X. Wang, X. Qi, S. Li, Y. Lu, L. Zhong and Y. Sun, "Fischer-Tropsch synthesis to olefins: catalytic performance and structure evolution of Co₂C-based catalysts under a CO₂ environment," *ACS Catalysis*, vol. 9, no. 10, pp. 9554-9567, September 2019.
- [66] J. Su, H. Zhou, S. Liu, C. Wang, W. Jiao, Y. Wang, C. Liu, Y. Ye, L. Zhang, Y. Zhao, H. Liu, D. Wang, W. Yang, Z. Xie and M. He, "Syngas to light olefins conversion with high olefin/paraffin ratio using ZnCrO_x/AlPO-18 bifunctional catalysts," *Nature communications*, vol. 10, no. 1, pp. 1-8, March 2019.
- [67] J. Přeč, D. R. S. Pedrolo, N. R. Marcilio, B. Gu, A. S. Peregudova, M. Mazur, V. V. Ordonsky, V. Valtchev and A. Y. Khodakov, "Core-Shell Metal Zeolite Composite Catalysts for In Situ Processing of Fischer-Tropsch Hydrocarbons to Gasoline Type Fuels," *ACS Catal.*, vol. 10, no. 4, p. 2544–2555, February 2020.
- [68] A. A. Adeleke, X. Liu, X. Lu, M. Moyo and D. Hildebrandt, "Cobalt hybrid catalysts in Fischer-Tropsch synthesis," *Rev. Chem. Eng.*, vol. 36, no. 4, p. 437–457, May 2020.

- [69] R. E. Yakovenko, A. P. Savost'yanov, G. B. Narochniy, V. N. Soromotin, I. N. Zubkov, O. P. Papeta, R. D. Svetogorov and S. A. Mitchenko, "Preliminary evaluation of a commercially viable Co-based hybrid catalyst system in Fischer-Tropsch synthesis combined with hydroprocessing," *Catal. Sci. Technol.*, vol. 10, no. 22, p. 7613–7629, November 2020.
- [70] J. Li, G. Yang, Y. Yoneyama, T. Vitidsant and N. Tsubaki, "Jet fuel synthesis via Fischer-Tropsch synthesis with varied 1-olefins as additives using Co/ZrO₂-SiO₂ bimodal catalyst," *Fuel*, vol. 171, p. 159–166, May 2016.
- [71] M. Yang, L. Zhu, Y. Zhuo, J. Liang and S. Wang, "Selective Fischer-Tropsch synthesis for jet fuel production over Y 3+ modified Co/H- β catalysts," *Sustainable Energy & Fuels*, no. 7, 2020.
- [72] D. Ishihara, Y. Jin and N. Tsubaki, "Development of Bimodal Catalysts for Jet-fuel Synthesis via Fischer-Tropsch Synthesis," *J. Jpn. Inst. Energy*, vol. 93, no. 1, p. 113–118, 2014.
- [73] Y. Pei, S. Jian, Y. Chen and C. Wang, "Synthesis of higher alcohols by the Fischer-Tropsch reaction over activated carbon supported CoCuMn catalysts," *RSC Adv.*, vol. 5, no. 93, p. 76330–76336, September 2015.
- [74] Y.-P. Pei, J.-X. Liu, Y.-H. Zhao, Y.-J. Ding, T. Liu, W.-D. Dong, H.-J. Zhu, H.-Y. Su, L. Yan, J.-L. Li and W.-X. Li, "High alcohols synthesis via Fischer-Tropsch reaction at cobalt metal/carbide interface," *ACS Catalysis*, vol. 5, no. 6, pp. 3620–3624, June 2015.
- [75] E. Durham, S. Zhang and C. Roberts, "Diesel-length aldehydes and ketones via supercritical Fischer Tropsch Synthesis on an iron catalyst," *Appl. Catal. Gen.*, vol. 386, no. 1, p. 65–73, September 2010.
- [76] Y. Xiang and N. Kruse, "Tuning the catalytic CO hydrogenation to straight- and long-chain aldehydes/alcohols and olefins/paraffins," *Nat. Commun.*, vol. 7, no. 1, October 2016.
- [77] L. Wang, Y. Zhang, X. Gu, Y. Zhang and H. Su, "Insight into the role of UV-irradiation in photothermal catalytic Fischer-Tropsch synthesis over TiO₂ nanotube-supported cobalt nanoparticles," *Catal. Sci. Technol.*, vol. 8, no. 2, p. 601–610, January 2018.
- [78] W. Gao, R. Gao, Y. Zhao, M. Peng, C. Song, M. Li, S. Li, J. Liu, W. Li, Y. Deng, M. Zhang, J. Xie, G. Hu, Z. Zhang, R. Long, X.-D. Wen and D. Ma, "Photo-Driven Syngas Conversion to Lower Olefins over Oxygen-Decorated Fe₅C₂ Catalyst," *Chem*, vol. 4, no. 12, p. 2917–2928, December 2018.
- [79] H.-K. Wu, F. Zhang, J.-Y. Li, Z.-R. Tang and Y.-J. Xu, "Photo-driven Fischer-Tropsch synthesis," *J. Mater. Chem.*, vol. A, November 2020.
- [80] R. Chen, H. Su, D. Liu, R. Huang, X. Meng, X. Cui, Z. Tian, D. H. Zhang and D. Deng, "Highly Selective Production of Ethylene by the Electroreduction of Carbon Monoxide," *Angew. Chem. Int. Ed.*, vol. 59, no. 1, p. 154–160, 2020.

- [81] J. McDaniel, "Unlocking Biofuels with Microchannel Technology," in *CO2 Summit*, 2010.
- [82] Siluria, "Siluria Technologies Building with Natural Gas," Lummus Technology, 2020. [Online]. Available: <https://www.siluria.com/>. [Accessed January 2021].
- [83] GasTechno, "Convert Gas To Liquids In A Single Step," Gas Technologies LLC, 2020. [Online]. Available: <https://gastechno.com/>. [Accessed January 2021].
- [84] D. J. Arent, S. M. Bragg-Sitton, D. C. Miller, T. J. Tarka, J. A. Engel-Cox, R. D. Boardman, P. C. Balash, M. F. Ruth, J. Cox and D. J. Garfield, "Multi-Input, Multi-Output Hybrid Energy Systems," *Joule*, in press.
- [85] I. Dybkjær and J. B. Hansen, "Large-scale production of alternative synthetic fuels from natural gas," *Studies in Surface Science and Catalysis*, vol. 107, pp. 99-116, 1997.
- [86] I. Dybkjær and T. Christensen, "Syngas for Large Scale Conversion of Natural Gas to Liquid Fuels," *Studies in Surface Science and Catalysis*, vol. 136, p. 435-440, December 2001.
- [87] P. K. Bakkerud, J. N. Gol, K. Aasberg-Petersen and I. Dybkjaer, "Preferred synthesis gas production routes for GTL," *Studies in Surface Science and Catalysis*, vol. 147, p. 13-18, 2004.
- [88] M. Hunter, *Personal Communication*, Haldor Topsoe.
- [89] K. Aasberg-Petersen, T. Christensen, I. Dybkjær, J. Sehested, M. Østberg, R. Coertzen, M. Keyser and A. Steynberg, "Chapter 4 - Synthesis gas production for FT synthesis," *Studies in Surface Science and Catalysis*, vol. 152, p. 258-405, 2004.
- [90] Haldor Topsoe, "SynCORTM - Autothermal Reformer (ATR)," Haldor Topsoe, 2021. [Online]. Available: <https://www.topsoe.com/products/equipment/syncortm-autothermal-reformer-atr>. [Accessed January 2021].
- [91] Johnson Matthey, "Reforming technologies (ATR, GHR, SMR)," Johnson Matthey, 2020. [Online]. Available: <https://matthey.com/en/products-and-services/chemical-processes/core-technologies/reforming>. [Accessed January 2021].
- [92] Air Liquide, "Autothermal Reforming (ATR) - Syngas Generation," Air Liquide, 18 March 2016. [Online]. Available: <https://www.engineering-airliquide.com/autothermal-reforming-atr-syngas-generation>.
- [93] K. Radtke and I. Wulcko, "The Low Cost Gas Era Gasification versus Steam Reforming - a True Alternative?," in *Gasification Technologies Conference*, Colorado Springs, CO, 2015.
- [94] Casale, "SYNGAS," 2021. [Online]. Available: <http://www.casale.ch/markets/syngas>. [Accessed January 2021].
- [95] Air Products, "Air Products Engineered Membrane Systems," Air Products, 2020. [Online]. Available: <http://www.airproducts.in/Products/Gases/supply->

- options/prism-membranes/prism-membrane-engineered-systems.aspx. [Accessed January 2021].
- [96] Air Liquide Advanced Separations, "Hydrogen," Air Liquide Advanced Separations, 29 November 2016. [Online]. Available: <https://www.airliquideadvancedseparations.com/our-membranes/hydrogen>. [Accessed January 2021].
- [97] Linde Engineering, "Membrane plants," Linde Engineering, 2021. [Online]. Available: <https://www.linde-engineering.com/en/process-plants/adsorption-and-membrane-plants/membrane-plants/index.html>. [Accessed January 2021].
- [98] Evonik, "SEPURAN® Noble Membranes for efficient helium recovery," Evonik, undated. [Online]. Available: <https://www.membrane-separation.com/en/helium-recovery-with-sepuran-noble>. [Accessed January 2021].
- [99] GENERON, "Hydrogen Recovery Packages," Pioneering Gas Solutions, 2019. [Online]. Available: <https://www.generon.com/product/hydrogen-recovery-packages/>. [Accessed January 2021].
- [100] M. J. v.d. Burgt, C. J. van Leeuwen, J. J. del'Amico and S. T. Sie, "The Shell Middle Distillate Synthesis Process," *Studies in Surface Science and Catalysis*, vol. 36, p. 473–482, 1988.
- [101] C. Ortega, "Gas to liquids: historical development of GTL technology in Shell," *Green Process. Synth.*, vol. 3, no. 5, p. 393, October 2014.
- [102] Shell, "Pearl GTL," undated, [Online]. Available: https://www.shell.com.qa/en_qa/about-us/projects-and-sites/pearl-gtl.html. [Accessed January 2021].
- [103] Greyrock, "Technology," Greyrock, undated. [Online]. Available: <http://www.greyrock.com/technology/>. [Accessed January 2021].
- [104] Greyrock, "Greyrock Delivers M-Class Plant to Permian, Texas (USA)," Greyrock, 9 September 2019. [Online]. Available: <http://www.greyrock.com/news/greyrock-delivers-m-class-plant-to-permian-texas-usa/>. [Accessed January 2021].
- [105] Expander Energy, "Expander Energy announces Rocky Mountain GTL," Expander Energy, 30 November 2017. [Online]. Available: <https://www.expanderenergy.com/news-releases/>.
- [106] Rocky Mountain GTL Inc., "Projects," Rocky Mountain GTL Inc., undated. [Online]. Available: <http://rockymountaingtl.com/projects/>. [Accessed January 2021].
- [107] B. Cody, "Roll-out of commercial biorefineries," in *Gasification & Syngas Technologies Council Conference*, October 2017.
- [108] D. Ferris, "Velocys' reactor technology not at fault for Oklahoma plant's internal leak," *Bolsamania*, 4 July 2018. [Online]. Available: <https://www.sharecast.com/news/aim-bulletin/velocys-reactor-technology-not->

- at-fault-for-oklahoma-plants-internal-leak--3379857.html. [Accessed January 2021].
- [109] E. Voegelé, "Envia idles GTL plant, Velocys focuses on Mississippi project," *Biomassmagazine.com*, 9 September 2018. [Online]. Available: <http://biomassmagazine.com/articles/15606/envia-idles-gtl-plant-velocys-focuses-on-mississippi-project>. [Accessed January 2021].
- [110] R. Kotrba, "Velocys delivers 4 FT reactors to Red Rock Biofuels in Oregon," *Biodiesel Magazine*, 2 August 2020. [Online]. Available: <http://www.biodieselmagazine.com/articles/2517097/velocys-delivers-4-ft-reactors-to-red-rock-biofuels-in-oregon>. [Accessed January 2021].
- [111] Black & Veatch Company, "Black & Veatch, Emerging Fuels Technology Advancing Alternative/Renewable Transportation Fuels Industry Through Combination of Innovation and EPC Expertise," Company, Black & Veatch, 2014.
- [112] K. Foster, "Over 340 'sudden' layoffs announced at Westlake plant construction site," 31 May 2019. [Online]. Available: <https://www.wafb.com>. [Accessed January 2021].
- [113] NiQuan Energy, LLC, "FT Technology And Process Systems/Units," NiQuan Energy, LLC, 2021. [Online]. Available: <https://www.niquanenergy.com/content/ft-technology-and-process-systemsunits>. [Accessed January 2021].
- [114] NiQuan Energy, LLC, "First Commercial-scale Gas to Liquids Plant," NiQuan Energy, LLC, 2021. [Online]. Available: <https://www.niquanenergy.com/first-commercial-scale-gas-liquids-plant-western-hemisphere>. [Accessed January 2021].
- [115] J. P. Collins, J. J. Freide, H. M. Font and B. Nay, "A History of Fischer-Tropsch Wax Upgrading at BP—from Catalyst Screening Studies to Full Scale Demonstration in Alaska," *J. Nat. Gas Chem.*, vol. 15, no. 1, p. 1–10, March 2006.
- [116] Johnson Matthey, "CANS novel reactors technology," Johnson Matthey, 2020. [Online]. Available: <https://matthey.com/en/products-and-services/chemical-processes/core-technologies/cans-novel-reactors>. [Accessed January 2021].
- [117] M. Peacock, J. Paterson, L. Reed, S. Davies, S. Carter, A. Coe and J. Clarkson, "Innovation in Fischer–Tropsch: Developing Fundamental Understanding to Support Commercial Opportunities," *Top. Catal.*, vol. 63, no. 3, p. 328–339, July 2020.
- [118] Johnson Matthey, "JM and BP license waste-to-fuels technology to Fulcrum BioEnergy," Johnson Matthey, 2020. [Online]. Available: <https://matthey.com/en/news/2018/jm-and-bp-license-waste-to-fuels-technology-to-fulcrum-bioenergy>. [Accessed January 2021].
- [119] B. Jager, R. C. Kelfkens and A. P. Steynberg, "A Slurry bed reactor for low temperature Fischer-Tropsch," *Studies in Surface Science and Catalysis*, vol. 81, p. 419–425, 1994.

- [120] Sasol, "Gas to Liquids: Technology," Sasol, 2021. [Online]. Available: <https://www.sasol.com/innovation/gas-liquids/technology>. [Accessed January 2021].
- [121] Sasol, "Sasol Integrated Report 2018," Sasol, 2018. [Online]. Available: <https://www.integratedreport.sasol.com/ebook/19/>. [Accessed January 2021].
- [122] WebWire, "Qatar: Long-term supply agreement signed with Oryx GTL," WebWire, 2 November 2009. [Online]. Available: <https://www.webwire.com/ViewPressRel.asp?ald=106856>. [Accessed January 2021].
- [123] Y. Cui, "Synfuels China CTL Technologies," Synfuels China, undated. [Online]. Available: <https://usea.org>. [Accessed January 2021].
- [124] Synfuels China, "Product and Service," Synfuels China, 2016. [Online]. Available: <http://www.synfuelschina.com.cn/en/proServices/index.html?id=3&first=3>. [Accessed January 2021].
- [125] H. Ovrebekk, "Statoil, PetroSA, Lurgi GTL tech demo success," ICIS Explore, 10 November 2006. [Online]. Available: <https://www.icis.com/explore/resources/news/2006/10/11/1097662/statoil-petrosa-lurgi-gtl-tech-demo-success>. [Accessed January 2021].
- [126] R. Zennaro, F. Hugues and E. Caprani, "The Eni - IFP/Axens GTL technology. From R and D to a successful scale-up," Deutsche Wissenschaftliche Gesellschaft fuer Erdoel, Erdgas und Kohle e.V., July 2006. [Online]. Available: <https://www.osti.gov/etdeweb/biblio/20840759>. [Accessed January 2021].
- [127] T. G. Kaufmann, R. A. Fiato, G. C. Lahn and R. F. Bauman, "Advances In ExxonMobil AGC-21 Gas-To-Liquids Technology," in *16th World Petroleum Congress*, January 2000.
- [128] K. Agee, K. B. Arcuri and P. F. Schubert, "Large scale pilot plant demonstrates syntroleum's GTL process," *Am. Chem. Soc. Div. Pet. Chem. Prepr.*, vol. 45, p. 268–269, January 2000.
- [129] OGJ editors, "Marathon, Syntroleum to expand demonstration GTL plant," *Oil & Gas Journal*, 5 June 2002. [Online]. Available: <https://www.ogj.com/refining-processing/article/17248102/marathon-syntroleum-to-expand-demonstration-gtl-plant>. [Accessed January 2021].
- [130] J. Lane, "REG completes Syntroleum acquisition," *Biofuels Digest*, 3 June 2014. [Online]. Available: <https://www.biofuelsdigest.com/bdigest/2014/06/03/reg-completes-syntroleum-acquisition/>. [Accessed January 2021].
- [131] ConocoPhillips, "Qatar Petr. & ConocoPhillips to Work Together on GTL Project," 8 December 2003. [Online]. Available: https://www.rigzone.com/news/oil_gas/a/9824/qatar_petr_conocophillips_to_work_together_on_gtl_project/. [Accessed January 2021].
- [132] R. Ray, "ConocoPhillips test plant to close," *tulsaworld.com*, 30 October 2004. [Online]. Available: <https://tulsaworld.com/archive/conocophillips-test-plant-to->

- close/article_f13ac2b1-a3f9-59cc-9d1e-8c656baa48ee.html. [Accessed January 2021].
- [133] The Tashkent Times, "Uzbekistan GTL issues Notice to Proceed to EPC contractors to commence construction," The Tashkent Times, 26 January 2017. [Online]. Available: <https://www.tashkenttimes.uz/economy/489-uzbeksitan-gtl-issues-notice-to-proceed-to-epc-contractors-to-commence-construction-works>. [Accessed January 2021].
- [134] Green Car Congress, "ADB: Projected cost of Uzbek Oltin Yo'l GTL plant increases by 37% to \$5.6B," Green Car Congress, 3 March 2014. [Online]. Available: <https://www.greencarcongress.com/2014/03/20140303-oltin.html>. [Accessed January 2021].
- [135] UzDaily, "Uzbekneftegaz: OLTIN YO'L GTL project enters its final phase," UzDaily, 10 October 2020. [Online]. Available: <https://www.uzdaily.uz/en/post/60671>. [Accessed January 2021].
- [136] Waste Today Staff, "Fulcrum BioEnergy Secures Funding for Renewable Energy Project," Waste Today, 12 September 2012. [Online]. Available: <https://www.wastetodaymagazine.com/article/fulcrum-bioenergy-secures-funding-solid-waste-fuel/>. [Accessed January 2021].
- [137] J. Lane, "Fulcrum's \$200 million pick: Abengoa for EPC contractor of first MSW-to-jet fuel project in the US," *Biofuels Digest*, p. 4, 6 May 2015.
- [138] Red Rock Biofuels, "Lakeview Site," Red Rock Biofuels, 2021. [Online]. Available: <https://www.redrockbio.com/lakeview-site/>. [Accessed January 2021].
- [139] Financial News, "Turkmenistan inaugurates \$1.7bn GTL plant," Financial News, 2 July 2019. [Online]. Available: <https://www.energyreviewmena.com/article/financial-news/item/450-turkmenistan-inaugurates-1-7bn-gtl-plant>. [Accessed January 2021].
- [140] Green Car Congress, "Turkmenistan gas-to-liquids refinery ships first synthetic gasoline to Afghanistan," Green Car Congress, 9 July 2019. [Online]. Available: <https://www.greencarcongress.com/2019/07/20190709-turkmenistan.html>. [Accessed January 2021].
- [141] LG International Corp, "LG International Corp. – Hyundai Engineering Completion," LG International Corp, 13 October 2015. [Online]. Available: http://www.lgicorp.com/en/company/bulletins/812;jsessionid=KYxzBkT3d9iLs1RP_rtORzyhMyLdY3jt9NH_NOM4GywIMnvyTwyd!-233035870. [Accessed January 2021].
- [142] S. Writer, "New synthetic diesel plant near Carseland," *Strathmore Times*, 18 January 2018.
- [143] S. K. Gangwal and K. McCabe, "Small-Scale Coal-Biomass to Liquids Production Using Highly Selective Fischer-Tropsch Synthesis," Southern Research Institute, Durham, NC, 2015.

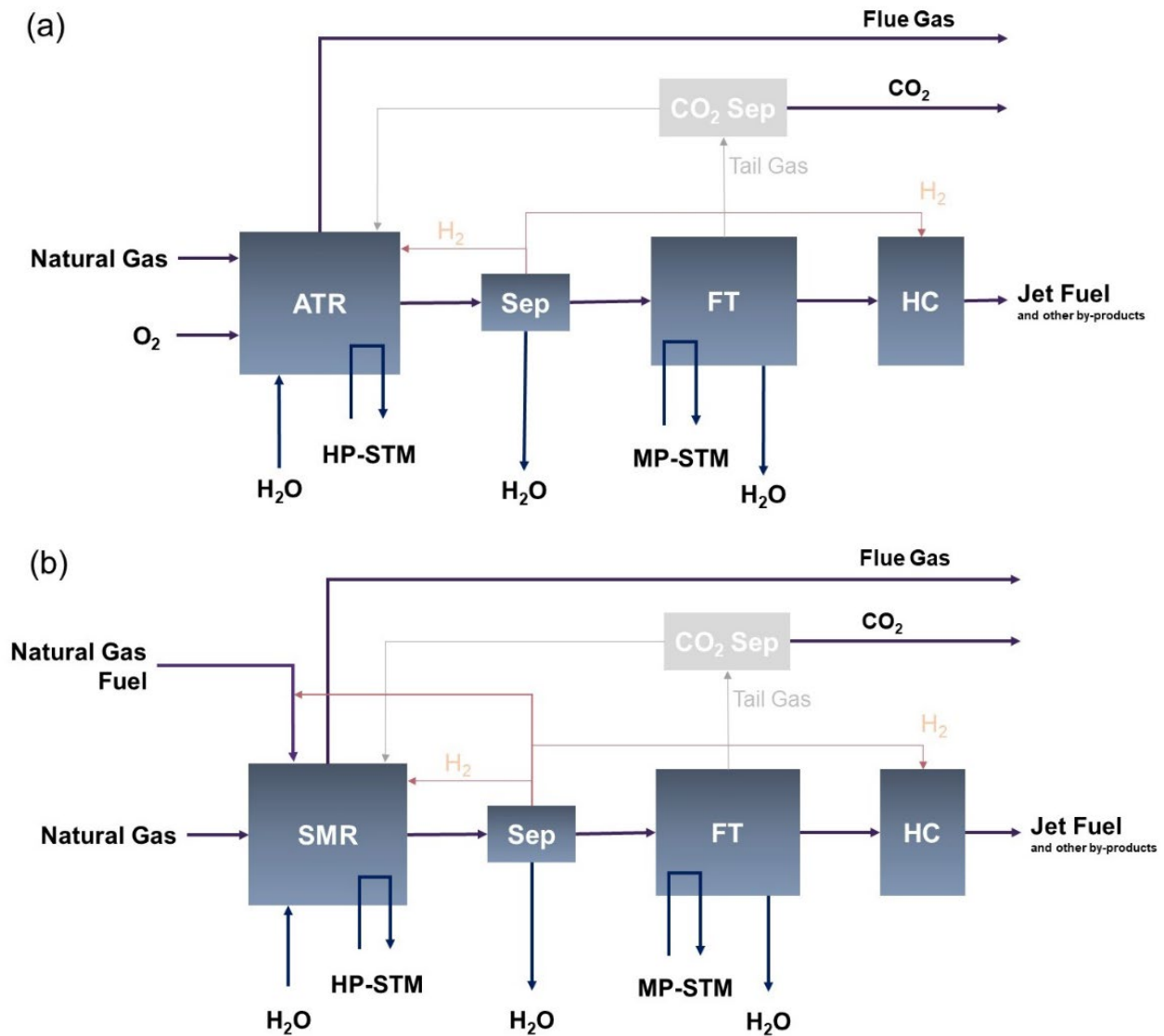
- [144] A. Lucero, B. Koob, B. Cline, K. McCabe and S. Gangwal, "Highly Selective FT Synthesis for Production of JP-8 Jet Fuel from Biomass, Coal, or Coal/Biomass Mixtures," in *Symposium on Thermal and Catalytic Sciences for Biofuels and Biobased Products*, November 2016.
- [145] H. W. Hildinger; E. D. Carlson, "Process for recycling and purifying condensate from a hydrocarbon or alcohol synthesis process". United States Patent US5053581A, 1 October 1991.
- [146] H. W. Hildinger; E. D. Carlson, "Process for recycling and purifying condensate from a hydrocarbon or alcohol synthesis process". United States Patent USRE37046E1, 6 February 2001.
- [147] P. E. J. Abbott; M. McKenna, "Production of hydrocarbons by steam reforming and Fischer-Tropsch reaction". United States Patent US7323497B2, 29 January 2008.
- [148] R. Schuetzle; D. Schuetzle, "Catalysts, related methods and reaction products". United States Patent US10260005B2, 16 April 2019.
- [149] L. Debter, "Delta's Computer Outage To Cost Them \$150 Million," *Forbes*, 7 September 2016. [Online]. Available: <https://www.forbes.com/sites/laurengensler/2016/09/07/delta-computer-outage-flight-cancellations-eats-into-profits/?sh=25818a5144a2>.
- [150] Shell, "The World's Largest Gas-to-Liquids Plant," 2021. [Online]. Available: <https://www.shell.com/about-us/major-projects/pearl-gtl/the-world-s-largest-gas-to-liquids-plant.html>. [Accessed 6 February 2021].
- [151] ASTM International, "ASTM D7566-20c, Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons," West Conshohocken, PA, 2020. [Online]. Available: <https://www.astm.org/DATABASE.CART/HISTORICAL/D7566-20C.htm>. [Accessed August 2021].
- [152] Spectrum News Staff and City News Service, "LAX: Power Restored After Four Hour Outage Disrupts Airport Operations," 6 June 2019. [Online]. Available: <https://spectrumlocalnews.com/tx/san-antonio/news/2019/06/06/lax--power-restored-after-four-hour-outage-disrupts-airport-operations>. [Accessed February 2021].

APPENDIX A: PROCESS SIMULATION

A.1 MODEL SETUP

The entire Fischer-Tropsch (FT) gas-to-liquids (GTL) process scheme, starting from natural gas and ending with the jet fuel and other auxiliary products is simulated using Aspen Plus® (Aspen) V11. Both the steam methane reformer (SMR) and autothermal reformer (ATR) are simulated for analysis and comparison (Exhibit A-1). The FT and hydrocracking sections were kept similar in both the cases.

Exhibit A-1. Block flow diagram using (a) ATR for syngas generation; (b) SMR for syngas generation



Based on the process schemes shown in Exhibit A-1, a total of four cases were explored in this study: SMR-1, SMR-2, ATR-1, and ATR-2. The cases have been described in Exhibit A-2 and Exhibit A-3. In all four cases, **no carbon dioxide (CO₂) is removed from the flue gas.**

For the two SMR cases

- FT tail gas used for two purposes
 - Recycled to the SMR
 - Used as a fuel in the fired heater
- Amount of FT tail gas recycle is adjusted to achieve hydrogen (H₂) to carbon monoxide (CO) ratio of 2–2.1
- CO₂ is removed from the entire FT tail gas before use
 - 95% CO₂ capture is assumed from the FT tail gas

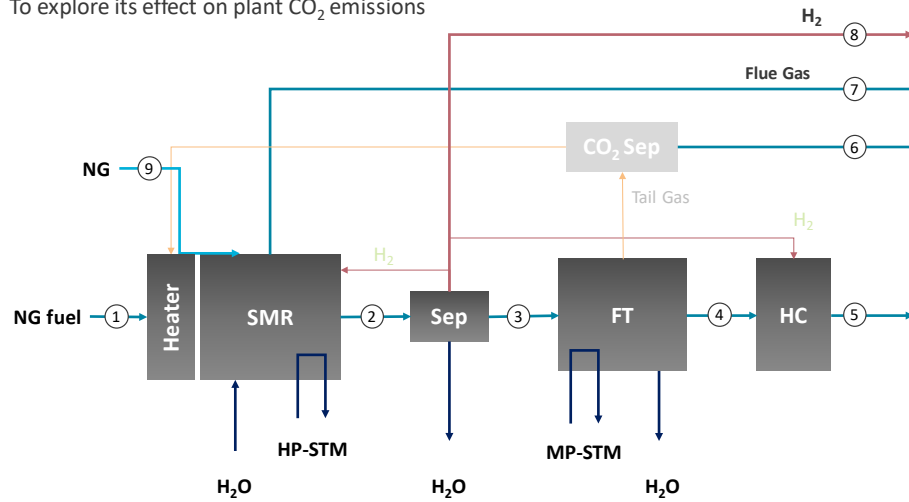
For the two ATR cases

- FT tail gas used for two purposes
 - Recycled to the ATR
 - Used as a fuel for feed preheating
- Amount of FT tail gas recycle adjusted to achieve H₂/CO ratio of 2–2.1
- CO₂ captured from FT tail gas with 95% removal
 - CO₂ is removed at different points from the tail gas in ATR-1 and ATR-2 cases

Exhibit A-2. Description of the different SMR and ATR cases considered in the study

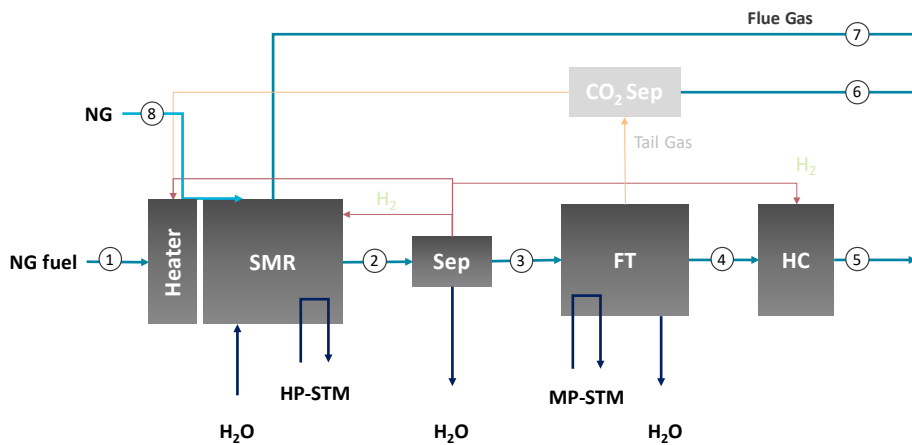
Rationale

To explore the economics of SMR if excess H₂ is sold as a product rather than in situ utilization as a fuel
 To explore its effect on plant CO₂ emissions



SMR - 1

- After the reformer, required H₂ is used for the HDS and HC
- **Excess H₂ is sold as a valuable by-product**
- **No H₂ is used as a fuel in the fired heater**
- Natural gas, along with some FT tail gas, is used as fuel in the fired heater



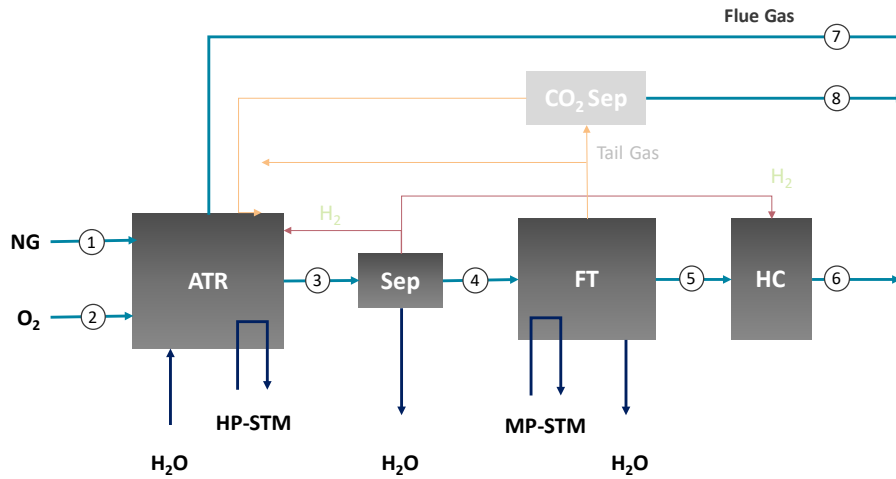
SMR - 2

- After the reformer, required H₂ is used for the HDS and HC
- **Excess H₂ is recycled for use as a fuel in the fired heater**
- Natural gas + recycled H₂ + some FT tail gas = fuels the fired heater

JET FUEL PRODUCTION AT THE PITTSBURGH AIRPORT: GTL VIA FISCHER-TROPSCH SYNTHESIS

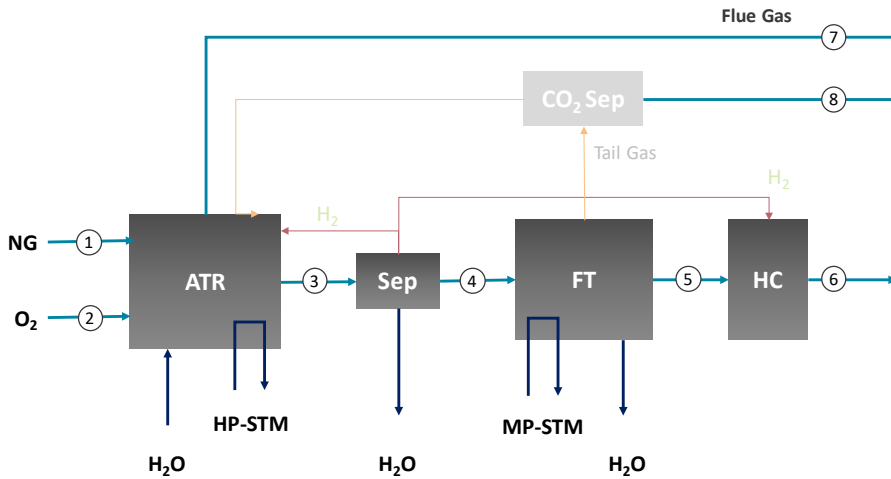
Rationale

To explore the effect of recycling CO₂-containing FT tail gas to the ATR



ATR - 1

- The required amount of FT tail gas is used as fuel for the fired heater, after CO₂ removal
- FT tail gas remainder is recycled to the ATR without CO₂ removal



ATR - 2

- All FT tail gas goes through CO₂ removal step
- Post CO₂-removal, required FT tail gas is used as fuel for fired heater
- FT tail gas remainder is recycled to the ATR

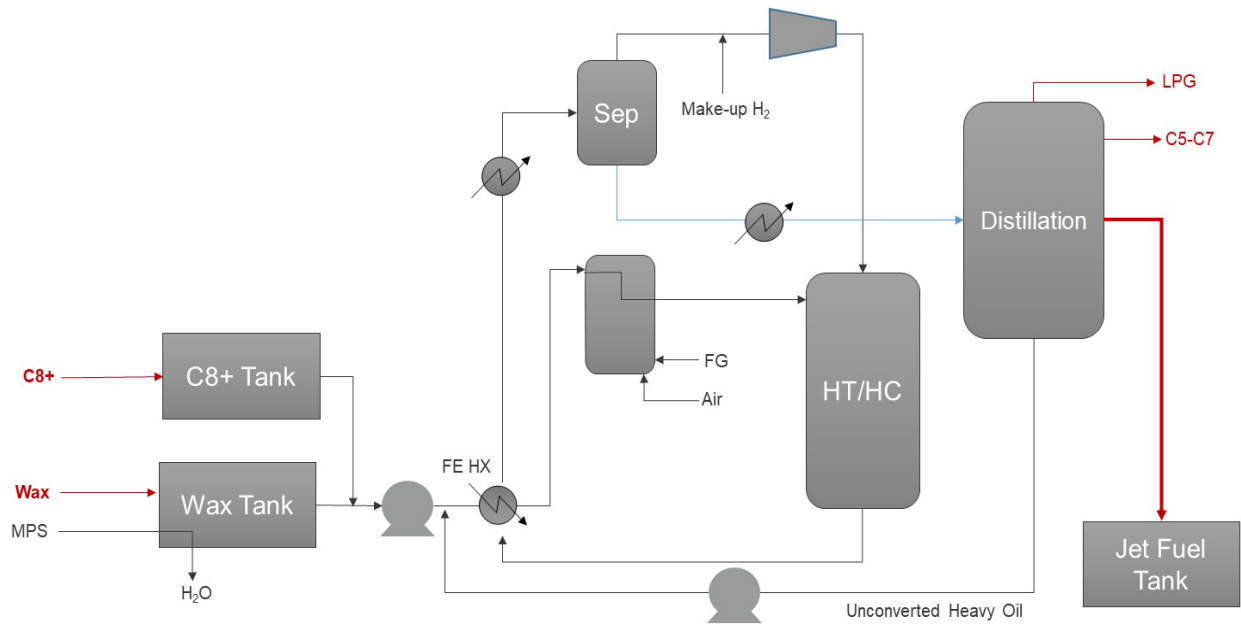
The assumed product distribution is presented in Exhibit A-3, which contains the feed natural gas, jet fuel, and auxiliary products. For the process model, a steady-state sequential modular approach was used. A REFINERY method filter with PENG-ROB base method was used with ASME 1967 steam tables. The following databanks were used for the simulation: PURE37, AQUEOUS, SOLIDS, INORGANIC, and NIST-TRC. Exhibit A-4 lists the major Aspen models that are used.

Exhibit A-5 shows the block flow diagram of the entire process, which formed the basis of the Aspen model.

JET FUEL PRODUCTION AT THE PITTSBURGH AIRPORT: GTL VIA FISCHER-TROPSCH SYNTHESIS

Exhibit A-3. Compositions of the products and feed

Mole Fractions		LPG	C5-C7	Jet Fuel	HC Feed	Natural Gas
	N ₂					0.35
	H ₂ O				0.07	
n-alkanes	H ₂	3.17				
	CO ₂	0.34			0.05	0.09
	C ₁	0.50			0.01	79.62
	C ₂	2.15			0.00	13.96
	C ₃	22.10			0.00	4.02
	C ₄	71.73	1.53		0.01	1.31
	C ₅		14.46		0.02	0.39
	C ₆		34.65		0.03	0.26
	C ₇		39.47		0.03	
	C ₈		9.89	11.91	2.18	
	C ₉			14.72	2.81	
	C ₁₀			14.45	2.99	
	C ₁₁			15.20	3.06	
	C ₁₂			12.04	3.09	
	C ₁₃			10.55	3.10	
	C ₁₄			8.67	3.10	
	C ₁₅			6.54	3.10	
C ₁₆			5.39	3.10		
C ₁₇			0.49	2.89		
C ₃₅			0.03	70.36		



A.3 PROCESS TARGETS

The entire process model was optimized in Aspen to closely match the industrial state-of-the-art operation. The optimization was performed to obtain certain prime process targets (Exhibit A-6).

Exhibit A-6. Major process targets used for various sections in the simulation

Basis: 5000 bbl/day of Jet Fuel		
Syngas Generation	ATR	<ul style="list-style-type: none"> • Steam-to-carbon (S/C) ratio = 0.7 • O₂-to-carbon (O₂/C) = 0.5–0.6 • H₂ for HDS = 3% of feed natural gas • Adiabatic operation of PRF and ATR • PRF temperature = 500–550°C • ATR temperature = 1050°C • ATR pressure = 420 psig • Heat loss in ATR = 5% • Hydrogen-to-carbon (H₂/CO) ratio at ATR exit = 2.1–2.15 • H₂ required for HDS and HC separated from syngas
	SMR	<ul style="list-style-type: none"> • S/C = 3 • H₂ for HDS = 3% of feed natural gas • Adiabatic operation of PRF • PRF temperature = 500–550°C • SMR temperature = 870–890°C • SMR pressure = 420 psig • H₂/CO ratio at SMR exit = 3 • H₂ required for HDS and HC separated from syngas; rest used as fuel for fired heater

Basis: 5000 bbl/day of Jet Fuel	
FT	<ul style="list-style-type: none"> • H₂/CO ratio for feed = 2–2.05 • FT reactor temperature = 210°C • FT reactor pressure = 350 psig • CO conversion (per pass) = 60% • CO conversion (overall) = 91% • Product selectivity • CH₄ = 7% • CO₂ = 0.6% • C₅₊ = 88%
HC	<ul style="list-style-type: none"> • Based on obtained product distribution of FT product, everything C₁₈ and higher represented as C₃₅ alkane • HC reactor temperature = 345°C • HC reactor pressure = 1100 psig • C₁₆₋ conversion = 100% • C₁₇₊ conversion = 50% • Most of unconverted C₃₅ (heavy oil) recycled • Target product distributions as shown in Table 1

ATR performance was based on detailed published performance data from Haldor Topsoe. [85] [86] [87] SMR and FT performance was based on previous experience. Hydrocracking (HC)/Hydroisomerization (HI) performance was based on actual plant data provided by Haldor Topsoe. [88]

High-pressure steam (HPS) was generated using the ATR/SMR product stream, whereas medium-pressure steam (MPS) from the reaction heat removal in the FT reactor. A part of the FT tail gas was recycled to the FT reactor to get the desired overall CO conversion. After separating CO₂ from the remaining tail gas, a portion was used as a fuel gas to meet the energy demands of the fired heater for syngas generation. The remaining tail gas was recycled to the ATR/SMR. Two product streams were obtained in the FT section: a) knock-out wax + hot separator (HS) and cold separator (CS) bottoms, and b) straight-run naphtha (SRN). The wax/hydrocarbon mixture was fed to the HC, which produces jet fuel and other liquid products. A series of flash columns followed by distillation columns were used to sequentially remove unconverted heavy oil (which is recycled to the HC), jet fuel, C₅–C₇ naphtha, and liquefied petroleum gas (LPG).

A.4 REACTOR SIZING

To size the FT reactor for daily production of 5000 bbl of jet fuel, a reaction rate of 300 m³ CO/m³ catalyst volume/hr has been used. These are related as:

$$\text{Productivity (volume/volume/hr)} = \text{GHSV} * Y_{\text{CO}} * X_{\text{CO}}$$

where

GHSV = Total feed gas hourly space velocity (volume/volume/hr)

Y_{CO} = Mole fraction of CO in the feed

X_{CO} = Fractional conversion of CO

Using a CO reaction rate of ~6,000 pound mole (lbmol)/hour (hr), which equals ~2,300 thousand standard cubic feet (Mscf)/hr, the required catalyst loading is estimated to be ~7,700 ft³. With 1” OD (0.875” inner diameter [ID]) tubes, which are 40 ft long, this amount of catalyst would require ~46,000 tubes. Exhibit A-7 summarizes the details of the various reactors. The GHSV values of the syngas generation are based on total dry feed gas flow. The flows are based on the values reported in Appendix C: Aspen Plus® Flowsheets, obtained from the Aspen simulations. Note that the dimensions are for catalyst bed only and are at assumed length-to-diameter (L/D) ratios—indicative values only, especially for the HDS and pre-reformer (PRF). Since the ATR catalyst bed is typically short and squat, an L/D ratio of ~1 was used, while for the SMR, the tubes were 6 in. ID and 40 ft long. For the HC/HI reactors, the ratio is ~5–8, so a value close to 8 was chosen.

Exhibit A-7. Reactor sizing and catalyst requirement for various sections of the plant

Parameter	Units	Syngas Generation						FT	HC/HI
		HDS		PRF		Reformer			
		ATR	SMR	ATR	SMR	ATR	SMR		
Reaction Rate	hr ⁻¹	3500		5000		8000	3500	300	1
Mole Flow	kmol/hr	2696	2222	3193	5295	4363	6801	6000 ^A	44664 ^B
	Mscf/hr	2251	1855	2666	4421	3643	5678	2300 ^A	2131
Catalyst	ft ³	643	530	533	884	455	1622	7700	2131
Diameter (ID)	ft	6	6	6	7	8	0.5	0.073	7
Height	ft	23	19	19	23	9	40	40	55
Number of Tubes		N/A	N/A	N/A	N/A	N/A	207	46000	N/A

^ACO flow rate; ^Bmass flow in kg/hr

A.5 RESULTS

A.5.1 Process Output Variables

All four cases were analyzed to produce syngas for the FT section. The FT section followed by the HC and purification, was identical in all cases, leading to the production of equal amounts of jet fuel and other liquid products. Exhibit A-8 shows the CO₂ emissions from the four cases in detail. In all the cases, no CO₂ is removed from the flue gas. Based on the case definition, different amounts of CO₂ are removed from the FT tail gas. As can be seen below, for the SMR, use of H₂ in the fired heater (SMR-2) reduces the flue gas emissions from 102 to 70 ton/hr. For the ATR, since most of the FT tail gas is used as a fuel for preheating, there is not much difference between ATR-1 and ATR-2. Significant changes in the ATR feed and operating conditions need to be made to observe differences in the two ATR cases, which is beyond the scope of this study.

Exhibit A-8. CO₂ captured and emitted from different streams for all four cases

Property	Stream	SMR-1	SMR-2	ATR-1	ATR-2
Flow (ton/hr)	FT tail gas	18	18	45	47
	Flue gas	846	877	147	144
CO ₂ conc. (vol basis)	FT tail gas	58%	58%	39%	39%
	Flue gas	8%	5%	9%	9%
CO ₂ flow (ton/hr)	FT tail gas	14	14	28	29
	Flue gas	102	70	20	20
CO ₂ captured (ton/hr)	FT tail gas	13.2	13.2	27	28
	Flue gas	0	0	0	0

Having a low carbon footprint is a key objective of this study. To simplify further analysis, based on the CO₂ emission intensity, two cases are used for comparison: SMR-2 and ATR-2. SMR-2 simulations show roughly 30 percent lower CO₂ emissions than SMR-1. Although ATR-1 and ATR-2 are similar, ATR-2 shows lower emissions. The Aspen flowsheets with detailed mass balances and conditions of the streams for the simulations are presented in the Appendix C: Aspen Plus[®] Flowsheets and supplementary information document.

Among the four cases, ATR-2 has the lowest carbon intensity: 20 ton/hr in the flue gas with 28 ton/hr already captured from the FT tail gas.

The key results of the simulation, optimized based on the targets presented above, are listed in Exhibit A-9. Apart from the targets mentioned in Exhibit A-6, Exhibit A-9 includes output variables like steam generation and H₂ production along with captured and emitted CO₂.

Exhibit A-9. Key process output variables from the simulation (using both ATR and SMR)

Parameters	Unit	ATR	SMR
Natural gas feed	MMscfd	52.6	43.3
Natural gas fuel for fired heater	MMscfd	0	20.7
S/C ratio		0.7	3.07
O ₂ /C ratio		0.57	
Exit Temperature	°C	1050	880
	°F	1927	1616
HPS for reformer	tonne/hr	46.7	199.2
KO water	tonne/hr	46.7	138.0
FT water	tonne/hr	49.5	51.1
Excess H ₂	MMscfd	1.55	
H ₂ for HDS	MMscfd	1.59	1.3
H ₂ for HC	MMscfd	3	3

Parameters		Unit	ATR	SMR
H ₂ /CO ratio	before H ₂ removal		2.15	3.06
	after H ₂ removal		2.05	2.05
FT recycle/feed ratio	mole basis		0.98	1.74
	mass basis		2.07	3.37
CO ₂ captured		tonne/hr	27.8	13.2
CO ₂ emitted in flue gas		tonne/hr	20.4	68.9
MPS generated		tonne/hr	150.5	146.7
Wax (211°C, 50 psig)		bbbl/day	5,100	4,685
HS hydrocarbons (114°C, 40 psig)		bbbl/day	1,280	1,171.5
CS hydrocarbons (53°C, 30 psig)		bbbl/day	1,160	1,355.4
Jet fuel		bbbl/day	5,000	
C ₅ -C ₇ and SRN		bbbl/day	920	
LPG		bbbl/day	659	

In an SMR, to reduce the CO₂ emissions in the flue gas, it is beneficial to utilize the excess H₂ as a fuel in the fired heater. Hence, SMR-2 is chosen as the preferred option for analysis. For ATR-1, it was observed that the process variables mentioned in Exhibit 3-5 have to be significantly modified to achieve the required jet fuel output. Hence, ATR-2 was chosen, where CO₂ is removed from all of the FT tail gas, before being used as a fuel and recycle as ATR-feed. In Exhibit A-9, for SMR, all the excess H₂ is used as a fuel for the fired heater. There is a slight excess of H₂ in the ATR case, since all the CO₂ has been removed from the FT TG before recycling; thus, raising the syngas H₂/CO ratio slightly.

A.5.2 Major Equipment List

The major equipment list is provided in Exhibit A-10.

Exhibit A-10. High-level list of the major equipment required for the entire plant

Section	Equipment
Syngas Generation (ATR)	Hydrosulfurization and H ₂ S adsorbers
	Pre-reforming reactor
	ATR reactor
	FT tail gas-fired heater
	Syngas waste heat boiler – HP steam generation
	WHB steam drum, feed water pre-heat (economizer)
	Syngas cooler and water knockout
	Gas compressors for product hydrogen
FT	FT reactor feed-effluent cross exchanger

Section	Equipment
	4–5 multi-tubular FT fixed bed reactors: 40 ft tube length, 11–12 ft shell diameter
	Reactor cooling/temperature control Wax knock-out drum
	Tail gas cooler LPS generation 3-phase hot separator Air-fin/cooling water exchanger 3-phase cold separator
	Hydrocarbons to flash tanks followed by distillation
	Product water flash tanks
HC	HC/HI reactor feed-effluent heat exchanger
	HC/HI feed trim heater (FT TG and/or natural gas fueled)
	HC/HI reactor (LHSV ~ 1 on total feed as liquids, sulfided base metal)
	HP H ₂ -liquid 2-phase separator
	Nominal 4-column distillation unit for separation

A.5.3 Utility Requirements

The utility requirements list is provided in Exhibit A-11.

Exhibit A-11. List of utility requirements from various sections of the process

	Equipment	ATR	SMR	Unit
Fuel Balance	HDS preheater	42.8	34.4	MMBtu/hr
	PRF preheater	54.7	183.8	MMBtu/hr
	Reformer preheater	40	106.3	MMBtu/hr
	Reformer	0	785.5	MMBtu/hr
FT TG to Fuel	LHV	11.7	13.2	MBtu/lb
	Mass flow	10.8	4.5	tonne/hr
Electrical Power	FT recycle compressor	2.1	4.43	MW
	FT TG to ATR recycle compressor	0.21	1.81	MW
	HDS compressor	0.26	0.21	MW
	HC H ₂ compressor	0.86	0.86	MW
	HC recycle compressor	0.33	0.33	MW
	HP steam pump	0.3	0.55	MW
	MP steam pump	0.126	0.126	MW
	Total	4.186	8.316	MW

A.5.3.1 Steam and Electricity

Generally, the steam would need to be superheated—typically in the waste heat recovery unit (WHRU) and/or fired heater. It could also be standalone. At this scale it is possible to use HPS (from the waste heat boiler [WHB] for main compressor duties with turbine drivers) and FT MPS in separate turbine driver gensets. In all cases the turbine exit low-pressure steam (LPS) is condensed and sent to the de-aerators. Cost of a small-scale power plant fall in the range of \$1,000/kW. Condensers are required since we have steam available onsite. In the current set-up, the turbine and genset need to be added. For 20 MW, this adds up to ≤ \$20 million (MM) @ \$1,000/kW. This would not result in a major cost considering the total cost of roughly \$600 MM for the entire GTL plant.

A.5.4 Estimated Environmental Performance

Exhibit A-12 describes the environmental performance of the main solid, liquid, and gaseous components of the plant. In case of the solids, almost all the spent catalyst will be moved to the metal reclamation section. This leads to little or no direct cost to the plant but also offers less economic benefit of the metals. The metals recovery plus profit margin is typically about the same as the value of the recovered metals.

Exhibit A-12. Description of the various categories of environment impact sources

Category	Component	Description
Solids	Spent ZnO H ₂ S adsorbents	Depends on natural gas sulfur content Possible regenerability of absorbents
	HDS, PRF, ATR/SMR spent catalysts	Co-Mo HDS, nickel-based PRF, ATR
		3–5+ year replacement estimate
	FT spent catalyst	Co-based, small amount of PGM
		3-year replacement
HC/HI spent catalyst	Co/Ni/etc.-based 3–5-year placement cycle	
Liquids	ATR product water	Generally clean Can be easily upgraded to BFW
	FT product water	1–2% oxygenate content Requires treatment prior to disposal Can be easily treated onsite and re-used for BFW make-up
	Bio-sludge	From the FT wastewater treatment plant
	Hydrocarbons	Generally limited to spills/incidents No continuous source
Gases	CO ₂	From fired heater, boiler flue gases
	Fugitive plant emissions	Per refinery/chemical plant standards
	Hydrocarbon emissions	From tankage per refinery standards

APPENDIX B: FISCHER-TROPSCH TECHNOLOGIES

B.1 FISCHER-TROPSCH FTL TECHNOLOGY SECTIONS

B.1.1 Syngas Production

Overall plant flowsheets and simulations were developed for both a pure steam methane reformer (SMR) and a pure autothermal reformer (ATR) syngas production unit. There are many variations in syngas generation technologies, including combinations of these processes in series and/or parallel configurations. [89] Despite large differences in various feed ratios and the main features of each technology, the front ends of both units are almost identical.

Feed natural gas is combined with a small amount (typically 1–3 percent) of hydrogen (H_2) and preheated to approximately 650°F before passing through a hydrodesulfurization (HDS) reactor where all sulfur compounds are converted to hydrogen sulfide (H_2S). The H_2S is then reacted with zinc oxide (ZnO)-based absorbents where it is removed almost quantitatively. The standard H_2S absorbent materials are not regenerable and must be replaced once saturated. Dual beds are typically employed in a lead/lag configuration. The need to periodically replace H_2S absorbents, in turn, leads to a maximum tolerable natural gas sulfur content of 50–100 parts per million. Significantly higher sulfur levels would require more conventional acid gas treatment (amine-based) plants upstream of the HDS/ZnO unit, which then become the final purification/polishing step.

The desulfurized natural gas is then combined with steam at a fixed steam-to-carbon (S/C) ratio, which is dependent on the syngas generation technology (SMRs require much higher S/C ratios than ATRs) and vendor specific recommendations. Some amount of tail gas from the Fischer-Tropsch (FT) unit is usually added to the steam and methane (CH_4) mixture to provide feed CO_2 and to reduce the need for fresh CH_4 . The amount of added FT tail gas and the location of the addition vary with technology and with technology vendors. In this study, the addition occurs downstream of the HDS system.

The combined feed is then preheated to a temperature of 900°F after which it goes to another catalyst bed where higher hydrocarbons (C_{2+}) are reformed to CH_4 and syngas products over a normally nickel-based pre-reforming catalyst. In principle, a pre-reformer (PRF) is not required for natural gas feeds with relatively low C_{2+} contents, but this will generally require a lower reformer feed temperature as any C_{2+} species will tend to decompose to carbon at temperatures above 1,000°F. With the C_{2+} converted during pre-reforming, higher reformer preheat temperatures are possible, which improves the overall reformer efficiency. This study assumes the pre-reformed gas is heated to 1,200°F, although some technology vendors allow significantly higher values (up to at least 1,400°F). The pre-reformed and preheated gas is then sent to the reforming reactor.

In an ATR-based plant, these three heating services typically take place in individual coils in a single-fired heater that may also be employed for other heating purposes, especially steam generation and/or steam superheating. In an SMR-based plant, these and other heating services typically occur in individual coils in a waste heat recovery unit (WHRU) heated by hot flue gas from the main SMR firebox.

For the reformers themselves, ATR and SMR configurations and operations are significantly different. In an SMR, the feed gas goes to a number of parallel tubes filled with (generally nickel-based) catalysts. Tube dimensions vary but diameters are usually 4–8 in. and tube lengths are 40 ft or more. All of these tubes are configured in a low-pressure “firebox” with multiple fuel gas burners.

The energy (heat) for the endothermic reforming reactions is supplied by the burners and must be transferred from the burners through the tube walls and then to the catalyst/gas mixture inside. Downstream FT synthesis prefers relatively high pressures (generally 300–500 psig) but CH₄ conversion in an SMR (which is limited by thermodynamic equilibrium) is favored at low(er) operating pressures. Hence the SMR may be operated at a higher than ideal pressure while the FT synthesis unit may be operated at a lower than ideal pressure.

Most SMR units in the world are designed to produce H₂ and or syngas where the H₂/carbon monoxide (CO) ratio is not a constraining variable (such as for methanol synthesis). For FT synthesis, however, the H₂/CO ratio must typically be ~2.0. This is lower than conventional SMR processes can achieve with existing commercial catalysts, so, in reality, a great deal of excess H₂ (and consequently carbon dioxide [CO₂]) is produced using an SMR for an FT-based GTL plant. Typical minimum H₂/CO ratios for conventional SMRs are usually 3.0 or higher. The excess H₂ must be removed between the SMR and FT units. The combined goal of maximizing CH₄ conversion and minimizing syngas H₂/CO ratios results in pushing the reaction temperature as high as possible while at the same time minimizing feed S/C ratios. Temperatures are generally limited by metallurgical constraints of reformer tubes and catalyst coking/deactivation considerations, while S/C ratios are also limited by the latter. In general, the maximum SMR process outlet gas temperature is 1,600–1,650°F.

Production scale in an SMR is largely determined by the number of tubes and burners, as well as the geometric size of the firebox, so although very large capacities are possible there is little economy of scale in the SMR itself, especially in the expensive and exotic tube alloys that must be employed to operate at these conditions.

An ATR operates under very different conditions. The top of the ATR contains a burner, where the feed gas mixture is combined with an oxidant, generally pure O₂, enriched air or air. Oxygen-to-carbon (O₂/C) ratios are sub-stoichiometric, leading to partial oxidation of the feed to a combination of H₂, CO, and CO₂. Below the burner flame zone, the hot gases go through a bed of Nickel-based reforming catalyst. Methane conversion is typically much higher in an ATR compared to an SMR, while it is possible to directly produce a syngas of H₂/CO ratio as desired for the FT synthesis unit (~2). Because no heat is transferred in the ATR itself, the actual reactor is a refractory lined low-alloy shell (typically carbon steel) that shows excellent economies of scale and is much smaller than an SMR of comparable syngas production capacity. Higher process gas temperatures (generally 1,900–2,000°F) are, therefore, quite possible. Similarly, operating pressure can be chosen based on downstream synthesis requirements. Higher operating pressures in ATR improve CH₄ conversion and minimize H₂/CO ratio and CO₂ production. Therefore, on almost all considerations, an ATR is greatly preferred over an SMR for an FT-based GTL plant, with a single exception—the need for O₂. Pure O₂ production by cryogenic air separation units (ASUs) is a well demonstrated and commercialized process, but it is relatively expensive. At smaller scales, adsorbent-based production of 90–95 percent purity O₂ is possible by pressure swing adsorption (PSA) and/or vacuum swing adsorption (VSA) technologies but these do not scale up well and are generally less economic than a cryogenic ASU at FT plant capacities above ~2,000–3,000 barrels per day (BPD). There have also been a number of efforts using air as the oxidant for an ATR-based syngas production plant, but air compression costs (capital and power) are prohibitively expensive, and the product syngas is highly diluted with nitrogen (N₂). Therefore, pure or nearly pure O₂ is generally preferred.

Despite these very different reactor configurations and modes of operation, the backend of each process looks very similar. In both cases, the hot syngas leaving the reactor goes into a shell and tube heat exchanger with the process gas on the tube side and boiler feed water (BFW) on the shell side.

The gas is cooled well below the metal dusting temperature region (above 800–900°F) by generation of high-pressure steam (HPS). Steam pressure is adjustable based on overall plant design and integration, but the pressure is typically around 600 psig. This is usually referred to as a waste heat boiler (WHB). The gas exiting the WHB can be used for other heating purposes, typically including heating the WHB BFW from the usual ~220–230°F de-aerator temperature to just below the boiling point of the water in the WHB. This exchanger is typically referred to as an economizer. The moderate temperature syngas could be further utilized for other plant heating purposes but would ultimately be cooled to near ambient temperature using air-fin and/or cooling water exchangers. A great deal of water is condensed in these coolers and the 2-phase syngas-water stream then goes into a 2-phase separator/knock-out drum where liquid water is removed.

B.1.2 Hydrogen Separation Unit

As described above, a small amount of H₂ is required for the natural gas HDS system in the reformer front-end. In addition, more H₂ is required as make-up for the hydrocracking (HC)/hydroisomerization (HI) unit further downstream. The H₂ demand for these processes can be easily met by excess H₂ that is separated from the SMR-generated syngas, and it is also common to operate an ATR to produce just enough H₂ for these processes and still meet the H₂/CO ratio required in the FT unit; although, again, the amount of H₂ to be removed from an ATR syngas is very small compared to that from an SMR. H₂ removal from the syngas can be conducted by H₂ specific membranes and/or by conventional PSA units. However, the HC/HI catalyst typically requires high H₂ purity so a single-stage membrane will likely not be sufficient in this case. Depending on exact unit configuration, the product H₂ may or may not be at the desired syngas pressure and will require compression for both HDS and HC/HI steps, while PSA offgas will generally be at low pressure and compression may be required to add it back into the syngas, especially in the case of an SMR.

B.1.3 Fischer-Tropsch Synthesis Unit

The H₂/CO ratio-adjusted syngas then goes to the FT unit. First, it is combined with some amount of recycled FT unit tail gas. This is required because essentially all the FT catalysts have a maximum per pass (or once-through) CO conversion limit beyond which product selectivities drop (higher light gas make, lower liquid make) and catalyst deactivation increases. The exact CO conversion limit varies with catalyst and process specific constraints but is typically 50–75 percent. This, in turn is too low a final CO conversion value for overall plant economics, largely because syngas generation is by far the most expensive part of the plant. The ratio of recycle to fresh feed (R/F) required depends on both the per pass and overall CO conversion targets (the closer these are the less recycle is required) and the syngas purity (H₂ and CO versus inert gases such as CH₄, CO₂, N₂, or argon [Ar]). Because an SMR syngas will contain significantly more CH₄ and CO₂ than an ATR syngas, higher R/F ratios are required in an SMR-based plant, everything else being equal. In reality, it may be necessary to lower overall CO conversion targets in an SMR-based plant, while somewhat lower liquid and higher gas selectivities would likely be the case given the higher overall inert levels.

Next the combined syngas feed is preheated to near the FT reactor operating temperature, which will typically be 400–450°F depending on process specifications. The preheating can be done in a feed-effluent heat exchanger using the hot process gas exiting the reactor, or in a separate gas preheater. For the latter, heating is usually done by condensing medium-pressure steam (MPS) generated by removing the exothermic heat of reaction in the FT reactor itself.

The preheated syngas is then fed to the FT reactors. This study considers a multi-tubular fixed bed (MTFB) and slurry bubble column reactors (SBCRs) for the study plant. An MTFB consists of a large number of parallel small diameter tubes that are packed with relatively small catalyst particles (typically 0.5 to ~2 millimeters in diameter). Tube diameters are generally around 1 in., and tube lengths around 40 ft. The tubes are welded to tube sheets at the top and bottom, and the whole assembly is inside a pressure vessel with top and bottom heads. In practice these are simply large shell and tube heat exchangers with the catalyst and process gases in the tube side and BFW/steam in the shell side. Gas is fed at the top, and a mixture of unconverted syngas, hydrocarbon liquids and gases ranging from CH₄ to as high as C₁₀₀, or higher, and a large amount of water (steam) produced from the O₂ in the CO feed comes out the bottom. It usually makes sense to send the reactor outlet mixture directly to a wax knockout drum operating at or near reactor temperature to avoid 2-phase flow issues at low elevations further downstream.

An SBCR is more or less the inverse of a MTFB. Here, a mixture of product liquids (molten wax) and small diameter (75–100 micron) catalyst particles are contained in the reactor shell, with a smaller number of larger diameter tubes containing BFW/steam. Feed gas is bubbled into the slurry at the reactor bottom using some type of gas distributor that will vary with technology supplier. Lighter liquid products and gases leave the slurry at the top and go to downstream cooling and separation. Heavier products—those that are liquid at reactor T and P—are removed from the slurry by filtration, commonly with sintered metal-type filters. These may be located inside the reactor vessel, outside the reactor vessel with circulating slurry, and/or a combination of both. The filtered wax is more or less equivalent to the MTFB wax removed at the MTFB reactor exit.

In both type of reactors, the exothermic heat of reaction is removed by MP steam generation, with fairly tight temperature control. A MTFB reactor is considerably less thermally stable than an SBCR, which makes it attractive for commercial use. However, SBCR scale-up is not well documented or understood, and catalyst-wax separation can be challenging. Catalyst regeneration, typically by reduction/oxidation/reduction (ROR) processing may be required in addition to catalyst activation (reduction) and changeout. MTFB reactors are typically loaded, activated, regenerated, and unloaded in situ, with the reactor off-line. SBCR catalyst addition and removal, as well as regeneration, can be conducted in external equipment with the reactor on-line, which can have significant service factor advantages. Similarly, much larger capacity SBCR reactors can be fabricated compared to MTFB reactors.

The hydrocarbon saturated and steam containing reactor effluent gas then goes through a cooler where the temperature is brought to an intermediate level, typically 220–250°F. This is required because a significant fraction of the hydrocarbons in the gas phase is solid at (much) higher than ambient temperatures. The gas may be cooled by a feed-effluent exchanger as described above, preheating the FT reactor to near reactor operating temperature, and/or by generation of low-pressure steam (LPS). The 3-phase (gas, hydrocarbon liquid, and water) mixture exiting the cooler goes to a 3-phase separator where the denser water goes to the bottom (often in a water “boot”), while the less dense hydrocarbons float on top of the water and are removed by passing over an internal weir. This 3-phase vessel is typically referred to as a hot separator (HS). The gas leaving the HS goes to one or more additional heat exchangers for further cooling, ultimately being cooled to near ambient temperature in air-fin and/or cooling water exchangers. The resulting 3-phase mixture goes into another 3-phase vessel, generally referred to as a cold separator (CS), which is configured almost exactly the same as the HS for production of lighter hydrocarbon liquids and additional liquid water. The non-condensable gas leaving the CS is the FT tail gas as discussed above. A certain fraction is compressed and recycled to the FT reactor as described above. This stream is completely

internal to the FT unit and can be ignored from a plant material balance perspective. Based on the overall conversion and selectivities to different species, a portion of the tail gas must exit the FT unit. A portion of this is typically recycled to the reformer as described earlier, while the rest is sent to an LPS plant fuel system as the main plant purge gas. The rate of purge gas can be determined by a number of considerations, especially including plant fuel requirements and plant inert buildup, especially in cases where significant N₂ and/or Ar may be present in the feed natural gas and/or the (ATR) O₂ supply.

The FT hydrocarbon products are typically depressurized (“flushed”) to remove dissolved gases and then sent to an intermediate distillation column for preparation for further processing. The FT product water is also depressurized (flushed) and sent for additional processing. It is very important to note that small, but non-negligible quantities of oxygenated species, mainly alcohols but also ketones, aldehydes, and acids, are produced in the FT synthesis. These are typically relatively light (C₁ to perhaps C₁₀) and a significant fraction of the lighter species are present in the product water, although some partition into the hydrocarbon liquids. The FT product water will generally contain ~0.5–2.0 percent total oxygenates and may have a pH of 3–4. It is critically important to prevent FT product water condensation in carbon steel piping and vessels, as these will quickly corrode. Mild stainless-steel alloys are commonly applied for this service, which includes the overhead piping from any process water flash drums. This FT water must be treated/cleaned up before use for any conventional BFW make-up or for disposal on or offsite, which can be treated by conventional commercially available technologies.

B.1.4 Intermediate Hydrocarbon Distillation

As described above, there are typically three hydrocarbon liquid product streams from the FT unit: hot wax, intermediate temperature HS, and (near) ambient temperature CS liquids. Because these separators are at best equivalent to a single stage/tray, there are long overlapping tails on both the low- and high-temperature sides for each. Distillation conditions depend very strongly on downstream processing requirements. For the production of jet fuel by HC/HI, the main separation is the removal of C₅–C₇ light naphtha from the C₈₊ majority of the products. This can be done by conventional distillation involving heating by steam condensation or hot oil circulation. The heavier hydrocarbons will start thermally degrading at temperatures above ~550°F, and rapidly at 600°F or higher, so distillation bottoms temperatures should be below 550°F in all cases. Depending on plant configuration and distillation targets, this may require the use of vacuum distillation columns and/or steam strippers. This consideration generally holds for the C₁₇₊ portion of unconverted oil (UCO) in the HC/HI unit described below. The C₅–C₇ light naphtha, referred to as straight-run naphtha (SRN), is sent to tankage as a final product. The C₈₊ liquids go to the HC/HI unit.

B.1.5 Hydrocracking/Hydroisomerization Unit

Although the details vary with catalyst type and process vendor specifications, the HC/HI unit operates at relatively high pressures—generally above 600–700 psig using platinum group metal (PGM) based catalysts and higher still (900–1,200 psig) for sulfided base metal catalysts. The C₈₊ liquids, generally consisting of a hot wax product from the FT wax knockout and the lower temperature C₈₊ material from the HS and CS after distilling/removing the C₅–C₇ are compressed in charge pumps to the pressure required for HC/HI. Like operating pressure, operating temperature will be a function of catalyst type and process vendor specific requirements, but will generally be 500–700°F. The feed from the FT unit is combined with UCO, which is heavier material from the HC/HI reaction that is only partially converted per pass, typically 50 percent. The combined feed is

heated against the HC/HI reactor outlet stream in a feed-effluent cross exchanger. Some additional trim heating will generally be required to meet the final operating target, and for this service concerns about maximum wax exposure temperatures are much lower than for distillation because the residence time in this heater would be very short, and the wax is going directly to a hydrogenation process immediately downstream of the heater. The hot pressurized liquids are sent to the HC/HI reactor along with the HP H₂. The majority of the H₂ is recycled from the backend of the HC/HI unit, but continuous addition of make-up H₂ (from the syngas H₂ separation unit) is required to make up for H₂ consumption in HC/HI. FT liquids HC/HI operating temperatures and pressures, as well as H₂ consumption rates, are much lower than for a conventional petroleum-based unit.

The reactor outlet stream is cooled against the feed stream in the feed-effluent exchanger discussed above, and then may be further cooled as required prior to H₂ separation from the liquids. This H₂ is compressed and recycled to the reactor inlet. The H₂ depleted gases are depressured as required (which is generally to a very low value) prior to further separation by distillation. There the heavier UCO (typically C₁₇₊ for a jet fuel plant) is recycled back to the HC/HI feed, while the C₁₇ goes for further separation/distillation. The final products would be a C₈–C₁₆ jet fuel, a C₅–C₇ light naphtha, and other lighter products. There is normally a significant amount of liquefied petroleum gas (LPG) (propane and butane) produced that could also be purified as an additional product, although very low, sub-ambient temperatures using a chiller would be required. Whether this is economically justified for a GTL plant with relatively low-cost natural gas is uncertain. Nevertheless, the LPG containing light fraction can be recycled to the reformer to make additional syngas and/or reduce the required natural gas feed rates.

B.2 FISCHER-TROPSCH GTL PROCESS AVAILABILITY AND VENDORS

B.2.1 Steam Methane Reformers

As described above, SMRs are older, well-established process technology and are available from numerous vendors, including many major catalyst/process technology suppliers and engineering, procurement, and construction (EPC) companies. Each technology provider has any number of different variations including firebox and burner configurations, process tube types, and heat integration, as well a different combination of multiple technologies such as gas heated reformers and combined reformers. Details of these variations were beyond the scope of this project.

However, most SMRs are employed for H₂ production, where high S/C feed ratios are used and where high pressures and temperatures may not be required. Because a GTL-based SMR will be pushed to very aggressive conditions, especially high pressures and temperatures at relatively low S/C ratios, any additional project scoping should be limited to those suppliers who have designed and operated SMR plants at these conditions.

B.2.2 Autothermal Reformer

ATRs are newer and less common processes, and the number of technology vendors is consequently much smaller than for SMRs. Some of the more established process suppliers include Haldor Topsoe, [90] Johnson Matthey/Davy, [91] Air Liquide/Lurgi, [92] ThyssenKrupp, [93] Casale, [94] and others.

B.2.3 Oxygen Air Separation Unit

While it is virtually certain that constructing and owning an ASU will result in the lowest overall project costs for O₂ supply, it is also certain that this will significantly increase the total plant capital costs. There are other options to consider. O₂ is not the only product from an ASU, N₂ is virtually automatic, and Ar is also possible with some additional investments. While a GTL plant would require some non-trivial amount of N₂ for purging and blanketing the equipment, the amounts of N₂ produced in an ASU sized to produce the desired amounts of O₂ for an ATR would dwarf the plant requirements. Again, it is possible to consider that the ASU plant sells N₂ and possibly Ar as separate products, but this would require a large additional increase in sales and marketing capabilities in a business area quite different than the GTL hydrocarbon production. In some cases, it may be possible for an industrial gas supplier to design, construct, and operate a standalone ASU close to a reasonably-sized GTL plant, selling O₂ and some N₂ to the plant “over the fence” while also using their prior knowledge and experience to sell additional O₂, as well as N₂ and Ar to other local users. The largest production expense for an ASU is typically power to run the air compressors. A GTL plant without an ASU has much more HPS and MPS available for power generation and/or turbine driven rotating equipment (especially compressors) than all of the other loads in the plant combined. It could be advantageous for both parties if the GTL plant supplied excess steam and/or power to the ASU operator in return for lower cost O₂.

B.2.4 Hydrogen Separation Units

H₂ separation by selective membranes and/or PSA technologies are well-known and available from multiple vendors, especially the large industrial gas suppliers such as Air Products, [95] Air Liquide, [96] Linde, [97] Evonik, [98] and Generon. [99]

For a conventional SMR-based GTL plant, there will always be a large excess of H₂ in the syngas, so considering a different source of H₂ for the HDS and/or HC/HI units would not make a great deal of sense. An ATR, however, can make the desired FT H₂/CO ratio directly, so there is the possibility of considering other options. For example, a small SMR could be added in parallel to the ATR to generate the H₂ required for these services, as well as for intermittent FT catalyst activation and regeneration. The most attractive part of this scheme results in decoupling the HC/HI unit operation from the ATR and FT units. While it is impractical to store large amounts of syngas to allow FT operations without the ATR running, it is highly practical to add intermediate liquid product storage/tankage to allow the HC/HI unit to operate when the ATR and FT are down, for example on turnaround. However, in the base plant configuration, this would not be possible as the HC/HI H₂ comes from the ATR syngas. Adding a small standalone SMR would almost certainly involve higher capital costs than a membrane/PSA H₂ harvesting system but could prove economically beneficial by decoupling the units as described. This could be investigated in later project phases.

B.2.5 Fischer-Tropsch Synthesis Technology

The number of commercially proven FT technologies is much smaller than those for any of the other processes considered in this plant.

For MTFB technology, Shell is a proven leader with long-time operating plants in Malaysia and Qatar. [100] [101] [102] Greyrock has built and operated at least one moderate size (450 BPD) GTL plant in West Texas with Advantage Midstream, [103] [104] and Canada’s Expander Energy currently is constructing a very similar, if not identical, plant in Alberta, Canada. [105] [106] Operational and

cost data for Greyrock's technology are not widely available. Velocys supplied their microchannel catalyst and reactors to an approximately 250 BPD joint venture landfill gas (LFG) to FT products plant (Envia Energy) in Oklahoma City, Oklahoma, several years ago. [107] This plant had operational issues, mainly with the LFG clean-up system initially, but was reported to be running well later. Unfortunately, one of the two FT reactors was irreparably damaged during off-spec operations (reportedly by a poorly designed reactor cooling system), and the plant was eventually shut-down, dismantled and removed from the site. [108] [109] Velocys is supplying FT catalyst and reactor to the Red Rock Biofuels waste wood to FT products plant that is currently under construction in Oregon. [110] Emerging Fuels Technology (EFT) was supplying FT catalyst for a ~1,100 BPD specialty wax plant designed and under construction by SGC Energia in West Lake, Louisiana. [111] Unfortunately, that plant recently declared bankruptcy prior to completing construction and beginning operations. [112] (Based on Exhibit B-1, the entire plant is ~300 ft by 400 ft [120,000 square feet (ft²), or ~2 acres].)

Exhibit B-1. SGC Energia ~1,100 BPD GTL plant in West Lake, Louisiana



Source: Google Earth

JET FUEL PRODUCTION AT THE PITTSBURGH AIRPORT: GTL VIA FISCHER-TROPSCH SYNTHESIS



Source: Google Earth

EFT is also supplying the FT catalyst and technology to Niquan Energy's ~3,200 BPD GTL plant [113] also currently under construction in Trinidad (actually the old World GTL plant from the early 2000s). Niquan has projected operations beginning in late 2020 to early 2021. [114] (EFT is also supplying some catalyst and reactor technology to Red Rock Biofuels for the Oregon BTL plant.) Niquan Energy's GTL plant has a reformer (SMR), fixed bed FT (EFT), and HC/HI upgrader. (Based on Exhibit B-2 and Exhibit B-3, the process plant area is ~500 ft by 700 ft [350,000 ft², or ~8 acres], also a tank farm and wastewater aeration/evaporation pond.)

Exhibit B-2. Niquan Energy ~3,200 BPD GTL plant in Trinidad and Tobago (under re-construction)



Note: Shows tank farm and wastewater aeration pond

Source: Google Earth

Exhibit B-3. Niquan Energy ~3,200 BPD GTL plant in Trinidad and Tobago (under re-construction) (zoomed)



Source: Google Earth

Johnson Matthey/Davy/British Petroleum (BP) operated a ~ 300 BPD GTL plant in Alaska in the early 2000s, [115] and more recently developed a newer radial flow FT (“CAN”) technology that is going to be employed at Fulcrum Bioenergy’s municipal solid waste (MSW) to FT product plant, which is currently under construction in Nevada. [116] [117] [118] There are also many other FT offerings from a significant number of vendors that have not operated at any significant scale, certainly not commercially to date. This could change in the future.

Although MTFB reactor scale-up is extremely simple and straight forward, simply increasing the number of identical parallel reactor tubes, while catalyst manufacturing scale-up is a significant hurdle to be demonstrated and overcome. For fixed bed catalyst manufacturing, equipment availability and configuration often varies, sometimes significantly, with production capacity, and there are cases where major hurdles were encountered in scaling up the actual catalyst manufacturing process.

There are also a number of SBCR reactor and technology suppliers. Sasol has operated SBCRs since the mid-1990s in South Africa, Qatar, and Nigeria. [119] [120] Although Sasol recently stated that they will not be pursuing new GTL or coal-to-liquids (CTL) plants, their process is available for license. [121]

Sasol’s Oryx is a ~34,000 BPD GTL plant in Qatar with two Haldor Topsoe ATRs, O₂ plants, two Sasol slurry FT reactors, and Chevron HC/HI. [122] (Based on Exhibit B-4, the entire plant area is ~3,000 ft by 2,000 ft [6,000,000 ft², or ~140 acres].)

Exhibit B-4. Sasol Oryx ~34,000 BPD GTL plant in Qatar



Source: Google Earth

The Chinese technology supplier Synfuels China has a handful of CTL plants in operation in China, although these employ iron-based catalysts that are generally not well suited for GTL plants. Whether they have developed and demonstrated a cobalt-based SBCR process is not known. [123] [124] The Synfuels China/Yitai Coal 5,000 BPD CTL demonstration plant in Da Lu, Inner Mongolia, China has a coal gasifier, O₂ plant, single Synfuels China slurry FT reactor, and Synfuels China Hydrocracker. (Based on Exhibit B-5, the entire plant area is approximately 4,000 ft by 2,400 ft [9,600,000 ft², or ~220 acres].)

Exhibit B-5. Synfuels China/Yitai Coal 5,000 BPD CTL demonstration plant in Da Lu, Inner Mongolia, China

Source: Google Earth

The GTL.F1 consortium, originally Lurgi, Statoil, and PetroSA demonstrated a ~1,000 BPD cobalt-based GTL process at Statoil's GTL refinery in Mossel Bay, South Africa. [125] This process is also available for license from Air Liquide. Axens and its partners demonstrated a SBCR reactor process at ~22 BPD in Italy, which is rather small for a SBCR demonstration. However, they also conducted extensive non-reactive hydrodynamic studies at much larger scales and are now offering this process for license as well. Energy Security Partners/GTL Americas plans to employ the Axens SBCR technology in their proposed 30,000 BPD GTL plant in Arkansas, but that has not reached project financing at this time and construction has not begun. [126] Both ExxonMobil [61] [127] and Syntroleum [128] [129] developed and demonstrated SBCR technologies at 200 BPD and 100 BPD scales in the 1990s and early 2000s. ExxonMobil has decided not to deploy it for its own use. Syntroleum was actively offering their process for license but ended up more-or-less bankrupt and was sold to REG several years ago. REG still maintains this GTL process on their website and in literature, but the actual current status of it is unclear. Most of REG's production comes from conventional biodiesel plus an old Syntroleum joint venture (originally Dynamic Fuels) renewable diesel plant in Geismar, Louisiana. [130] Similarly, Conoco demonstrated a ~200 BPD SBCR technology in Ponca City, Oklahoma, in the early 2000s, but following the merger with Phillips, that plant and technology were sold at auction. [131] [132]

Comparing the 2 broad FT technology options, the SBCR reactors employed by Sasol and Synfuels China can produce ~18,000–20,000 BPD each. These are very large reactors—nominally ~10 meters in diameter and to 60 meters tall. As such, there are only a very limited number of facilities that can construct them, and transportation is very challenging. For a ~6,000 BPD plant considered in this study, the required reactor size would be smaller, but still extremely large at ~6 meters in diameter that would still be challenging for fabrication and transportation. Several (2–3) smaller reactors might be more desirable than a one for these reasons. Similarly, solids handling is a particular

challenge with SBCRs, especially if a complicated, multi-step, and usually batch catalyst activation and/or regeneration facility is required.

The maximum production capacity for the largest MTFB reactors in operation today (at Shell’s Pearl plant in Qatar) is ~6,000 BPD of product—in theory, one reactor could be used in this GTL plant. However, Shell’s reactors contain ~30,000 1” diameter tubes each, are over 20 ft in diameter, and are extremely heavy. As a result, only 1–2 fabrication shops in the world can manufacture them, and plant locations to date have been on the coast due to transportation limitations. Shell’s Pearl GTL is a 140,000 BPD GTL plant with Shell thermal partial oxidation, O₂ plants, SMRs, Shell fixed bed FT, and Shell HC/HI/HT. (Based on Exhibit B-6, the entire plant site is approximately 8,000 ft by 5,000 ft [40,000,000 ft², or ~920 acres].)

Exhibit B-6. Shell Pearl GTL 140,000 BPD GTL plant in Qatar



Source: Google Earth

OLTIN Y’OL in Uzbekistan is a nominal 37,000 BPD GTL plant using a Haldor Topsoe ATR, Sasol slurry FT, and either a Haldor Topsoe or a Chevron hydrocracker (Exhibit B-7). The original total price tag was announced at \$2.3 billion (B) (\$61,162/BPD); more recently, they have been reporting \$3.7 B (\$100,000/BPD), [133] although another reference claims it was \$5.6 B (\$151,000/BPD). [134] Though the plant was announced in 2009–2012, it is unclear when design engineering work actually started. Construction started in 2016, and it is nearly complete now. It should be completed in 2021, indicating 4–5 years of construction time. The location is less than ideal, as everything needed to be imported from far away, [135] and either expensive ex-patriot and/or low-productivity local labor was employed. The FT is certainly 2 trains (like Qatar or Escravos/Nigeria). ATR and HC could be 1 or 2 trains.

Exhibit B-7. OLTIN Y'OL 37,000 BPD GTL plant in Uzbekistan



Fulcrum Bioenergy's Sierra BioFuels Plant is a ~800 BPD MSW gasifier and BP/JM/Davy fixed bed FT based plant in Nevada. There is currently no upgrader. The total cost was originally announced at \$200 million (MM) (\$250,000/BPD); [136] [137] it appears to stand at \$300 MM, (\$375,000/BPD), maybe more. Announced in 2014 (but not fully funded then), the plant began construction in 2018. It should be completed in 2021. The syngas generation includes the gasifier/reformer, tar conversion, water gas shift (WGS), and extensive clean-up. There is also a rather enormous wastewater treatment plant. The entire plant site is ~1,500 ft by 400 ft (600,000 ft², or ~14 acres). The process area (in the lower center of Exhibit B-8) is only a small fraction of acreage (less than 1,000 ft by 200 ft).

Exhibit B-8. Fulcrum Bioenergy 800 BPD Sierra BioFuels Plant (MSW to liquids) in Storey County, Nevada, United States



Source: Google Earth

JET FUEL PRODUCTION AT THE PITTSBURGH AIRPORT: GTL VIA FISCHER-TROPSCH SYNTHESIS

Red Rock Biofuels is a ~1,100 BPD waste wood gasifier (Frontline Bioenergy) plus FT (Velocys and EFTI), Topsoe HC/HI. It is located in Oregon. They announced \$320 MM total cost in 2019 (\$290,000/bbl). [138] It is unclear when the plant began work or had funding, but construction started in 2018; it is due to be completed in 2021.

Turkmenistan GTL is a ~15,500 BPD natural gas to gasoline plant with Haldor Topsoe ATR, and Haldor Topsoe TIGAS™ (which is essentially methanol synthesis and methanol-to-gasoline) (Exhibit B-9). Its official total price is \$1.7 B (\$110,000/BPD), [139] [140] but at least 1 reference claims it is \$3.9 B (\$250,000/BPD). [141] Construction started in 2016; it was complete and operational in 2019. Like Uzbekistan, a very high cost-location factor is expected.

Exhibit B-9. Turkmenistan ~15,000 BPD gas to gasoline plant



Greyrock/Advantage Midstream is a ~450 BPD GTL plant in West Texas containing SMR and Greyrock fixed bed FT reactors, with no upgrading, but distillation. Announced in 2014, the plant was completed and operational in 2019. Construction paused for at least 1, possibly 2 years in 2015–2017 due to low oil prices. The total cost is unclear (not public) but based on Greyrock's claims and Expander Energy's numbers, it is probably \$45–55 MM (\$100,000 to 122,000/BPD). The total plant rectangle without the parking and buildings (on bottom right in Exhibit B-10) is less than 400 ft by 800 ft (320,000 ft², or ~7 acres).

Exhibit B-10. Greyrock/Advantage Midstream 450 BPD GTL plant in West Texas



Source: Google Earth

Expander Energy/Rocky Mountain GTL is a near carbon copy of the Greyrock/Advantage Midstream GTL plant, at 470 BPD (Exhibit B-11). The original cost estimate was \$42 MM; it now stands at \$60 MM (\$89,000–128,000/BPD). [142]

Exhibit B-11. Rocky Mountain GTL plant in construction in Alberta, Canada



Source: Google Earth

Most cobalt catalysts require periodic regeneration, typically yearly, while the entire catalyst charge would be replaced every 3–5 years. As these procedures require the reactor be offline and would require multiple weeks at a minimum, the service factor (production) debit for a single reactor plant would be large. Shell has four reactors at their Malaysian plant, and 24–26 at their Qatar plant. With these numbers, it is reasonable to consider installing a spare reactor such that production is unaffected by these requirements. For this 6,000 BPD GTL plant similar considerations apply. At the same time, the MTFB reactors are really just large shell and tube heat exchangers, which many fabrication shops can design and construct up to some limiting size, typically 10–12 ft in diameter. It would be preferable to install several (4–5) reactors in this size range rather than 1–2 very large ones. This increases the possibility of local construction, minimizes transportation distances, and reduces reactor weight significantly. The larger number of potential manufacturers also increase the likelihood of competitive bidding. At the same time, with 4–5 reactors installed, when one is taken offline for catalyst regeneration or replacement, it would be relatively easy to increase the operating temperature of the other reactors to make up for the lost CO conversion, albeit at somewhat higher light gas and somewhat lower liquid product selectivities. MTFB activation and regeneration would then be conducted using a dedicated system employing hot oil for heating (to avoid extremely high pressure with BFW/steam heating) and a dedicated gas circulation compressor sized for these duties. This would be much smaller than the FT tail gas recycle compressor used in normal operations during FT synthesis.

At least 3 technology vendors have produced cobalt-based FT catalysts that make very little wax, typically less than 5 percent. These are Greynock, as discussed above, the Russian company Infra Technology, and Chevron. Infra built a 100 BPD demonstration plant outside of Houston several years ago but was unable to get their self-designed SMR operational. Their U.S. subsidiary declared bankruptcy and the plant was sold at an auction to another small-scale GTL developer, Greenway Technologies. [55] Chevron appears to have lost interest in small-scale GTL solutions, but the catalyst was operated at pilot scale by Southern Research Institute (SRI) as part of a DOE program, and SRI now offers this for license. At least one developer, Agra Energy, announced plans to build a demonstration plant using manure-based anaerobic digester gas as the feed to a Chevron FT-based GTL plant. This demo plant may be in operation in 2021. [52] [143] [144] [53]

These wax-free catalyst developments are extremely promising for very small-scale GTL units where the HC/HI unit would be prohibitively expensive (it is relatively complicated and does not scale down well), where wax is more of a problem to deal with than any useful product. Small-scale developers are generally interested in liquid fuel they can move through existing networks. All three catalysts produce a great deal of C₁–C₄ light gas and a lot less C₅₊ liquids compared to high wax (high Anderson-Schulz-Flory distribution) catalysts, and for larger plants where the cost of an HC/HI unit is low relative to syngas generation and FT production, the higher C₅₊ selectivity with a conventional, high wax FT catalyst almost always outweighs the cost of processing the wax by installing an HC/HI unit. Hence, there are no known plans for large plants employing these catalysts.

The typical cobalt FT catalyst makes mostly n-paraffin products. There are, however, almost always non-trivial amounts of (mainly) 1-olefins, as well a much smaller amounts of branched paraffins and olefins, and the various oxygenates discussed in the FT water composition section above. The primary products formed in the FT reaction depend mainly on the chemical composition of the catalyst itself, especially the nature of the support and additives other than base or PGM metals such as rare earths and/or alkali metals. Reaction temperature and H₂/CO ratios are also important. The major differences in FT product chemical compositions involve different concentration of olefins.

Under reaction, rather than diffusion, controlled conditions olefin content tends to be higher, especially in the C₃–C₈ (or so) carbon number range. Using very small catalyst particles, such as in a SBCR, or in a MTFB reactor operating at some combination of low reaction rates and/or very large catalyst pores or low diffusional distances (for example eggshell metal deposition), the maximum olefins to paraffins ratio, which is at C₃ and C₄, can be significantly higher than 1, sometimes 5–8. With moderate diffusional resistances, olefins tend to be caught up in the catalyst pores long enough to be re-incorporated in growing carbon chains and/or hydrogenated, while at strongly diffusion-limited conditions, characterized by low effective H₂ and CO concentrations and high H₂/CO ratios, they are mainly hydrogenated. Thus, there is really no such thing as a representative FT product composition; these will depend very strongly on individual vendor designs. The olefin content mainly varies in the FT composition; higher olefin content results into less H₂ consumption in FT but more in HC/HI. Oxygenate concentrations are much lower, and have much smaller effect, other than notably on the amounts of oxygenates in the product water.

B.2.6 Fischer-Tropsch Water Treatment Options

As discussed above, there are a number of commercially proven technologies for treatment of the acidic, oxygenate containing FT process water. These typically involve pH neutralization, aerobic and/or anaerobic digestion (including membrane-based processes) potentially after a steam stripping or other distillation type step to concentrate the oxygenates in a smaller water stream for treatment.

A potentially more effective strategy would be to use the FT water “as is” for generating steam for the ATR or SMR process. A number of such routes have been proposed and/or developed. These include using FT water in a heated humidification system to supply some or all of the reformer steam, generating HP steam in a segregated “dirty” boiler system directly fed with FT process water, heating FT process water at high pressure and flashing it into the hot process gases, etc. There are patents in this area from ExxonMobil, [145] [146] Johnson Matthey, [147] and Greyrock. [148] Johnson Matthey/BP/Davy offer their version of this technology for license. Such a system greatly reduces the wastewater treatment load for a GTL plant, and recaptures the carbon in the oxygenates within the overall process, somewhat reducing feed natural gas requirements.

B.2.7 Hydrocracking/Hydroisomerization Technologies

HC/HI is a fairly well-known and common petroleum refinery process that is available from any number of catalyst and/or technology suppliers. However, as discussed above, operating conditions for FT feeds are very different than those used for petroleum, and inquiries should be restricted to those vendors/suppliers who have operated with FT feeds at some meaningful (pilot and/or demonstration plant) scales, if not commercially. There are, however, a number that have such experience. Shell produces a number of FT products, including jet fuel, using their own in-house HC/HI technology. Chevron has done the same in the Sasol Oryx plant in Qatar as well as their own (Sasol FT based) Escravos plant in Nigeria. Both Haldor Topsoe and UOP have discussed operations and yields from FT-based HC/HI, and it is strongly believed that others such as Air Liquid/Lurgi, Johnson Matthey/BP/Davy, Axens, ExxonMobil, and others have done the same. Catalysts range from PGM-based processes to sulfided based-metal catalysts. PGMs may be hampered by the need to hydrotreat the FT feeds to convert olefins and alcohols to the corresponding paraffins, which sulfided base metal processes do not require. PGM catalyst are generally more expensive, but typically require less aggressive operating conditions, especially pressure.

Most earlier studies and efforts focused on converting the FT wax, which is typically the C_{21+} material, but could be C_{17+} for a jet fuel plant, leaving the lighter products from the FT unit as produced. Both the diesel and the naphtha are highly paraffinic, and for the diesel low temperature properties are poor. Similarly, the naphtha generally has a very low octane number. These schemes put very significant economic pressure on minimizing diesel and naphtha production (maximizing wax) in an FT unit. Upgrading the lighter material would require the addition of separate processing steps such as isomerization, aromatization, etc., to great economic detriment. Recent tests have fed the entire C_{8+} product stream from FT to a single stage by Haldor Topsoe, sulfided base metal HC/HH unit. This was able to produce jet fuel at a selectivity of 70–80 percent. [88] Given that the FT product C_5 – C_7 yield is very low, these results greatly improve jet fuel production relative to the old processing schemes.

B.2.8 Multiple Technology Suites

There are a number of vendors/companies that offer the entire GTL processing in a single package: Shell, Axens, Johnson Matthey/BP Davy, Air Liquide, and Haldor Topsoe/Sasol. Air Liquide could also supply the O_2 ASU for an ATR-based plant. There are potential advantages in such an approach, especially a more seamless marriage of the separate technologies without the need to separately design and engineer the handoffs from one supplier to another. A limited number of EPC companies have designed and constructed the small number of commercial GTL plants that are in existence today. These include Technip and KBR, although many others have conducted front end engineering and design studies for multiple GTL plants that were proposed in the past.

B.2.9 Carbon Dioxide Removal Options

The majority of CO_2 emissions in the GTL facility comes from burning fuel in the ATR-fired heater or the SMR firebox. At the same time, a significant amount of this fuel comes from FT tail gas purged to the fuel system. For an ATR, this is the majority of the plant fuel under normal operating conditions. As described above, the FT tail gas can contain 30–50 percent CO_2 ; so, if this is directly used as fuel, up to half of the total CO_2 released from its combustion enters the heater as CO_2 . The tail gas is, however, available at fairly high pressures (300–400 psig) and the CO_2 concentrations are relatively high. Therefore, a detailed investigation of CO_2 removal from the FT tail gas stream prior to depressurization into the fuel gas system is recommended. The remaining CO_2 emissions would be from LP flue gas and would be diluted with N_2 from the combustion air (typical CO_2 concentration will be 6–8 mole percent in this flue gas). Hence, this CO_2 would be much more difficult and expensive to capture, although a number of technologies are being commercially offered, such as Air Liquide's CryoCap and Svante's VeloxoTherm technologies for capturing CO_2 from an SMR flue gas.

While CO_2 is a diluent that can reduce CO conversion and liquid yields in FT, CO_2 removal from syngas feed to the FT unit is rarely economic compared to removing it from the purge tail gas as described above. First the absolute concentration of CO_2 is much lower (8–15 percent in the syngas), the total gas volume to be treated is consequently much higher, and the most common CO_2 removal systems, which employ amine-based solvents, are potential poisons for the commercial FT catalysts downstream.

Other options, such as oxy-fuel combustion, which would use pure O_2 or O_2 -enriched air rather than straight combustion air, could also be considered. O_2 , however, is expensive, and its use would

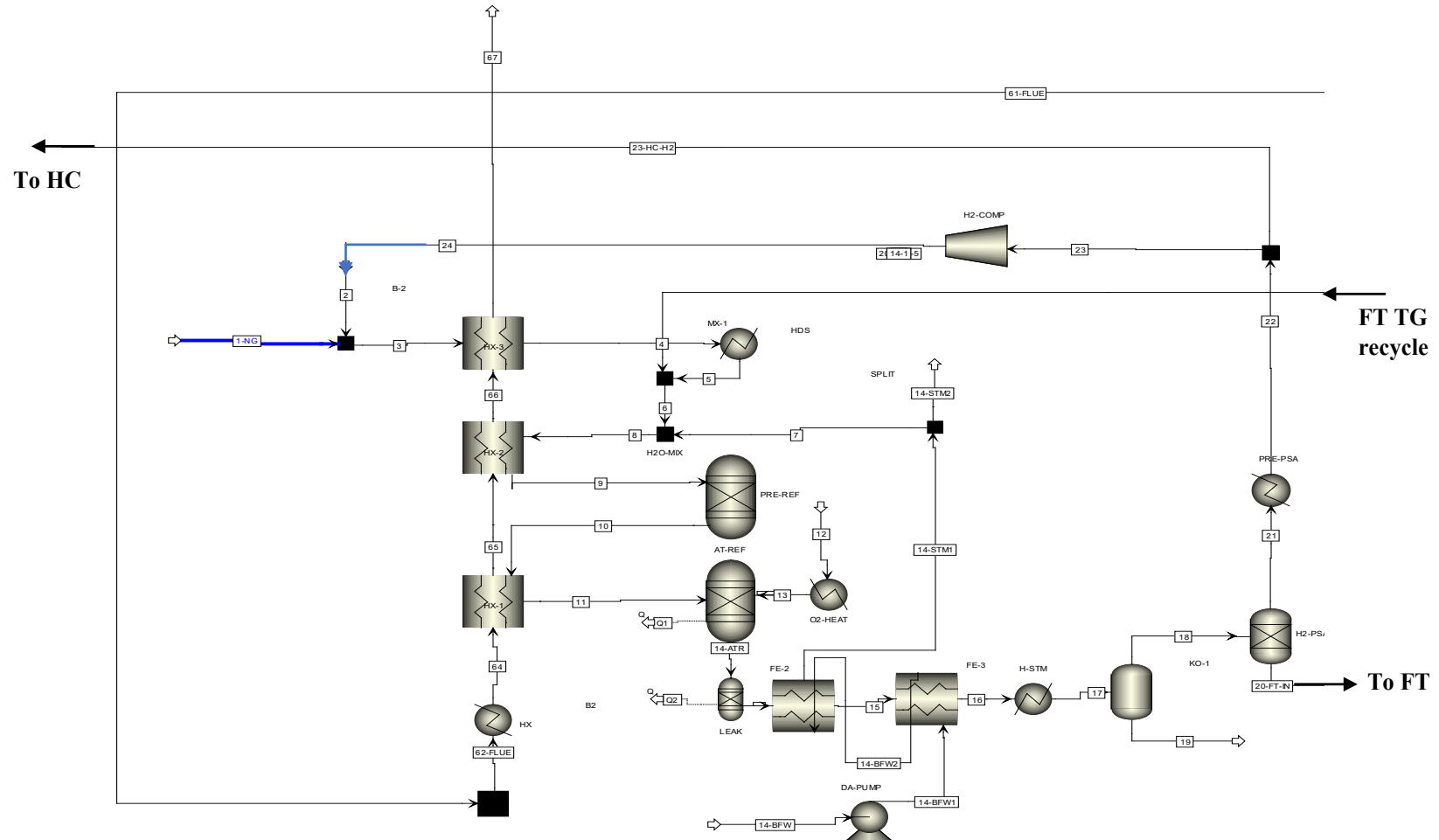
require significant modification to the typical conventional fired heater or SMR firebox design and configuration that may well result in prohibitively expensive costs.

SMR CO₂ emissions will almost always be higher than those from an ATR because all of the reforming reaction energy is supplied by fuel combustion. However, in a more remote, standalone GTL plant location, the excess H₂ removed from the SMR syngas has very little value, and it would normally be used as a fuel. In a more industrialized location, this excess H₂, which would be available at high purity, could be further purified for sales to local users such as for fuel cell vehicles. As H₂ is a relatively expensive commodity, this could well boost the overall GTL plant economics, perhaps by a large amount. However, this H₂ will have a relatively high CO₂ footprint of ~10 kilogram of CO₂ per kilogram of H₂ produced.

APPENDIX C: ASPEN PLUS® FLOWSHEETS

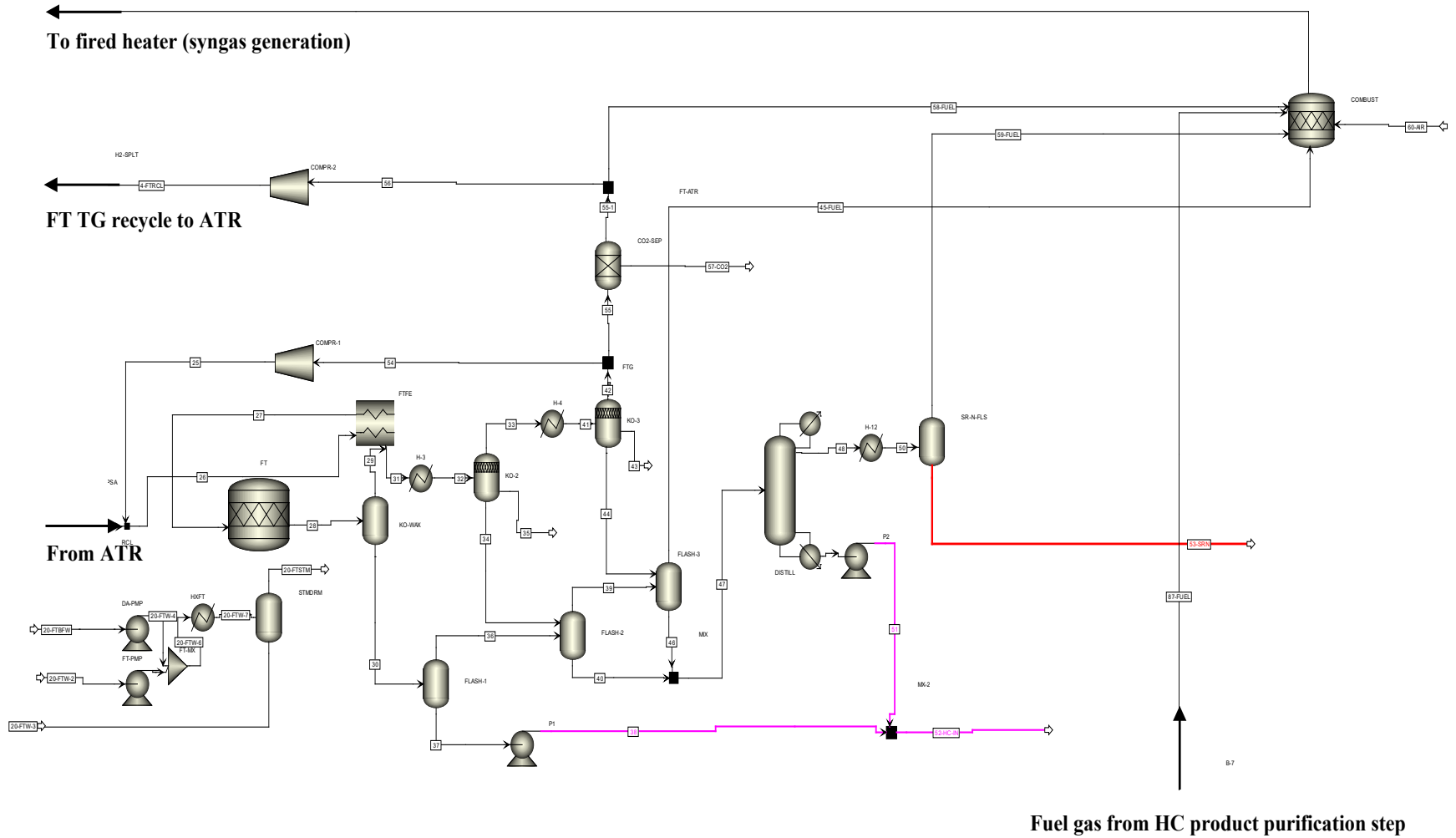
C.1 AUTOTHERMAL REFORMER ASPEN PLUS® FLOWSHEET

Exhibit C-1. Simulation flowsheet showing the syngas generation using ATR



JET FUEL PRODUCTION AT THE PITTSBURGH AIRPORT: GTL VIA FISCHER-TROPSCH SYNTHESIS

Exhibit C-2. Simulation flowsheet showing the FT section to produce wax



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