MULTI-OBJECTIVE ANALYSIS OF A GAS-TO-LIQUID (GTL) PROCESS FROM ECONOMIC, SAFETY, AND ENVIRONMENTAL PERSPECTIVES

A Thesis

by

JINYOUNG CHOI

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Chair of Committee,	Mahmoud El-Halwagi
Committee Members,	M. Sam Mannan
	Fadwa Eljack
Head of Department,	N. Nazmul Karim

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ABSTRACT

One of the most important challenges facing chemical engineers today is developing more efficient processes that reduce the discharge of greenhouse gasses (GHG) and the usage of material and energy resources. Furthermore, industrial manufacturers are making major efforts to incorporate inherently safer design concepts when developing or retrofitting processes. With the recent discoveries of shale gas, there is a growing interest in monetization pathways that convert gas to chemicals and fuels. The Fisher-Tropsch gas-to-Liquid (GTL) process is regarded as a promising alternative to producing liquid transportation fuels. A typical GTL plant requires substantial mass, energy, and financial resources. The syngas production section, in particular, accounts for approximately 50-75% of the total capital costs and about 60-70% of the total energy requirements. Also, the GTL plants have several trains for the syngas production section to accommodate large-scale capacities. Focus on this work is to investigate possible improvements to the GTL process in two areas: 1) tailgas recycling and 2) lower steam-to-carbon (S/C) ratio for autothermal reforming (ATR). The results from these cases are analyzed in terms of cost, inherent safety, and environmental sustainability. Ultimately, the aim of this research is to support the decision makers in understanding the multi-objective insights and in using these insights to make better decisions in design and operation.

This study provides a comparative approach for four different operating cases from various perspectives: economics, inherent safety, and environmental sustainability. In the inherent safety analysis, a fire and explosion hazard analysis are used to choose the least hazardous material for a fuel. The release rate is estimated at the failure case in order to evaluate the degree of containment loss. For the environmental sustainability, the carbon efficiency of the overall process and CO_2 emissions are evaluated. The operating conditions and results are validated against pilot test results from industry in order to verify the degree of carbon deposition during operation. The results are used to establish tradeoffs among the various objectives.

DEDICATION

I would like to dedicate my academic work to my family but especially to my **mother and father** who have always encouraged me to make every effort in every undertaken task and to always strive for happiness for my life.

I would also like to thank my sister **Jina**, brother **Deokjae**, and my lovely niece **Sian** for their support and love throughout this entire journey. They are the most precious for me and they will be with me forever.

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Contributors

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NOMENCLATURE

AIT	Autoignition Temperature
ATR	Autothermal Reforming
HTFT	High-Temperature Fischer-Tropsch
FT	Fischer-Tropsch
GHG	Greenhouse Gas
GTL	Gas-to-liquid
LHV	Lower Heating Value
LPG	Liquefied Petroleum Gas
LTFT	Low-Temperature Fischer-Tropsch
MIE	Minimum Ignition Energy
O_2/C	Oxygen to Carbon
POx	Partial Oxidation
SMR	Steam Reforming
S/C	Steam to Carbon
Syngas	Synthesis Gas, H_2+CO

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1 INTRODUCTION

1.1 Background

The growth of the global population and the size of economy increase the demand for fossil fuel. Since the energy reserve is limited, global demand also urges industries to improve processes targeting more efficiency. These demands lead to increase in greenhouse gas (GHG) emissions to the atmosphere. According to the IPCC [1], atmospheric GHG concentrations will more than triple in the next 50 years compared to pre-industrial levels if no action is taken. The concentrations of GHG increase the risk of climate change such as destruction of natural ecosystems and abnormal weather. As such, concerns about GHG emission increase, it calls for clean fuels increase. These encourage seeking alternatives from unconventional sources to prevent the depletion of conventional energy and to reduce the GHG emissions. Also, it is encouraged developing a process to increase efficiency and reduce the GHG emissions.

Moreover, it is desirable to incorporate safety issues, traditionally little regarded in the design objectives, to develop processes to be inherently safer. Although technologies have been developed, still a lot of incidents are reported in the plants. Numerous approaches from the various aspects have been performed to reduce or eliminate hazards, such as creating safety cultures, enforcing the regulatory, or enhancing the engineering design principles. Although these approaches have contributed to increasing the level of safety, inherent safety approach is believed to be more fundamental and logical way of eliminating the risks by reducing the hazard that causes the significant incidents[2]. Inherent safety or inherently safer design in a chemical process is defined as “a concept, an approach to safety that focuses on eliminating or reducing the hazards associated with a set of conditions” [3]. It prevents incidents fundamentally rather than relies on the instrumentation and control systems, or operating procedure because inherently safer processes should be tolerant of any errors and reliable at any conditions

[4]. Therefore, it is an essential step to make every effort to achieve inherently safer design when developing processes.

As mentioned before, it is necessary to seek for an alternative energy, to develop the process with incorporating the inherent safety and environmental sustainability. Among the several alternatives, natural gas is regarded as one of the best potential energy sources in the future. It is abundant, affordable, and environmentally clean. The report of the Outlook for Energy [5] says that by 2040, the demand for natural gas will account for more than 25% of the major energy demand and will rise by 50%. The current exportation of the natural gas to the market is done via pipe or LNG (Liquefied Natural Gas). For the future, Gas-to-Liquid (GTL) process is regarded as an alternative to LNG because it is proven to have substantial benefits in terms of economic and environmentally sustainable development. This clearly indicates that study on improvement of the GTL process is required to meet the global demands.

Figure 1 shows the schematic flow of process converting natural gas to various products. Of them, the GTL process to produce Syncrude by the FT reaction is one of the three main processes. It is believed to be an attractive way to produce energy in terms that it can produce the synthesis crude comprising naphtha, diesel, and jet fuel overcoming the transportation issue of natural gas.

Previous studies have been done with the following objective to develop the GTL process addressing the economic or process efficiency, operating philosophy or sustainability on GHG emissions:

- To evaluate the potential CO_2 capture and conversion to GTL products by dry reforming[6].
- To maximize heat recovery and power generation of GTL process [7]
- To evaluate the GTL process for single or various syngas technologies related with heat, mass, power, and GHG emissions [8, 9].
- To reduce the GHG gas emission through the utilization of tailgas and moderate operating constraints at Oryx GTL plant[10].

- To optimize and select reforming technologies for syngas generation from natural gas and shale gas[11].

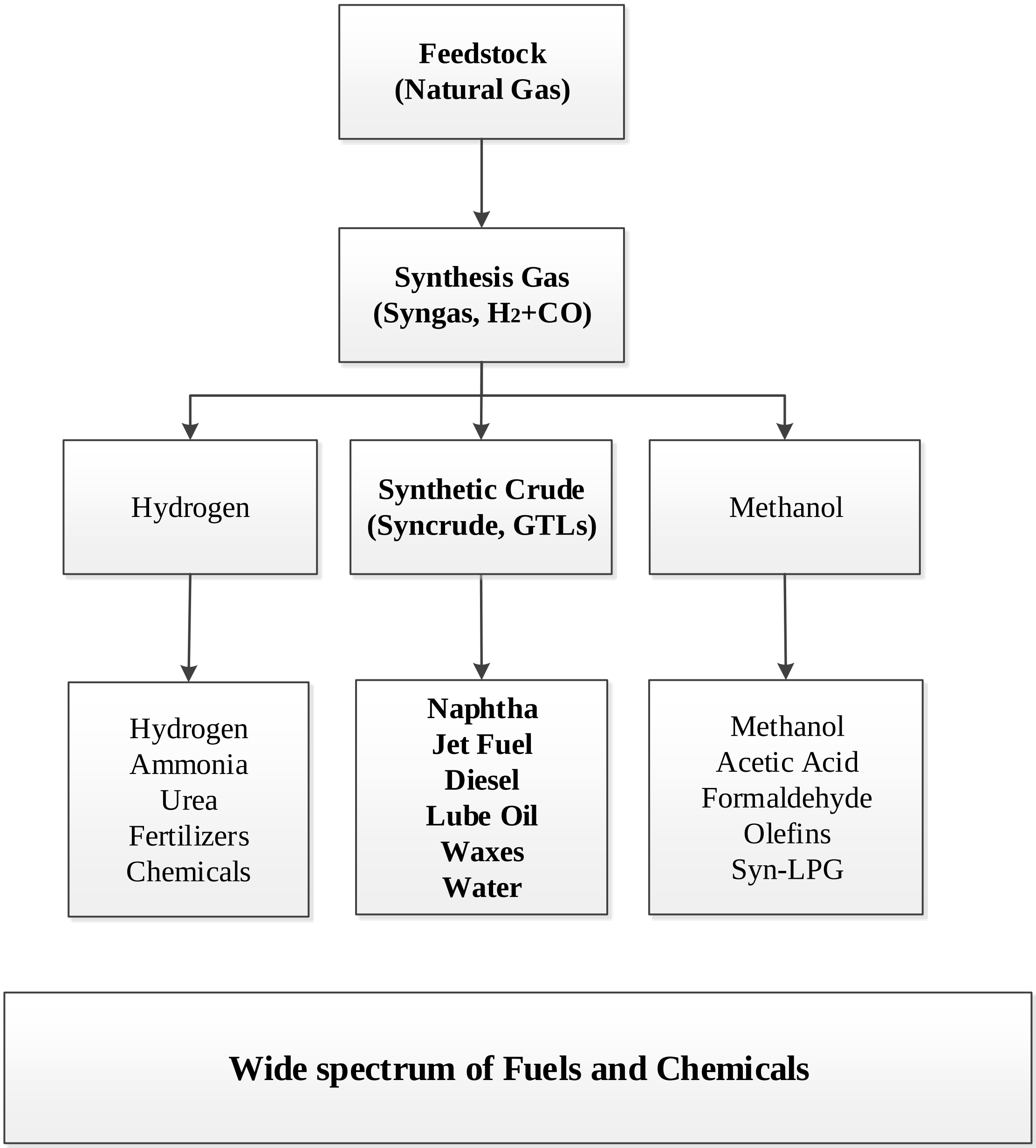

Figure 1. The Schematic Flow of Processes Converting Natural gas to Products

1.2 Objectives

The objectives of this study are to provide information for an effective decision making among various operating options by analyzing the process performance, economic achievement, safety, and sustainability level of the process. It is desired to develop as much as practically and industrially possible in terms of followings:

- To identify the contributions of various process options
- To evaluate the tradeoffs among various implications
- To present effective insights to help to make a decision

The results from these opportunities show various implications as per process options. The trade-off analysis of these implications ultimately provides the integrated insights to help us make a decision for better design and operations. Detailed perspectives are mentioned in **Table 1.**

Table 1. Direction of Process Improvement from each Perspective

Cost-Effectiveness		**Safety**	**Environmental Sustainability**		
Capital Costs	Operating Costs	Inherent Safety	Emission/ Waste	Carbon Efficiency	Energy Usage
↓	↓	↑	↓	↑	↓

It differs from the previous studies [8, 10, 12, 13] in those corporates trade-off evaluations with adding the inherent safety perspectives to improve GTL process.

2 PROCESS BACKGROUND

The process configuration of the GTL process, a description of process technology, and the background information of each of the process section are addressed. The GTL process converts natural gas into high-performing and clean liquid fuels by Fischer-Tropsch (FT) reaction[10], which is composed of three sections: (1) syngas production by reforming natural gas, (2) Fischer-Tropsch (FT) reaction to produce long chain hydrocarbons, and (3) product upgrading and separation to produce syncrude (LPG, naphtha, diesel, waxy product, etc.). The schematic GTL process overview is shown in **Figure 2.** The diagram is made with referenced to the GTL process with autothermal reforming technology. This describes the theoretical backgrounds on the GTL plant and its development learning from reviewing the previous studies. In a practical point of view, industrial practices and perspectives are mainly addressed.

2.1 Feed Preparation Section

The objective of feed preparation process is to eliminate potential poisons from natural gas affecting adversely the performance or reliability of overall GTL plant. Typically, most of the reforming and F-T synthesis technologies that are industrially operated require catalysts for a better efficiency and performance. Therefore, it is necessary to remove poisons from the feedstock before service into the process.

The feed preparation process enables catalysts themselves to protect and to ensure that the catalysts can maintain their performance as long as they can. Deactivation of catalysts is a critical problem not only with the product quality but also with the reliability of the plant. This process reduces the concentration of poison, such as sulfur, mercury, and mercaptans to the acceptable levels designed by the catalyst lifetime and reliable performance [14, 15].

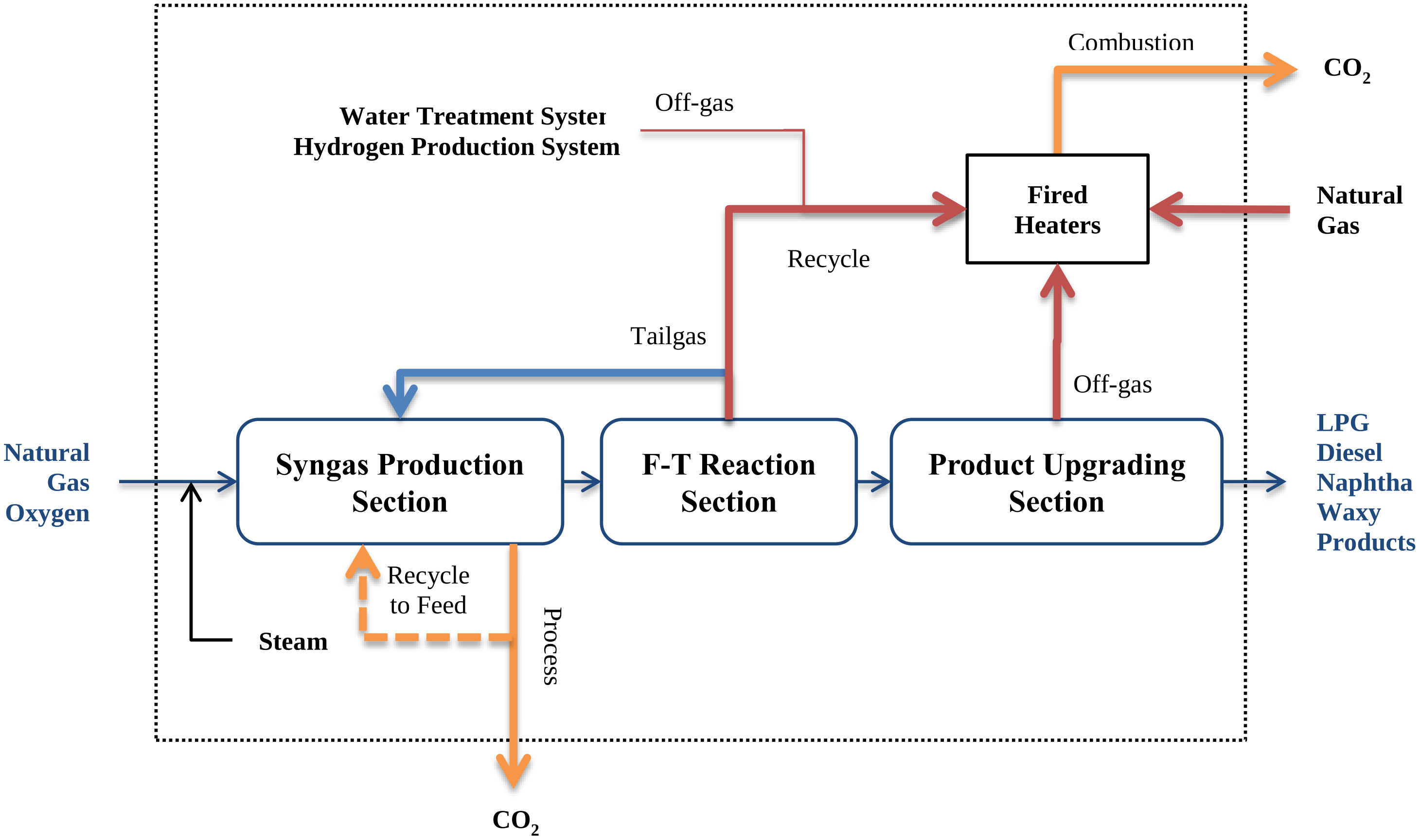

Figure 2. Overview of the GTL process

2.2 Syngas Production Section

The syngas production section produces syngas (H_2+CO) by reforming natural gas. There are three major reforming technologies used in the commercial GTL plants: Steam Reforming (SMR), Partial Oxidation (POx), and Autothermal Reforming (ATR). These three technologies are successfully implemented in the different scales[16].

ATR is one of the adiabatic oxidative reforming routes, which is intensified with partial combustion and steam reforming. It is believed that ATR is the best option of three technologies for large scale F-T reaction in various aspects: efficiency, economic achievement, GHG gas emission, and operability [8, 16-22]. **Table 2** shows the key performance indicators of each reforming technology in the GTL process.

Table 2. Key Performance Indicator (KPI) for the GTL process with different Syngas production technologies [8, 9, 16]

KPI	Unit	SMR	POx	ATR
Natural gas conversion	scf/bbl. GTL	1	0.82	0.81
Net water (Note 1)	lb/bbl. GTL	-1	+1.23	+1.17
CO_2 (Note 2)	lb/bbl. GTL	1	1.01	0.62
O_2	lb/bbl. GTL	-	1	0.93

Notes:

1. +: generated internally, -: required from external sources
2. The generated amount of CO_2 by reaction and combustion.

In industrial fields, the application of ART for the FT reaction has been developed to enhance the efficiency and reliability in three points: (1) catalysts, (2) reformer design, and (3) operation.

- Catalysts: the reliable performance, the stabilities on poisoning and thermal effects, and reasonable pressure drop across the catalyst bed
- Reformer design: mechanical design (including burners) and heat transfer with coupling of catalysts

- Operation: reliable and safe operation without carbon formation and thermal back mixing of hot gas

Catalysts in the reforming system enable to moderate the operating temperature. Typically, nickel is used as a catalyst for the reforming process. A typical process technology for the syngas production with ATR require pre-reformer to convert the higher hydrocarbons (n >1) into CH_4 and CO. Pre-reformer also enables to save the cost by reducing the O_2 consumption in ATR [14, 23, 24]. Pre-reformer is a reactor with a fixed catalyst bed where the reactions are performed as shown below and are recommended operating at lower temperature ranged from 350 to 550°C to avoid the carbon formation [21, 23, 24]:

$$\mathrm{C_nH_m} + \mathrm{nH_2O} \rightarrow \mathrm{nCO} + {}^{(2n+m)}\!/_{2}\, \mathrm{H_2},\ \Delta \mathrm{H_{298K}}(n = 7) = 1175\ {}^{\mathrm{kJ}}\!/_{\mathrm{mol}} \qquad (1)$$

$$3\mathrm{H_2} + \mathrm{CO} \leftrightarrow \mathrm{CH_4} + \mathrm{H_2O}, \qquad \Delta \mathrm{H_{298K}} = -206\ {}^{\mathrm{kJ}}\!/_{\mathrm{mol}} \qquad (2)$$

$$\mathrm{CO} + \mathrm{H_2O} \leftrightarrow \mathrm{CO_2} + \mathrm{H_2}, \qquad \Delta \mathrm{H_{298K}} = -41\ {}^{\mathrm{kJ}}\!/_{\mathrm{mol}} \qquad (3)$$

Pre-reformed gas is additionally reformed with steam in the ATR. This ATR consists of a burner, a combustion chamber, and a fixed catalyst bed within a refractory lined pressure shell[25]. This refractory lining enables to reduce the risk caused by thermal shock or corrosion by H_2 and CO[20]. In the burner and combustion section, natural gas and O_2 (or air) are fed and do partial combustion reaction. In the fixed catalyst bed, the steam reforming and water gas shift reaction are performed. Syngas from ATR should be free of oxygen and soot. The detail reactions are given below [8, 21, 25]:

<u>Combustion Zone:</u>

Partial Combustion:

$$\mathrm{CH_4} + 1.5\mathrm{O_2} \rightarrow \mathrm{CO} + 2\mathrm{H_2O}, \Delta \mathrm{H_{298K}} = -519\ {}^{\mathrm{kJ}}\!/_{\mathrm{mol}} \qquad (4)$$

Thermal and Catalytic Zone:

Steam Reforming: $$\mathrm{CH_4 + H_2O \leftrightarrow CO + 3H_2, \Delta H_{298K} = +206\ {}^{kJ}/_{mol}} \tag{5}$$

Water Gas Shift Reaction: $$\mathrm{CO + H_2O \leftrightarrow CO_2 + H_2, \Delta H_{298K} = -41\ {}^{kJ}/_{mol}} \tag{6}$$

The thermal neutrality of reaction in pre-reformer and ATR is theoretically performed when the net heat is zero:

$$\Delta H_T = \sum_i n_i H_i(T) = 0 \tag{7}$$

The exothermic and endothermic reactions balance the heat to maintain adiabatically. The final syngas ratio of H_2 /CO is determined by thermodynamical equilibrium. The typical operating temperature in the ATR is ranged from 950°C to 1100°F[21]. A large amount of CO_2 is generated in the water gas shift reaction. The syngas properties and CO_2 emissions can be controlled by operating conditions. The desired syngas ratio of H_2/CO is recommended to be around 2.0 for the FT reaction[26].

Since the reforming process is carried out at a high temperature, the catalysts have a thermal stability and a resistance to carbon deposition. Carbon deposition is one of the critical operating concerns in the reforming system. Carbon formed during the reforming process (1) deactivates the catalyst performance, (2) causes the frequent change-out of catalysts, and even, (3) affect the reliability of the overall process. The detail reactions of carbon formation in the reformer are given below[20, 23]:

$$2CO \leftrightarrow \mathrm{C + 2CO_2, \Delta H_{298K} = +172\ {}^{kJ}/_{mol}} \tag{8}$$

$$CO + H_2 \leftrightarrow \mathrm{C} + \mathrm{H_2}O, \mathrm{\Delta H_{298K} = +131\ {}^{kJ}/_{mol}} \tag{9}$$

$$C\mathrm{H_4 \leftrightarrow C + 2H_2, \Delta H_{298K} = -75\ {}^{kJ}/_{mol}} \tag{10}$$

$$\mathrm{C_nH_m \rightarrow nC + {}^{m}/_{2}\, H_2} \tag{11}$$

The probable reasons of carbon deposition during reforming are (1) operating temperature, (2) feed composition, longer chain hydrocarbon than CH_4, and (3) steam to carbon ratio. Several approaches have been taken to avoid carbon formation and deposition during the reforming. Firstly, It is recommended that pre-reformer and ATR be operated at a certain temperature range[23] to avoid any carbon deposition. Higher or lower temperature in both reformers is known to increases the risk of it. Secondly, pre-reformer is equipped for eliminating the longer hydrocarbon. The higher rate of longer hydrocarbon is in the ATR also increases the risk [23], which is also proven by the results of the pilot test. Therefore, as much longer hydrocarbon as possible should be reduced to avoid any carbon deposition in the ATR. Thirdly, sufficient steam is serviced. Typically, steam is used as an agent for catalysts to be regenerated or to avoid the deactivation. The higher S/C ratio is, the lower risk of carbon formation arises [23]. The industry has researched the minimum required S/C ratio avoiding carbon deposition. In the large scale reforming process, 0.6 as the S/C ratio is applied. Haldor Topsoe A/S, an ATR technology provider, commercialized at the S/C ratio of 0.6 in a large scale production and demonstrated the stable operation by the pilot plant at the S/C ratio of 0.2 as with free of carbon deposition [27]. The application of lower S/C ratio can be a big challenge to reliable and continuous operation. The carbon deposition on catalysts decreases on-stream service factor caused by regeneration or change-out of catalysts.

As mentioned before, syngas ratio for the FT synthesis is known as 2.0. This ratio can be achieved only at very high temperature in the reformer (more than 2500°F) or low S/C ratio in reformer [28]. At higher temperature, it demands too high heating energy to be considered as an economic process. According to the industrial practice[29], ATR applies with the low exit temperature and higher S/C ratio with CO_2 recycling to meet the syngas ratio around 2.0. It is estimated relatively economic and reliable way without carbon deposition while maintaining process performance.

Produced syngas from the reformer contains a large amount of H_2O and CO_2, which is inert to low-temperature FT reaction (See section 2.3 in detail). Typically, H_2O is removed by gravity and CO_2 is removed by amine absorption. This removal process enables to reduce the size of the downstream system by removing inert gas. Moreover, it should be removed for preventing corrosion to the piping and equipment materials caused by syngas with H_2O. Moreover, it is beneficial to prevent any the deactivation of cobalt catalyst and lead to methane formation in the FT reactor by reducing the partial pressure of H_2O in the FT reactor [30].

2.3 Fischer-Tropsch Reaction Section

The FT reaction is to convert syngas into hydrocarbon condensates; the product distribution and detail reactions depend on the Anderson-Schulz –Flory (ASF) model[1]. This model also depends on the operating condition and catalyst used. The FT reaction is highly exothermic converting CO to syncrude, generating heat about 140~160 kJ/mol of CO[8]. So, the reliable heat removal system is required for avoiding any thermal runaway. The detail reactions in the FT reactor are given below[8].

Alkenes: $$\mathrm{nCO} + 2\mathrm{nH_2} \leftrightarrow (\mathrm{CH_2})_\mathrm{n} + 2H_2\mathrm{O} \tag{12}$$

Alkanes: $$\mathrm{nCO} + (2\mathrm{n}+1)\mathrm{H_2} \leftrightarrow \mathrm{H(CH_2)_nH} + \mathrm{nH_2O} \tag{13}$$

There are major three types of the FT reactors: fluidized reactor, tubular fixed bed reactor slurry bed reactor. These reactors are proven industrially two operating temperature categories: Low-Temperature (LTFT, 220~240 °C) and High-Temperature (HTFT, 300~350°C). The corresponding pressure range is 2~2.5 Mpa [8, 31, 32]. In the low-temperature FT process, the water shift gas equilibrium (Eq.10) is not promoted, so CO_2 cannot be a reactant in the synthesis; whereas, high-temperature FT process, the water shift gas is active and CO_2 is a reactant for synthesis process. The detail features of each reactor are shown in **Table 3**. Several technologies have emerged in last three decades, which have applied to the GTL process. The commercialized GTL plants made

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[1] Anderson-Schulz-Flory (ASF) model equation $x_n=(1-\alpha)\cdot \alpha^{(n-1)}$
Where, x_n= molar fraction of each carbon number (n), α= the chain growth probability.

a technical decision considering economic, operational, and environmental implications[16].

Table 3. Comparison between Major commercial FT reactor Categories[33, 34]

	Category 1	**Category 2**	**Category 3**
Reactor	Fluidized-bed reactor	Tubular Fixed-bed reactor	Slurry bed reactor
Operating Temperature	HTFT	LTFT	LTFT
Products **(Note 1)**	Gasoline, Olefin, Specialty chemical	Middle distillate (Kerosene, Diesel), Naphtha, Waxed	Middle distillate (Kerosene, Diesel), Naphtha, Waxed
Catalyst	Iron	Cobalt	Cobalt
Advantage	Higher heat efficiency	Easy to operate and separate wax from the products	Better heat transfer, Reasonable pressure drop
Disadvantage	Complex to operate, Narrow range of products	Poor heat transfer, Poor temperature control, High-pressure drop	Difficult to separate wax from the products
Industrial Technology	Sasol SAS, Sasol Synthol	Shell SMDS, BP	Sasol SPD, ExxonMobil AGC-21, Eni/IFP/Axens Gasel, Statoil, ConocoPhillips

During the FT synthesis, a large amount of tailgas is generated, which is mostly unconverted syngas with a trace of CH_4. To maximize the use of internal sources, this tailgas is directly recycled and reused as a feed. To avoid inert accumulation, 3~5% of tailgas is purged to fuel gas system.

2.4 Product Upgrading Section

Product upgrading section is composed of hydrocracker to convert longer chains into shorter chain molecules with the addition of H_2, and fractionator to refine the desired products. Hydrocarbon condensates (FT condensate and waxy product) from the FT reaction are hydrocracked and separated to light ends and liquid sync rude. This syncrude is composed of LPG, diesel, naphtha, and waxy product according to the Sasol Oryx GTL process. In the separation process, light ends are separated, which is mostly unconverted syngas with a trace of CH_4. To maximize the use of internal sources, this off-gas is directly recycled and reused as a fuel with some part of tailgas.

3 PROBLEM STATEMENT

The GTL plants are quite capital intensive in that they require a large scale more than 30,000 bbl./day to return their investment and to ensure their profits [30]. Particularly, the syngas production section accounts for 50~75% of total capital costs [21, 26, 28]. It has several trains to accommodate the large scale due to the small single line capacity of ATR. **Table 4** shows the multi-phasing or trains of large scale GTL plants. Moreover, the operation at high temperatures requires high heating energy, which accounts for about 60~70% of total energy requirements [8].

Table 4. Multi-phasing/trains of Commercial GTL plants

Commercial Projects	**Total Capacity (Phase * Capacity/phase, bbl./day)**	**No. of Train * Capacity/ train(bbl./day)**		
		Syngas Production	**FT Reaction**	**Product Upgrading**
Sasol Oryx (2006)	2 *17,000	1*17,000	1*17,000	1*17,000
Sasol Canada (Planning)	2 *48,000	3*16,000	2*24,000	1*48,000

With different operating options for syngas production section, it is desired to improve the GTL process in terms of economic achievement, maintaining process performance. It is also desirable to incorporate safety and environmental sustainability issues to develop the GTL process. The issues to be addressed are as follows:

- How could contribute to the development of the process by controlling process conditions?
- How could the process be retrofitted to enhance the profitability by maximizing the use of internal sources?
- What are the inherent safety implications of each operating option?

- What are the environmental sustainability implications of each operating option?

4 PROCESS DEVELOPMENT

A detailed description of each of the process section, the simulation techniques used, and assumptions made are addressed. The GTL process ultimately produces syncrude from natural gas. The natural gas is reformed to be synthesis gas. Syngas is an intermediate product as well as a reactant for the FT synthesis. The hydrocarbon condensates from the FT reactor are hydrocracked and fractionated to refine liquid products (syncrude) separating light ends. Syncrude is composed of LPG, naphtha, diesel, and wax product. This research does not address the further separation for the each of final commercial product. Overall process configuration and product distribution are referred to Oryx GTL plant in Qatar, specifically, for syngas production section, Haldor-Topsoe's design and engineering practice are referred. Process flow diagram of the GTL process for this study is shown in Appendix A.

Table 5. Feedstock Conditions

Properties	Units	Value
Temperature	°F	78.8
Pressure	psia	310
Density@78.8°F	lbm/ft^3	0.935
Molecular Weight	-	16.77
LHV	Btu/lb	21,070.2
Composition	lbmole%	CH_4 95.39 C_2H_6 3.91 C_3H_8 0.03 CO 0.59 N_2 0.08 Sulfur nil. O_2 nil.

Detail conditions[8] of natural gas as a feedstock are shown in **Table 5.** Since any potential poisons to the catalyst in the natural gas are not seen, the facility for the feed preparation is not considered. O_2 is supplied from outside and steam is internally produced; however, it is not addressed specifically in this study. H_2 used for hydrocracker is internally supplied by separated from the syngas in the PSA[2]. The production capacity of syncrude is set as 50,000 bbl. /day for the study considering the industrial practice[8, 30]. The steady state simulation for flowsheets is performed using Aspen Plus V8.8, thermodynamical property package is Soave-Redlich-Kwong-Kabadi-Danner (SRKKD) as per industrial practice[35].

The base case is with Autothermal Reformer (ATR) using nickel catalysts as a syngas producing technology and slurry bed reactor for the FT synthesis using cobalt catalysts.

4.1 Syngas Production Section

The syngas production section produces syngas by reforming natural gas with steam and O_2. This section is equipped with saturator, pre-reformer, an autothermal reformer, heaters, and CO_2 removal unit. This section operates with natural gas and recycled CO_2 to produce the syngas with ratio 2.0. Both reformers equilibrate adiabatically, simulated using R_{Gibbs} model.

Natural gas is pressurized to 370 psia and heated to 300 °F before being fed to saturator, where natural gas is saturated with water. The water for saturator is serviced at a 30% of serviced carbon contents. It is for removing any impurities by washing with water. The discharging stream is mixed with saturated steam at 370 psia at reforming system pressure and then heated to 700◦F. The stream is fed to pre-reformer for the primary reforming the gasses. Steam is a reactant as well as a heating source, whose enthalpy give a heating energy to the mixed process stream at the system pressure with the saturated state. For the modeling of pre-reformer, only six components (CH_4, O_2, CO, CO_2, H_2, and H_2O) and one inert (N_2) are limited as products to be free of O_2. The

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[2] Pressure Swing Adsorption: a kind of H_2 production facility by gas adsorption and desorption.

stream from the pre-reformer is combined with directly recycled CO_2 and heated to the desired temperature for autothermal reforming. Where the recycled tailgas combines is determined by considering an economic achievement, process performance, and operating enhancement.

In the ATR, O_2 is supplied for partial combustion to generate the heat for steam reforming. It is set as a certain ratio 0.6 of O_2 to carbon contents in the feed stream. This ratio is set as per the engineering practice [20]. The ATR is thermally neutral and outlet temperature is adjusted by the heat duty of upstream fired heater. The target of syngas H_2/CO is set by 2.0 for the low-temperature FT reaction. Syngas ratio to the F-T reactor, is achieved by manipulating CO_2 recycling rate or steam rate as per operating cases. The reformed syngas is cooled to 122 °F to remove efficiently the water and residual water is removed from cooled syngas.

The CO_2 removal system separates CO_2 from cooled syngas to reduce the inert contents for the LTFT reactor and thus to reduce the size of the following equipment. CO_2 removal efficiency is set as 99.95% as per previous study[8]. Separate simulation of syngas conditioning system is not carried out. A part of conditioned syngas is used for hydrogen production in the PSA. Conditioned syngas is sent to the FT reaction section.

4.2 Fischer-Tropsch Reaction Section

The Fisher- Tropsch reaction section produces hydrocarbon condensate (FT condensate and waxy product) from the conditioned syngas. This section is equipped with the F-T reactor and light hydrocarbon vapor (tailgas) separation system. FT reactor is simulated using an R_{Stoic} model with conversion 70% [8]. The catalyst for synthesis has a α-value of 0.92. As per applied α-value, the product distribution is from C_1 to C_{100}, however, for convergence of the balance, only products ranged C_1~C_{30} are considered [8].

Conditioned syngas is fed to the FT reactor, which is operated highly exothermically at 428°F with 363 psia. The waxy product from the FT reactor is sent to the product upgrading section to hydrocracker. The light hydrocarbons from the FT reactor are sent to the separation system and divided to three streams: light liquid hydrocarbons, residual water, and light hydrocarbon vapor (tailgas). The FT condensate is sent to the product upgrading section to hydrocrack the longer hydrocarbon chain. The tailgas is reused as a hydrocarbon feed or fired heaters as a fuel source.

4.3 Product Upgrading Section

The product upgrading section hydrocracks the FT condensate and waxy product with H_2 and fractionates the mixed hydrocarbon stream into syncrude with separating light end gasses. This section is equipped with hydrocracker, fractionator, coolers, fired heater and PSA. Hydrocracker is simulated using an R_{Stoic} model with conversion 65% and fractionator is modeled using RADFRAC[8]. The FT condensate and waxy product from F-T reaction section are pressurized to 1015 psia and heated to 662°F for hydrocracking process. The liquid product from the hydrocracker is cooled down. Light hydrocarbon and H_2 is separated. H_2 is made up for the feed of hydrocracker with H_2 generated by PSA. The liquid product is heated in the fired heater to above 700°F and then sent to the fractionator. In the fractionator, the final product (syncrude) is separated from the light hydrocarbon and cooled down to 122◦F. The separated light carbons (off-gas) from the hydrocracker and fractionator are recycled as a fuel for fired heaters.

4.4 Utility Section

4.4.1 Water and Steam

The residual water is removed from cooled syngas and from the FT reactor and then sent to water treatment system for the reuse of water. This treated water is used as a source to produce Steam and saturates the feed and as a cooling medium.

A large amount of Steam is generated and used in the GTL process. Steam is generated in the process of power generation. Steam is used the main feed for steam reforming in ATR and the heating medium as well.

4.4.2 Fuel gas

Natural gas is the main fuel for fired heaters in the GTL process. As an approach to improve the carbon efficiency of the process, a part of tail gas and off-gas are recycled to be a fuel gas. The amount and composition of fuel gas depend on tailgas recycling ratio. Where the heating duty in fired heaters is higher than those of fuel gas, natural gas is made up to meet the demand.

5 APPROACH AND METHODOLOGY

To provide insights from various perspectives for a decision-making, utilizing the opportunities to develop the GTL process should be maximized and major efforts should be performed with the systematical procedures. The systematic approach used in the research for getting inherently safer, environmentally sustainable and cost-effective design is given by the following steps with schematic diagram shown in **Figure 3**.

- Define the overall GTL flow sheets from literature and public data sources
- Simulate each GTL flow sheet of various process options using Aspen Plus V8.8
- Conduct process development from simulation results
- Apply economic evaluation of the integrated process
- Perform safety and environmental sustainability assessment of integrated process
- Provide the integrated insights for decision making from the trade-off analysis

It is estimated that GTL process has many opportunities for process improvement: (1) by maximizing the internal use of material sources to achieve higher carbon efficiency and lower carbon footprint, and (2) by reducing the steam to carbon ratio of feed for reformer to achieve a more compact size of equipment and to reduce capital and operating costs.

For the GTL process, natural gas is used as a feed to produce the syngas and as a fuel to heat the process streams to the higher temperature which steam cannot approach. Considerable amount of light-end gasses are generated during the separation of products. These are mostly CO, H_2, and CH_4, which are unconverted gasses in the reformer and reactor. It can be used as a feed or a fuel by direct recycling to the reformer or fired heaters.

The fuel gas is light ends generated from the overall process, which is combined with tailgas and off-gas. Tailgas is the light ends separated to get liquid products from the FT reactor. It is mainly composed of unconverted syngas in the FT reactor with few of CH_4.

Off gas is the light ends generated during refining products from hydrocracker and fractionator in product upgrading section. It is also composed of unconverted syngas and a few of CH_4. Most of the tailgas is mainly recycled to syngas production section as a feed. The rest of tailgas is combined with off-gas and then, it is used as an alternative fuel for fired heaters. Internal recycles of tailgas and off-gas as hydrocarbon sources enable the GTL process to be more efficient.

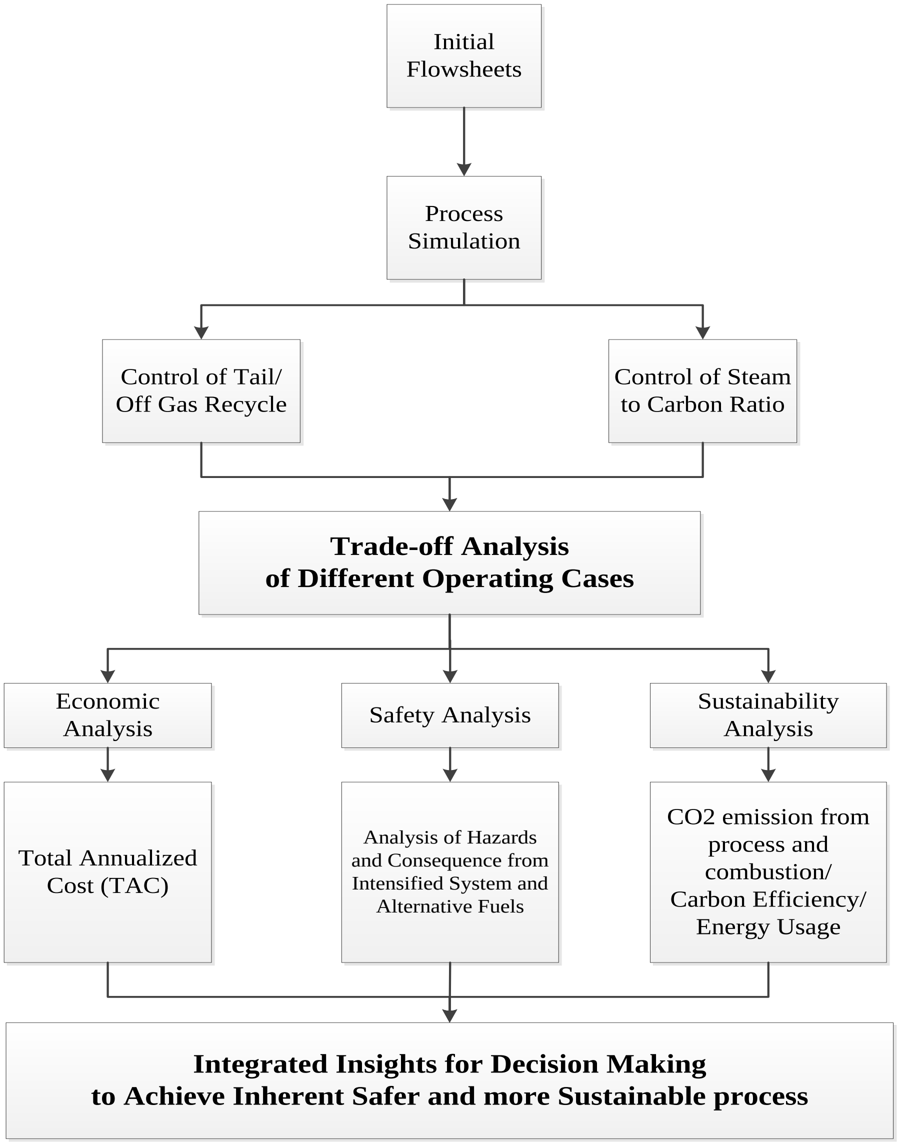

Figure 3. Approach and Methodology for Systematic Analysis

When the tailgas and off-gas are recycled as an alternative to natural gas, it reduces the fresh carbon source requirement and then, increases the profitability of the plant. Moreover, reduces the GHG emissions by reusing the waste gas, instead of burning in a flare[10]. The effects of the fuel gas recycling to the plant's profitability, safety, and environmental sustainability are addressed.

Steam is used as a reactant for steam reforming reaction as well as an inert gas for removing a carbon on the catalysts in the ATR. So, excessive steam is estimated to decrease the risk of carbon formation during reforming. With the agreement with industrial practices, the S/C ratio is set as 0.6; however, this value is higher than the adiabatically equilibrium requires to minimize a Gibbs free energy in the ATR. It is regarded as "safety margin" to avoid carbon deposition. Obviously, complex factors work to prevent or cause the carbon deposition. In this study, however, major efforts focus on reducing the steam to carbon ratio, maintaining concerns on other factors affecting carbon deposition such as operating temperature, pressure, feed composition, reformer design including burner, and operation.

The reduction of S/C ratio to as low as the equilibrium requires contributes to energy savings in the reduced heat input to the preheaters and in the reduced system volume. In fact, since steam and residual water are sufficiently generated to be stand-alone in the GTL process, the reduced steam consumption is not that much impact on the profitability of the process; however, from the reduced system volume point of view, the capital cost is saved as well as loss of containment is saved in case of failures in the system. The effects of the reduced S/C ratio to the process's profitability, safety, and sustainability are addressed.

The operating conditions of ATR technology that are used in industry for the FT synthesis are shown in **Table 6.** Typically, there are two categories of operating conditions. It is estimated that the targeted syngas ratio is important factor to determine operating conditions. For the higher syngas ratio than 2.5, the higher S/C ratio should be applied because steam is an H^+ source for reforming reaction. To study the comparative analysis on the effects of tailgas recycling and the lower S/C ratio, the operating conditions (shown in **Table 7)** of the reforming system are set within the range that are proven by large scale or pilot scale. Since the reforming process is an endothermic reaction, it is known that the higher temperature and lower pressure increase the CH_4 conversion. So, the outlet temperature of reformer and system pressure of reforming system are 1950°F with 370psia for the most efficiency of carbon conversion.

Table 6. Comparison of Operating Conditions of ATR technology
for the FT synthesis [14]

Parameters in ATR	Unit	Reference 1	Reference 2
O_2/C ratio	mol/mol	0.55~0.6	0.6
S/C ratio	mol/mol	1.5~2.5	0.6
Outlet temperature	°F	1,742~1,922	1,868~1,949
Outlet pressure	psia	~362.6	362.6~420.6
Syngas ratio (H_2/CO)	mol/mol	2.5~3.5	2.2~2.3

In the case of S/C ratio 0.6, CO_2 is recycled to meet the syngas ratio 2:1. CO_2 sink is an inlet of ATR. The recycling ratio is determined by adiabatic equilibrium in the reforming reaction to meet the syngas ratio. In the case of lower S/C ratio, CO_2 recycling is not required to meet the syngas ratio 2.0. Instead of, the steam rate is determined by equilibrium in the reforming reaction. It is aimed to reduce the S/C ratio to the level which the equilibrium requires.

Obviously, it is more cost-effective that as much tailgas as possible is recycled to the feed considering the added value for products in the process, however; the increased recycling ratio affects the accumulation of inert (particularly, N_2) in the ATR and the FT reactor. This decreases the efficiency in the reaction. In the decreased ratio, the inert accumulation can be seen in fuel. This decreases the fuel quality and increases NOx emissions. Purging of 4% of the tailgas to fuel gas system enables not only to achieve the stand-alone in the heating energy requirement, but also to prevent much inert accumulation.

Table 7. Operating Parameters for Cases Studies

Parameters	Unit	Case 1	Case 2	Case 3	Case 4
Product capacity	bbl./day	50,000	50,000	50,000	50,000
Syngas ratio **(Note 1)**	-	2.0	2.0	2.0	2.0
O_2/C ratio **(Note 2)**	mol/mol	0.6	0.6	0.6	0.6
Temperature **_ATR outlet**	°F	1950	1950	1950	1950
Pressure_Reformer	psia	370	370	370	370
S/C ratio (Note 2)	mol/mol	0.6	0.6	By equilibrium	By equilibrium
CO_2_recycling ratio **(Note 3)**	-	By equilibrium	By equilibrium	N.A.	N.A.
Tailgas (Note 4) **(ATR:FT, Note 5)**	-	0.96 (ATR:FT=1:0)	0.96 (ATR:FT=0.2/0.8)	0.96 (ATR:FT=0.2/0.8)	0.90 (ATR:FT=0.2/0.8)
Internal heating ratio (Note 6)	-	<1	<1	=1	1<

Notes:

1. H_2/CO, Based on the inlet of the FT reactor
2. Based on the inlet of the ATR
3. Recycling ratio of CO_2= $\frac{(molar\ rate\ of\ \ CO_2\ to\ feed\ )}{(total\ molar\ rate\ of\ CO_2\ generated\ )}$
4. Recycling ratio of tailgas = $\frac{(\text{ molar rate of tailgas to feed })}{(\text{total molar rate of tailgas })}$
5. Recycled tailgas is split to the ATR and the FT reactor as sinks.
6. The thermal efficiency of fuel gas and natural gas for burning is assumed to be 100%.

$$\text{Internal heating ratio} = \frac{\text{Heat Duty supplied by fuel gas, MMBtu}}{\text{Total Required Heat Duty, MMBtu}}$$

Additionally, when recycling the tailgas, it is split to the ATR and the FT reactor. Since the feed composition to ATR particularly, longer hydrocarbons can affect the possibility of carbon formation, the split recycling of tailgas is beneficial to avoid chance of carbon deposition and to reduce the size of ATR. The split ratio is determined by considering minimize reformers' size and preheaters' duty. 0.2 as the split ratio of recycled tailgas to the ATR and the FT reactor is set considering tailgas composition, which contains 90% of syngas and 10% of CH_4.Any heat recovery from the flue gas in the fired heater to estimate required heating duty is not addressed. The sinks of recycled tailgas to feed are determined by the gas composition and economic consideration.

The detail description of each case is as follows:

- **Case 1:** To meet the requirement of syngas ratio 2:1 at 1950°F, CO_2 is recycled to ATR. All tailgas excluding 4% of purge is recycled to the inlet of ATR.
- **Case 2:** To meet the requirement of syngas ratio 2:1 at 1950°F, CO_2 is recycled to ATR. Tailgas excluding 4% of purge is recycled to the inlet of the ATR or the FT reactor with ratio 0.2:0.8. The same configuration with Sasol plants.
- **Case 3:** To meet the requirement of syngas ratio 2:1 at 1950°F, the lower S/C ratio is applied, instead of CO_2 recycling. Tailgas excluding 4% of purge is recycled to the inlet of ATR or inlet of FT reactor with ratio 0.2:0.8.
- **Case 4:** To meet the requirement of syngas ratio 2:1 at 1950°F, the lower S/C ratio is applied, instead of CO_2 recycling. Tailgas excluding 10% of purge is recycled to the inlet of ATR or inlet of FT reactor with ratio 0.2:0.8.

With the comparison between Case 1 and 2, the effects of recycling sinks are highlighted with the same S/C ratio (0.6). With the comparison between Case 2 and 3, the effects of the reduced S/C ratio are highlighted with the same tailgas recycling ratio (0.96). For the comparison between Case 3 and 4, the effect of tailgas recycling ratio are highlighted with the same S/C ratio.

5.1 Process Analysis

In the process analysis, following approaches are addressed:

- Evaluation of process performance with comparing feed requirement.

- Evaluation of energy distribution of overall process and each equipment in syngas production section
- Estimation of volume of main equipment and the required number of trains in syngas production section.
- Validation of operating conditions to confirm the free of carbon formation

5.2 Economic Analysis

The economic data to dictate the decision-making are annualized capital and operating cost. The only cost for heating and raw material is considered to estimate the operating cost in this study. It is plausible that this study is to identify the effects of utilizing the internal source (tail gas, off-gas, or CO_2) and reducing the steam to carbon ratio.

For comparison of the economic performance of different operating options, annualized cost for producing the GTL syncrude of 50,000 bbl./day is illustrated. The plant is with on-stream factor 8,000 hours per year of continuous operation. Plant service life is set at 20 years.

Total annualized cost (TAC)
= annualized fixed cost (AFC) + annualized operating cost (AOC)
(14)

- Annualized fixed cost= yearly cost for equipment, piping, civil, steel, instrumentation, etc. estimated by Aspen Economic Analyzer
- Annualized operating cost= yearly cost for raw material (natural gas, steam, and oxygen) consumed + yearly cost of heating (natural gas and steam) and cooling (cooling water) energy consumed
  - The prices of raw materials are shown in **Table 8**. The price of raw material is referred to energy information administration and ICIS website and literatures.

Table 8. Raw-material Prices [36]

Parameter	Unit	Values
Natural Gas	US$/MMBtu	3.0
Steam	US$/kg	0.006
O_2	US$/kg	0.11

- Tailgas, off-gas, water and H_2 are assumed to be free of cost.
- Steam is a reactant and a heating utility. For the cost estimation, steam is regarded as a reactant for natural gas reforming, and the enthalpy from steam is considered to estimate the heating energy.

Through the economic data, the following issues are analyzed:

- Evaluation of estimated costs of each process option
- Evaluation of contribution of syngas production section to annualized fixed cost
- Evaluation of contribution of each heating utility to annualized operating cost

5.3 Safety Analysis

Safety analysis has been an emerging essential step with sustainability analysis in selecting alternative process options. Major efforts are being dedicated to achieving inherently safer processes or design by reducing or eliminating any hazards with a systematic approach and reviewing the implications in terms of inherent safety before making a decision.

Inherent safety is to prevent incidents in advance with facilitating the environment with fewer hazards or fewer possibilities of incidents to arise. Typically, inherently safer design can be achieved by four strategies (minimize, substitute, moderate, and simplify)[4] from different points during design works. Followings are typical techniques of each strategy:

- Minimize (intensification): Change large reactor to a smaller reactor
- Substitute (substitution): Use the materials that are less toxic or hazardous

- Moderate (attenuation and limitation of effects): Reduce process temperature and pressure
- Simplify (simplification and error tolerance): Select the equipment that requires less maintenance, that has low failure rates, and that has easiness to operate.

5.3.1 Effects of utilizing tailgas and off-gas as a carbon source

The efforts are made to consider less hazardous materials (the substitution) in the process as one of the strategies to achieve the inherent safety. It is shown by comparative analysis of the base and an alternative case. The implications in terms of fire and explosion hazards and toxicity are addressed when utilizing light ends as an alternative fuel for fired heaters.

Natural gas is a main carbon source for the GTL process. Since carbon sources are obviously combustible; they are flammable under the certain conditions. By comparative analysis of the used material for the fuel, it can be estimated which material is less or more hazardous. Materials themselves as well as their potentials to the hazardous outcomes are comparatively analyzed and assessed with the identification of fire hazards utilizing combustion and ignition properties of materials and with estimation of the risk from the systematic approach using a consequence modeling tool.

A risk analysis in this study is a process of quantifying the fire and explosion hazards motivated by the need to have a decision making for achieving the more inherently safer design. Detail procedure is shown in **Figure 4.**

The risk analysis begins by gathering process information of each material and then, proceeds to identify the fire hazards and to determine scenarios. The process information is from the process simulation (Aspen Plus V8.8). Once identifying hazards and determining the failure scenario, the probabilities of the events are estimated utilizing the event tree shown in **Figure 5**. The consequences of fire and explosive events are simulated by Process Hazard Analysis Software Tool (PHAST V6.7, Det Norske Veritas Co.), which is one of the most widely used processes hazard analysis tools in the estimation of flammable and toxic effects.

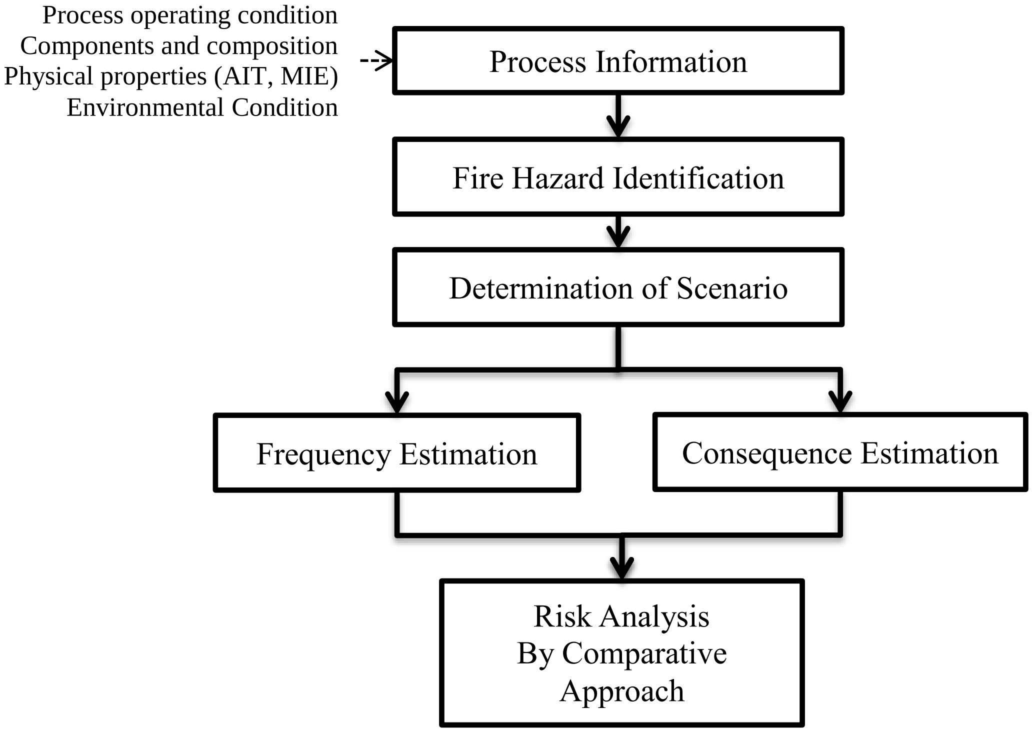

Figure 4. Procedure for Risk analysis

Quantitative risk analysis starts with the hazard identification. As much as possible information about design, operation, and environmental conditions enables to assess hazards effectively. For the determination of failure scenario, one of the typical failures, a leak in the pipe is selected [37]. Under the assumption that well-organized and regular maintenance is carried out in the plants, the leak with 2” hole in the pipe is given. It is assumed that fire and explosion result from the leak of the transferring gas fuel in the pipe. This study does not address additional toxic gas to be generated during a fire.

Once the scenario is set as a leak in the pipe, the source model is selected to describe the release incident with which material releases, how much material releases, and how long the release continues. Then, the dispersion model is selected considering the density of materials and environmental conditions, such as the wind or solar intensity. Through this procedure, the expected incidents such as fire and explosion are presented. For the estimation of consequence, both approaches are carried out. One is to estimate the probabilities of each incident. The other is to model the consequence of the incidents.

A simple event tree analysis applies for the estimation of probabilities of each top event (shown in **Figure 5**). Event tree analysis provides information on the cause and outcome of a failure with the probability of each top event[4]. The possible events are fires, explosion, and no fire, but environmental effects including human health.

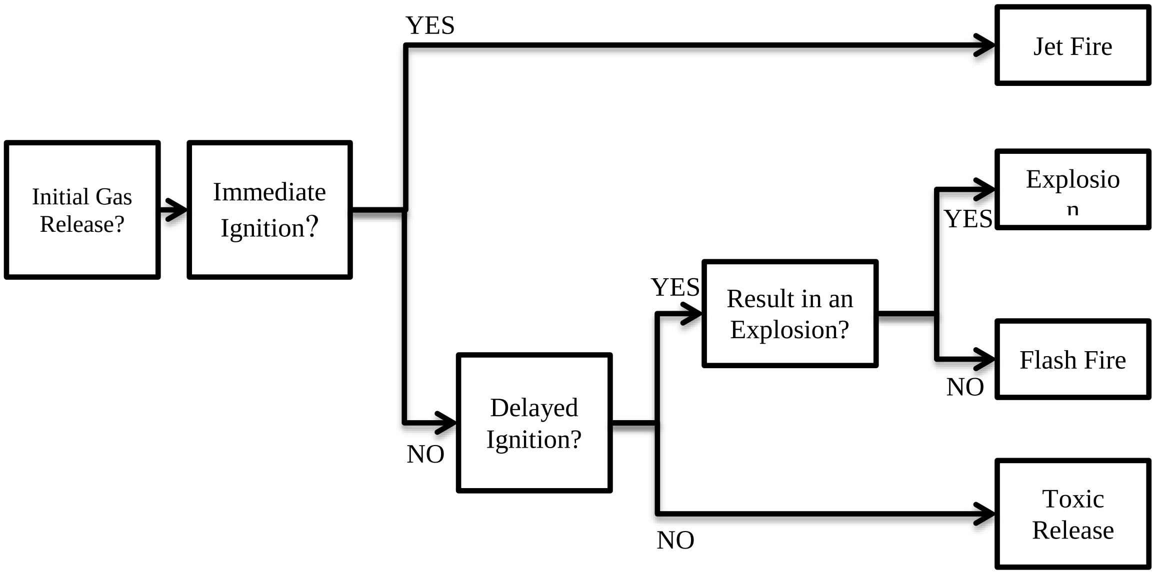

Figure 5. Event tree for Material release by pipe leak

Since the probabilities of the top events are highly dependent on the conditions of the material itself and the scenario, the careful considerations to calculate probabilities are required. The probabilities are calculated by following equations[38]:

P [Immediate ignition]
= Pai [Potential for auto-ignition] + Psd [Potential for static discharge]

$$= [1 - 5{,}000 \times \exp(-9.5 \times {}^{\mathrm{T}}/_{\mathrm{AIT}})] + [0.0024 \times {}^{\mathrm{P}_1^{1/3}}/_{\mathrm{MIE}^{2/3}}] \qquad (15)$$

- For ${}^{\mathrm{T}}/_{\mathrm{AIT}} < 0.9,$ (16)

$$P_{ai} = \left[1 - 5{,}000 \times \exp\left(-9.5 \times {}^{T}\!/_{AIT}\right)\right] = 0$$

- For ${}^{T}\!/_{AIT} > 1.2$,

$$P_{ai} = \left[1 - 5{,}000 \times \exp\left(-9.5 \times {}^{T}\!/_{AIT}\right)\right] = 1 \tag{17}$$

P [Delayed Ignition] $= 0.3 \times \prod\left(M_{mat} \times M_{mag} \times M_{dur}\right)$ (18)

- $M_{mat} = 0.6 - 0.85 \times \log \mathrm{MIE}$ (19)
- $M_{mag} = 7 \times \exp(0.642 \times \ln \mathrm{FR} - 4.67)$ (20)
- $M_{dur} = {}^{\left[1 - (1 - S_2) \times \exp\left((-0.015 \times S) \times t\right)\right]}\!\big/_{0.3}$ (21)

P [Delayed Ignition resulting in Explosion]= $P_{exp/g/ign} = 0.024 \times FR^{0.435}$ (22)

Where:

AIT= Autoignition temperature (°F),

FR= Flow rate from the hole (lbs/sec)

M_{mat}= Modifier on the materials being released

M_{mag}= Modifier on the magnitude of the release

M_{dur}= Modifier on the duration of the release, and the numbers/density and strength of ignition sources

MIE= Minimum ignition energy (mJ)

P= Releasing pressure (psig),

S= Probability of ignition in one minute (Strength S), 0.5 in this study

T= Releasing temperature (°F)

t= Duration time (sec)

Releasing temperature and pressure are same for both cases. The strength of the release is assumed to be 0.5 considering high equipment densities in the plant[38]. The reactivity of the process is assumed to be medium level [38].

Consequence modeling is investigated in two different weather data of corresponding day and night. The detail conditions are shown in **Table 9**. Conditions in day lead to worst- case scenario, and those in night lead to the most representative scenario.

Table 9. Weather data corresponding to Day and Night

Atmospheric parameters	**Unit**	**Day**	**Night**
Atmospheric stability class	-	D	F
Wind velocity	m/s	5	2
Ambient Temperature	°F	77	32
Relative humidity	%	50	70

For the dispersion modeling by PHAST, the duration of the release is assumed to continue for 10min, fire starts after the release of 10 min and lasts 20 min. It is considering that at least 10 min is required for operators to take an action to stop the release of materials. The release inventory is considered as 10^6 kg. The release elevation is considered to be 1m from the ground. The surface temperature of the pipe is assumed to be same as ambient temperature because thermal insulation is applied to avoid any condensate during transferring. The surface roughness of the environment is assumed to be medium crops with roughness length 0.16m. TNT is considered as the worst case scenario.

Risk analysis is performed by the probit functions associated with the deaths due to the radiation or overpressure. Detail equations are shown as follows:

Table 10. Probit Functions of Hazardous Consequences

Events	**Probit Parameter, k_1**	**Probit Parameter, k_2**	**Causative Variable, V**
Burn death from Thermal Radiation	-14.9	2.56	$t*I^{4/3}/10^4$
Burn death from Overpressure	-77.1	6.91	p^o
Death by CO inhale	-37.98	3.7	$\sum C * T$

Notes:

C= concentration (ppm)
I= effective radiation intensity (W/m^2)
p= overpressure (N/m^2)
T= time interval (min)
t= effective time duration (sec)

$$\text{Probit Variable, } Y = k_1 + k_2 \ln V \tag{23}$$

$$\mathrm{P} = 50\left[1 + \frac{Y-5}{|Y-5|} erf\left(\frac{|Y-5|}{\sqrt{2}}\right)\right] \tag{24}$$

The individual risk is determined by multiplying the frequency of initial events and probabilities caused by events. The sum of individual risks provides the total individual risk of a leak in the pipe.

$$\text{Individual Risk} = \sum_{i=1}^{n} f \times P \tag{25}$$

f= frequency of accident

P= Probability of affectation due an accident

5.3.2 Effects of reduced the steam to carbon ratio to syngas production system

The efforts are made to reduce the loss of containment (the intensification) when failures as one of the strategies to achieve the inherent safety. It is shown by estimating the effects of reduced the S/C ratio for syngas production systems. Typically, a lower feed rate for given amount of product makes the system volume to be smaller. The system with smaller volume is intensified in respect of cost and safety. Smaller inventories of hazardous material result in a less severe consequence when failures and smaller sized systems reduce the capital cost. However, it is not always for a system of smaller volume to lead to better results. Less volume of containments in the system reduces the surface area to absorb the heat from the external fire case, and then it moderates the loss of containment from the system. On the other hands, higher surface to volume causes more heat loss. Adiabatic reformer particularly might lose more heat to the surroundings, which requires additional O_2 or higher inlet temperature as much as it loses to the surroundings to generate heat for an endothermic reaction. As such, there can be multiple implications in a scenario of reduced system volume as follows:

- Process Performance:
    - Adiabatic equilibrium in lower temperature caused by higher heat loss leads to lower efficiency in reaction than intended. Additional O_2 or preheating is required.
- Operability and Availability:
    - More dependent on instrumentation and control system reliability to control the operating temperature in ATR.
- The risk and consequence by fire or explosion:
    - Less hazardous consequence due to the less system volume
    - Reduced heat absorb from the external fire

To avoid the worse situations in industrial plants, the system will be tripped with the reliable instrumentation and control when any carbon is detected on the catalysts. It is worthy reviewing the operating case with lower S/C ratio, without any carbon deposition.

Assumptions:

- Design pressure of the system is 10% more than operating pressure.
- Design temperature of the system is 45°F more than operating temperature.
- Reformer and pre-reformer are assumed to be vertical vessel with semi-elliptical head. The ratio of height to diameter is ranged from 4~5 as per industrial practice [39]. This study does not consider the volume that the catalysts in the pre-reformer and catalysts and combustion system in ATR are occupying.
- The volumes of both reformers are assumed to dictate only the inlet molar flow rate with the same GHSV in the reformers. GHSV is assumed to be 5,000hr^{-1} as per industrial practice [40].
- Wind velocity is not considered to the calculation of heat loss to the surroundings.
- Shell material is assumed to be stainless steel (SA-387 Gr.11) with thickness 3”.
- The insulation material is assumed to be rock mineral wool with 3” considering operating temperature. No credit of external insulation has been taken for the estimation of relieving load as per API 521 recommendations[41]. For ATR, refractory lined internally with several layers. It is functioned as heat insulation[20].
- **Table 11** shows the thermal properties of shell and insulation materials.

Table 11. Mechanical Information of both Reformers

Parameters	**Unit**	**Shell wall**	**Insulation**
Thickness	inch	3	3
Specific heat capacity	Btu/lb-°F (J/kg-K)	0.1120	 (840)
Density	lb/ft^3	486.9	6
Conductivity	Btu/hr-ft-°F (W/m-K)	30.5	 (0.0952)

Notes:

1. All information is from the engineering practices from manufacturers.

5.3.2.1 Heat absorption from external fires

When the equipment or pipes containing the materials are exposed to an external fire, the materials absorb the heat from the fire. The amount of the heat absorbed is determined by the surface area exposing to the fire at the same intensity of that. This heat makes the materials be thermally expanded. The volume or pressure can reach to the higher level than the system can tolerate. In this case, equipment or pipes can be leaked or ruptured. For preventing from any leaks or rupture in the system, pressure relieving devices such as rupture disks or relieving valves are considered. Typically, the relieved materials containing hydrocarbons are sent to and combusted in the flare. As low as possible relieved materials, the lower loss of containment from the system could be. The major factors to dictate the relieving load to protect the system are thermal expansion properties and the surface area of the equipment or pipes absorbing the heat from the external fire. Since this study is associated with the gas processing, the impact of thermal expansion coefficients can be negligible. With the lower S/C ratio, the lower system volume in the reforming system can be achieved. It is necessary to review the effects of the lower system volume in terms of the heat absorption from external fires.

API 521[41] recommends the practice about how to estimate the relieving load caused by the external fires as an overpressure source. The equations used to calculate the required relieving load in gas or vapor service are shown below. The estimation of relieving load is based on the recommendations by API 520[42] and 521.

$$W = 0.1406\sqrt{MP_1}\left(\frac{A'(T_w - T_1)^{1.25}}{T_1^{1.1506}}\right) \tag{26}$$

Where:

A'= exposed surface area of the vessel, ft^2

M= molecular weight of the gas

P_1= relieving pressure, psia

T_1= relieving temperature, R

T_w= equipment wall temperature, R

W= required relieving load, lb/hr

To show the effects of the smaller surface area caused by the smaller volume, the pre-reformer and reformer are selected as main equipment in syngas production system. The volume of both reformers is determined by volume index based on the volumetric flow rate to both reformers.

The actual size of pressure relief valves is determined by the required relieving rate, based on the ASME II specification by Aspen Plus V8.8, however; it depends on the manufacturer’s design.

5.3.2.2 Heat loss to the surroundings

In the ATR reforming of CH_4, the operating conditions determine the heat of reaction at adiabatic conditions at a defined temperature. Self-sufficiency of the heat for the reaction can be theoretically attained when the net adiabatic heat of reaction is zero (equation (7)); however, due to heat losses through the reactor walls, O_2 requirement or pre-heating should be slightly higher than stoichiometric ratio to account for any heat loss or to raise the gas temperature to maintain the performance. To avoid any heat loss, external or internal heat insulation is considered. It is also considered as a safety guard for personnel protection from the high temperature.

Practically, this heat loss thermally equilibrates among the materials, equipment wall, and the surroundings. The major factors to dictate the amount of transferred heat are the thermal properties of the materials, temperature difference, and the surface area. The typical equations for estimating the heat transfer are shown in equation (27) and (28).

With the lower S/C ratio, the smaller volume of equipment leads to the higher ratio of surface area to volume. The higher ratio increases the cooling flux per the material volume. Therefore, the effects of higher heat loss to the surroundings caused by smaller volume should be investigated. The rigorous heat loss from the system is modeled by Aspen HYSYS V8.8.

$$Q = UA\Delta T \tag{27}$$

$$U = \frac{1}{A\left\{ {}^{1}\!/_{A_i h_i} + {}^{\left[\ln\left({}^{r_o}\!/_{r_i}\right)\right]}\!/_{2\pi kL} + {}^{1}\!/_{A_o h_o} \right\}} \tag{28}$$

Where:

A= surface area

A_i= inside area

A_o= outside area

h_i= convective heat-transfer coefficient, inside

h_o= convective heat-transfer coefficient, outside

k=thermal conductivity

L= Length (height) of equipment

r_i= radius of equipment, inside

r_o= radius of equipment, outside

ΔT= temperature difference

U= overall heat transfer coefficient based on area A and temperature differenceΔT

5.4 Environmental Sustainability Analysis

The environmental sustainability assessment is based on the amount of fresh carbon resources (feeds for process and fuels for heating) used to produce syncrude , and the generated amount of GHG by the reaction and combustion. There are several factors affecting the environment, however, CO_2 emissions and carbon efficiency are regarded as typical factors differentiating the environmental sustainability among various process options.

This study tries to decrease energy usage for heating and to increase carbon efficiency by recycling tailgas and off-gas and by reducing the S/C ratio for the reforming system. The effects of the approaches are analyzed in terms of carbon efficiency and CO_2 emissions.

Recycling tail gas and off-gas reduce the amount of required fresh natural gas for the process. With the same production rate, the lower fresh natural gas is required. It enables to enhance the carbon efficiency of the overall process. Carbon efficiency can be estimated as a ratio of the amount of product to fresh feed to the system.

$$\text{Carbon efficiency} = \frac{Product\ Rate}{Fresh\ Feed\ Rate} \tag{29}$$

Where:

Fresh Feed Rate= Required Fresh Natural Gas Rate (lbmole/hr)

Product Rate = Produced syncrude capacity, 50,000 bbl./day

In the GTL process, CO_2 is generated from two sources, inherently produced by water gas shift reaction in the reformers and emitted as a part of the flue gas by combustion of fuels in fired heaters. The comparative analysis of CO_2 emission as per process options is performed to achieve the more environmentally sustainable design and operation. The amount of CO_2 generated by the reaction (equation 3) is estimated by process modeling (Aspen Plus V8.8), and CO_2 emission from burning fuels is estimated by the guidance from EPA[43]. EPA recommends the practice about how to estimate the CO_2 emissions utilizing the emission factors when carbon contents in fuels are combusted. The equations used to calculate the CO_2 emission from the fired heaters are shown below.

$$CO_2 \text{ emission} = \text{Fuel} \times \text{Carbon contents} \times 44/12 \tag{30}$$

Where:

CO_2 emission= rate of CO_2 emitted

Fuel= Mass or volume of fuel combusted

Carbon contents= Fuel carbon content including CO, in units of mass of carbon per mass or volume of fuel

44/12= ratio of molecular weights of CO_2 and carbon

6 RESULTS AND DISCUSSION

The results of the process performance analysis, economic analysis, safety analysis, and environmental sustainability analysis are shown and discussed separately. The results are highlighting their different requirement or outcomes as per the tailgas recycling and/or reduced S/C ratio with the same targets: syncrude production rate and syngas ratio at the same operating conditions in the ATR.

6.1 Process Analysis

The feed and fuel consumption of each operating case are summarized in **Table 10**. The results are shown separately as feeds for reforming reaction and fuels for heating energy. The steam rates decrease by more than 40% over the cases with S/C 0.6. The corresponding S/C ratios of case 3 and 4 are respectively 0.34 and 0.32.

The less natural gas requirement in case 2 than case 1 shows that considering split recycling of tailgas to sinks (the ATR and the FT reactor) is beneficial to decrease fresh natural gas consumption. This split recycling enables a large amount of unconverted H_2+CO in the tailgas to be used as a feed directly for the FT reactor. The higher natural gas requirement in case 3 than case 2 is because of the lower CH_4 conversion (from 0.98 to 0.97 in **Table 12**) by reduced S/C ratio. Increase in the natural gas requirement of case 4 over the case 3 shows that more natural gas is required due to the reduced tailgas recycling ratio (from 0.96 to 0.90).

O_2 and steam rate are directly proportional to the required natural gas, not tailgas. These are determined by the carbon contents in the feed to ATR with a certain ratio. Tailgas is composed of about 90% of syngas, which has little impact on the carbon contents.

Table 12. Feed and Fuel requirements of different Operating options

Parameters	**Unit**	**Case 1**	**Case 2**	**Case 3**	**Case 4**
S/C ratio (ATR inlet)	-	0.61	0.60	0.34	0.32
CO_2 recycling ratio	-	0.36	0.38	0	0
Tailgas recycling ratio (ATR:FT)	-	0.96 (1:0)	0.96 (0.2:0.8)	0.96 (0.2:0.8)	0.90 (0.2:0.8)
<u>Feeds for Reaction</u>					
Natural gas	lbmole/hr	45,637	45,306	45,667	47,485
Tailgas_recycled		54,130	57,032	59,531	54,467
Steam		30,561	28,727	16,198	15,712
O_2		31,052	29,229	29,845	30,603
<u>Fuels for Energy</u>					
Fuel gas (Note 1) (LHV)	lbmole/hr (Btu/lb)	3,422 (9,605)	3,647 (11,584)	3,747 (11,848)	4,128 (12,072)
Natural gas (LHV)		2,963 (21,070)	993 (21,070)	0	0
Internal heating ratio (Note 2)	-	0.33	0.68	1	1.77

<u>Notes:</u>

1. Fuel gas= a part of tailgas + off-gas
2. Internal heating ratio $= \frac{\text{Heat Duty supplied by fuel gas,MMBtu}}{\text{Total Required Heat Duty, MMBtu}}$

Even though the same ratio of tailgas is recycled over the case 1 to 3, they show the different internal heating ratio. The heating requirement of case 3 is self-sufficient by internally produced steam and recycled fuel gas without any makeup of fresh natural gas. For case 1 and 2, natural gas make-up is required to heat the process streams. This is because of the reduced heat duty in syngas production section (shown in **Figure 6**) and increased tailgas rate and its heating value (LHV) of the case 3 by split recycling of tailgas and the reduced S/C ratio. Increased CH_4 slips in the tailgas caused by the reduced CH_4 conversion in the ATR results in increase the heating performance of the fuel gas. So, the lower fuel gas rate is enough to meet the heat duty. The gradual decrease among case 1 to 3 in required natural gas rate as a fuel is supportive this discussion.

Case 3 is the most carbon efficient operating option among the cases even though lowers CH_4 conversion in the ATR. The process performance data of different operating cases are tabulated in **Table 13**.

Table 13. Comparison of Process performance indicators

Parameters	Unit	Case 1	Case 2	Case 3	Case 4
CH_4 conversion in ATR	mole basis	0.97	0.98	0.97	0.97
Carbon Efficiency in the GTL plant	bbl. GTL /lbmole	1.03	1.08	1.09	1.05

Notes:

1. $\mathrm{CH_4\ conversion} = \frac{\mathrm{CH_4\ lbmole\ in} - \mathrm{CH_4\ lbmole\ out}}{\mathrm{CH_4\ lbmole\ in}}$
2. $\mathrm{Carbon\ efficiency} = \frac{\mathit{Product\ Capacity},\ 50{,}000\ \mathit{bbl.\ per\ day}}{\mathrm{Required\ Natural\ Gas\ for\ reforming\ and\ heating},\ \mathrm{lbmole\ per\ hour}}$

Figure 6 illustrates the heat duty of each operating option and highlights the difference of total energy consumption for heating as well as the distribution of energy requirement for each section in the GTL process. It is seen that total heating energy requirement and the portion of syngas production section decrease gradually over the cases. It can be supportive evidence that heating duty of the two other sections (F-T reaction and product upgrading) are nearly constant among four cases; however, the heat duty of syngas production section significantly decreases about 50% and the contribution of this section decreases as well. **Figure 7** shows the contribution of heat duty of individual equipment in syngas production section. Reducing the S/C ratio and sending 80% of recycled tailgas to the FT reactor enables to reduce the heat duty of preheater for

ATR, which is the main contributor to the reduction of total heating duty of the overall plant.

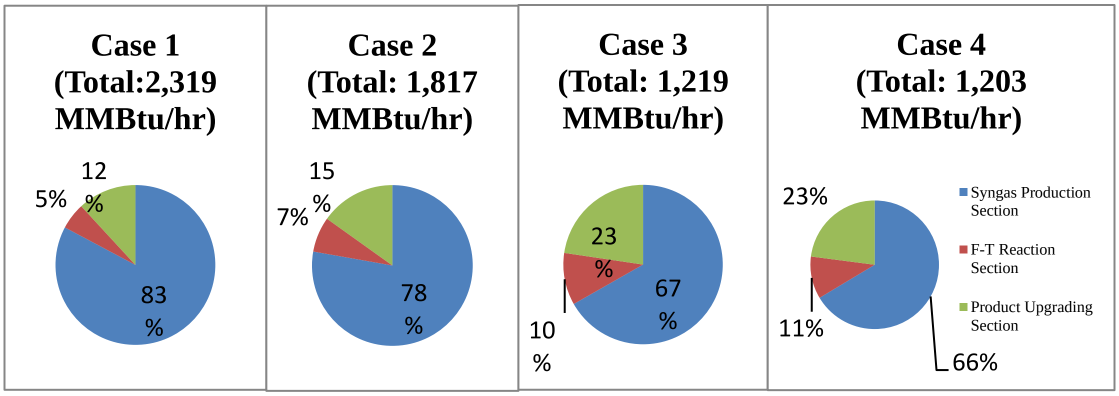

Figure 6. Heating duty of different Operating options

<u>Notes:</u>

1. Excluding the heat requirement for utility section or CO_2 removal system

Figure 8 shows the contribution of heating utilities used in the different operating options. The contribution of natural gas (external heating utility) to the total heating duty decreases gradually over the cases. For case 2 to 4, more than 80% of required heating duty is self-sufficient by internal heating utilities (steam and fuel gas). Case 3 and 4 have the lower contribution of steam to the total heat duty because of the reduced S/C ratio and higher contribution of fuel gas.

Splitting tailgas to recycle and reducing the S/C ratio enable to reduce the inlet flow rate to the main equipment in the syngas production section, such as pre-reformer, reformer, heaters, and piping. For efficient comparison, inlet flowrates to both reformers and their estimated volume and surface area are presented in **Table 14**. By splitting the tailgas and reducing the S/C ratio, inlet flow rate to major equipment in syngas production section decreases about 18% at most in pre-reformer and about 59% in the reformer. In existing GTL plants, several trains of syngas production section are applied to accommodate the large scale because of the limited single capacity of syngas production section[29]. Reducing the required volume of main equipment enables to reduce the numbers of the train and to reduce the capital cost.

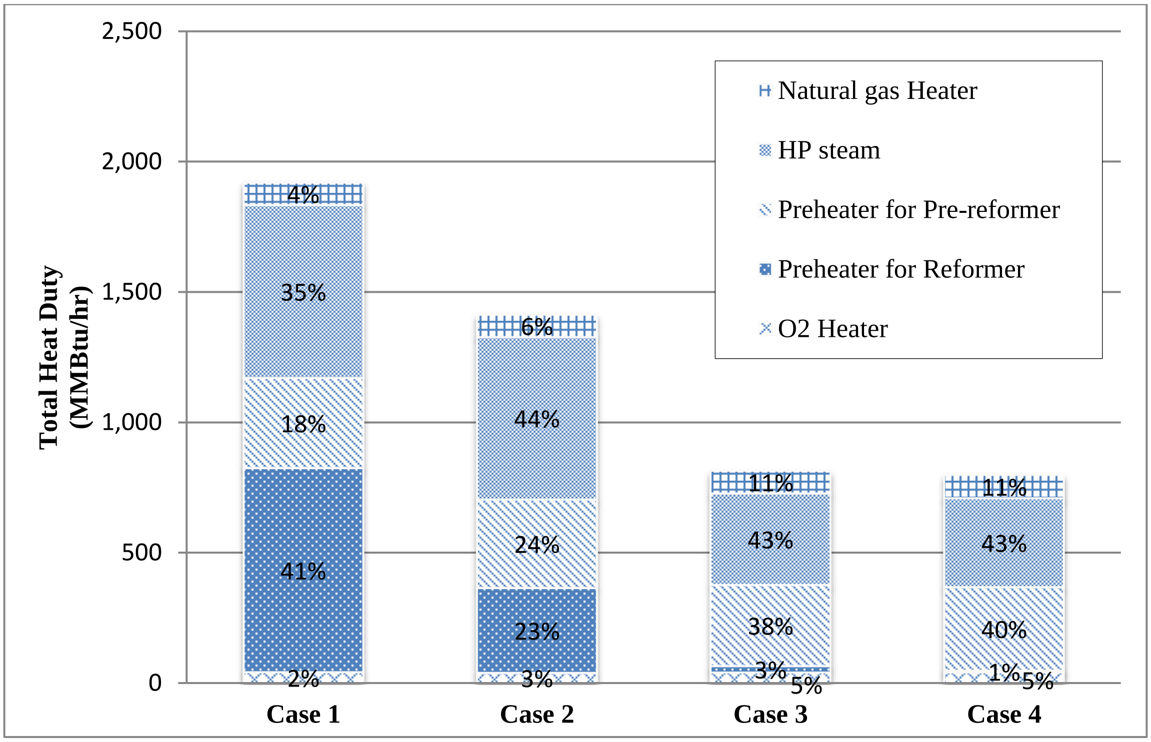

Figure 7. Heating duty of each equipment in syngas production section

Table 14. Inlet flow rate for Major equipment in Syngas production section

	Unit	Case 1	Case 2	Case 3	Case 4
Pre-reformer					
Flow rate	ft^3/hr	2,630,760	2,558,870	2,160,250	2,208,990
Flow, index	-	100	97	82	84
Auto-Thermal Reformer (ATR)					
Flow rate	ft^3/hr	6,101,820	3,759,800	2,506,590	2,490,780
Flow, index	-	100	62	41	41

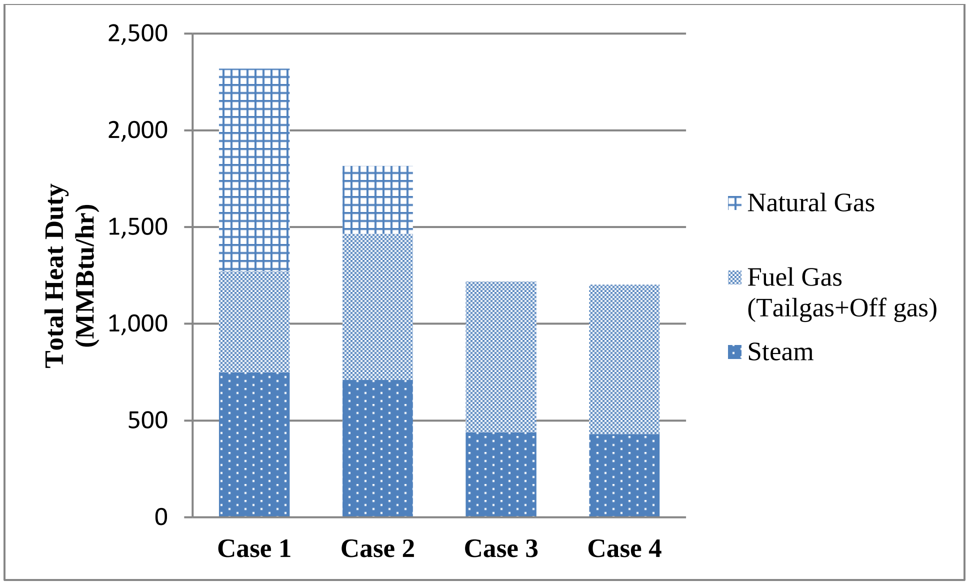

Figure 8. Contribution of Heating utilities to the Total heating duty of different Operating options

Supposed that case 2 has three (3) identical trains of ATR in syngas production section, same with Sasol Canada project, which considers the same design and similar capacity with case 2, case 3 and 4 have only two (2) identical trains of ATR. The number of trains of each section applied to this study is shown in **Table 15**. Supposed that the maximum single line capacity of ATR is limited to about 16,000 bbl. /day, case 1 has to consider five (5) identical trains of ATR. Increase or decrease in the number of trains in syngas production section contributes to estimating the capital cost of the GTL plant. Detail economic analysis is shown section 6.2.

To confirm the effectiveness of the reduce S/C ratio to process performance, operating conditions of the different cases should be verified to ensure the free of the carbon deposition. **Table 16** summarizes the pilot test results with parameters affecting the risk of carbon deposition and the operating conditions of four cases for comparative analysis to evaluate the risk of carbon formation. The pilot test explored the lowest S/C carbon ratio with free of carbon deposition by Haldor Topsoe. The results can be criteria to estimate the risk of carbon formation in this study; however, it is not the lowest limitation of carbon formation.

Table 15.Trains of each Operating option

Sections	Case 1	Case 2	Case 3	Case 4	Sasol, Canada
Syngas Production	5* 10,000	3* 16,667	2* 25,000	2* 25,000	3* 16,000
FT Reaction	2 *25,000	2 *25,000	2 *25,000	2 *25,000	2 *24,000
Product Upgrading	1* 50,000	1* 50,000	1* 50,000	1* 50,000	1* 48,000

Notes:

1. Includes O_2 supply system.
2. Includes utility systems (waste water treatment system, PSA, Fuel gas system, etc.)

The S/C ratio in ATR is typically lower than those in pre-reformer because of increased carbon contents by the recycling of carbons, CO_2 and/or tailgas at the same steam rate. According to the results from the pilot-scale test by Haldor Topsoe [20, 24], the tested S/C ratio in pre-reformer is about 0.25 at 743°F. This operation was proven to be free of carbon deposition. For the S/C ratio in ATR, the results from the pilot-scale test [20, 26]show the free-carbon deposition operation at the S/C ratio of 0.21 as a case operating at 1949°F with 355 psia. Since the values of all four cases are higher than the pilot test results, it could be estimated that there is no carbon deposition in the pre-reformer and ATR.

One of the critical causes to introduce carbon deposition is a higher hydrocarbon in ATR. The simulation results show that C_2+ contents per total carbon contents in the feed to ATR. For case 1, the value of C_2+/C is higher than the test result, however, it is estimated to be safe in the carbon formation because the S/C ratio is much higher than 0.21. As per the comparison analysis with the pilot test, it is estimated safe with carbon deposition in the four operating cases.

Table 16. Key Parameters for determining Carbon deposition with Criteria

Feed ratios (mole/mole)	**Case 1**	**Case 2**	**Case 3**	**Case 4**	**Pilot Test**
S/C ratio_$_{\text{Pre-reformer}}$	0.7	0.66	0.39	0.37	0.25
S/C ratio_$_{\text{ATR}}$	0.61	0.60	0.34	0.32	0.21
C_2+/C ratio_$_{\text{ATR}}$	0.08	0.04	0.04	0.03	0.06
O_2/C	0.6	0.6	0.6	0.6	0.6
Product gas					
Temperature	1950 °F				1949°F
Pressure	370 psia				355 psia
H_2/CO	2.0				1.96

6.2 Economic Analysis

Table 17 shows the estimated annualized cost of each operating case. From the comparative results, the economic performance of case 3 is better than other cases in totalized and individual annualized costs. This is because the lower S/C ratio reduces the size of ATR and the number of the train in the syngas production section and contributed to reducing the fixed cost of syngas production section. Reduced heating and cooling energy requirement from the reduced S/C ratio contributes to decrease in operating cost.

Table 17. Comparison of Estimated cost

Parameters (Million USD/yr)	**Case 1**	**Case 2**	**Case 3**	**Case 4**
TAC	924.8	867.9	856.3	883.6
AFC	14.6	13.6	11.4	13.1
AOC (Before Energy- Integration)	910.2	854.3	844.9	870.5

Economic analysis shows that reduced S/C ratio and split tailgas to the ATR and the FT reactor decrease the fixed cost by reducing the number of the train in syngas production section. On the other hands, there has not been much influence on the operating cost because the increase in CH_4 usage offsets the operating cost benefits from reduced steam consumption. The reduced tailgas recycling ratio results in an increase of both fixed cost and operating cost increase. This is because of higher natural gas and O_2 usage resulted from lower tailgas recycling ratio (0.9) and higher carbon rate. So, reducing the S/C ratio is beneficial to decrease both operating cost and fixed cost at the same tailgas recycling ratio. Utilizing tailgas as a feed is also beneficial to decrease both operating cost and fixed cost at the same S/C ratio. Controlling tailgas recycling ratio has more impact on the operating cost than controlling the S/C ratio because lower S/C ratio increase CH_4 and O_2 usage, while controlling tailgas recycling ratio has less impact on the fixed cost than controlling the S/C ratio because lower S/C ratio can decrease the number of train in the system. By reducing the S/C ratio from 0.6 to 0.32, about 11.6 million USD can be saved annually at the tailgas recycling ratio 0.96.

6.3 Safety Analysis

6.3.1 Effects of utilizing tailgas and off-gas as a carbon source

6.3.1.1 Comparative analysis of the physical properties

Table 18 shows the physical properties of both materials used as a fuel for fired heaters to evaluate their potential hazards. Natural gas is a flammable gas mixture comprising more than 95% of CH_4 and the rest is C_2H_6, C_3H_8, CO_2, and N_2; whereas, only about 10% of CH_4 is in the fuel gas. Instead, it is mainly composed of H_2 and CO about 80% and the rest is C_2H_6, C_3H_8, C_4+, CO_2, N_2, and a trace of water. Since the fuel gas has more than 40% of hydrogen, it is lighter than air. It will tend to rise and disperse easily in the air, whereas natural gas is heavier than air, which tends go and spread down to the ground. Fuel gas is relatively high in N_2, which is concerned with higher NOx emission in flue gas from fired heaters. However, it is less than 1%, which is estimated sufficiently reduced by low NOx burners' application in industry.

The range of flammability limit of natural gas is 4.34~16.43%, whereas that of the fuel gas is 5.48~58.49%. A wider range of flammable limit means that the material is able to be ignited under a wider range of conditions so typically poses a greater risk in flammability when they expose to air. However, as the gas mixture mixes with air and moves away from its release point, it is eventually becoming non-flammable once diluted below the lower limit.

The MIE of natural gas is 0.28mJ, whereas that of the fuel gas is about 0.024mJ. The most contribute composition to decrease MIE of the fuel gas is H_2. H_2 is regarded as clean energy for the future because it has no carbon emissions and low polluting properties. However, it has a quite low MIE (0.017mJ, [44]). Particularly, H_2 can even ignite spontaneously due to the shock wave from high-pressure release[45], without any ignition sources. Therefore, the fuel gas containing more than 40% of H_2 is more sensitive to ignition than natural gas when it exposures to air.

Typically, natural gas is not considered as toxic material. On the other hands, the fuel gas has more than 30% of CO, which are a flammable gas as well as toxic gas. Their toxic impacts are addressed in **Table 18**.

Table 18. Physical properties of Fuel for Fired heaters

Materials	**Unit**	**Natural Gas**	**Fuel Gas** **(Note 1)**
Composition **(Note 2)**	Mole %	CH_4 95.39 C_2H_6 3.91 C_3H_8 0.03 CO_2 0.59 N_2 0.08	CH_4 10.07 C_2H_6 1.39 C_3H_8 1.36 CO_2 0.07 N_2 0.97 H_2 43.98 CO 36.10 H_2O 2.03 C_4+ 4.02
Density **(Note 3)**	lb/ft^3	0.935	0.053
LHV	Btu/lb	21,070	11,848
Flammability Limit **(Note 4)**	vol%	4.34~16.43	5.48~58.49
AIT **(Note 5,7)**	°F	1,098.5	905.4
MIE **(Note 5,8)**	mJ	0.28	0.024

Notes:

1. Fuel gas = a part of tailgas + off-gas. Physical data of case 3.
2. C_4+ is considered as C_4.
3. Air density =0.074887 @ 70°F and ATM
4. Values from the PHAST
5. Values when exposure to the air
6. $MIE_{mix} = {}^{1}\!/\!\left(\sum\left({}^{y_i}\!/_{MIE_i}\right)\right)$ [4]
7. $AIT_{mix} = \sum y_i AIT_i$ [46]

6.3.1.2 Comparative risk analysis

Table 19 shows the probabilities of each top event caused by the leak on the pipe to evaluate their potential risk. The scenarios are based on the event tree shown in **Figure 5**. From the results, the probabilities of both materials that fire or explosion does not occur are respectively 95.9% and 86.5%. Looking into the individual probabilities of each top event, they have implications on the composition of materials.

Table 19. The probabilities of each Top event

Materials		**Unit**	**Natural Gas**	**Fuel Gas**
Releasing Pressure		psig	34.7	34.7
Releasing Temperature		°F	79	79
Releasing Rate		lb/sec	1.46	1.40
Probability	**Explosion**	-	<0.001	0.001
	Jet Fire	-	0.017	0.094
	Flash Fire	-	0.023	0.039
	No Fire (Note 1)	-	0.959	0.865

Notes:

1. Environmental impact

The possibility of jet fire by natural gas is lower than that by the fuel gas. The impact of lower MIE of the fuel gas contributes to increasing the probabilities to jet fire.

The possibility of flash fire by natural gas is lower than that by the fuel gas. The possibilities of the delayed ignition depend on various conditions, such as release flow rate, MIE, the duration of the release, and its strength. Since this comparative analysis is performed in the same condition in the duration of release and its strength, the MIE of the material and release flow rate dictates the possibilities of the explosion. The lower MIE of materials and the higher release flow rate, the higher possibilities of delayed ignition could arise. According to the equations for delayed ignition and explosion, the release flow rate is a more governing factor in determining the possibilities of the explosion. Since the releasing rates of both materials are almost same, there is no big difference in the probabilities of the explosion. Moreover, the fuel gas has a large portion of CO.

Figure 9. Probability of fatalities by CO toxicity

Fuel gas is more critical and hazard than natural gas to human health and the environment. Typically, natural gas is believed to be non-toxic and the results also show non-toxic effects. Toxic hazards with environmental impact attributes to CO in fuel gas, whose LC_{50} is 3760 ppm with 1hr exposure. As per dispersion modeling, at least 25 m (shown in **Figure 9**) away from the releasing source is necessary to be with free of fatalities caused by CO gas inhaling and more than 90 m is required to go down to LC_{50}.

Figure 10 shows the individual risk of both materials in fire and explosion hazards by the distance from the releasing source point. Individual risks of both materials get to zero at least 20 m away from the releasing source. According to the values from the figure, natural gas is inherently safer material in terms of fire and explosion hazards.

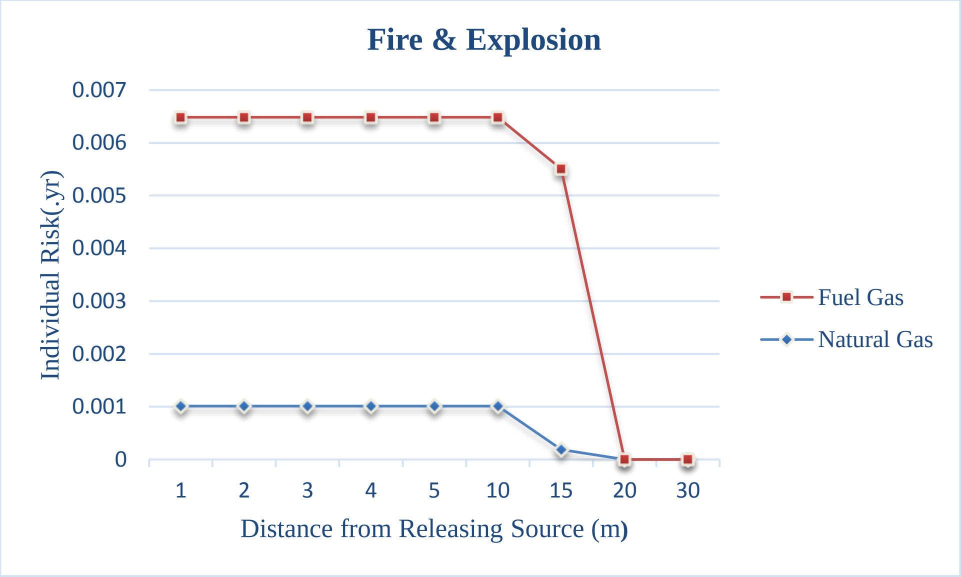

Figure 10. Individual risk of Natural gas and Fuel gas by Fire and explosion hazards

6.3.2 Effects of reduced the S/C ratio for syngas production system

For the estimating heat absorption from external fires and heat loss to the surroundings, the volume and surface area of both reformers are designed based on the inlet volume flow rates and are shown in **Table 20.** The results in the table illustrate the relieving loads in external fire case are reduced by 33% from the case 1. It is contributed to the lower volume of equipment and then, less surface area enables to reduce the heat absorption from the external fires. For the ATR, the relieving load in the external case is quite small to show the difference caused by lowered surface area. This is because the operating temperature (1950 °F) is quite high and the effect of the external heat is quite small. The API 521[41] also explains that the wall of ATR with 1 inch-thickness would take more than 21 min to reach to 1400°F when the plate is exposed to an external fire. It is estimated that much more time would take for ATR case.

Table 20. Geometric data of both Reformers

	Unit	Case 1	Case 2	Case 3	Case 4
Pre-reformer					
Flow rate	ft^3/hr	2,630,760	2,558,870	2,160,250	2,208,990
Volume	ft^3	5,936	5,774	4,874	4,984
Surface Area	ft^2	2,282	2,220	2,030	2,089
Surface/Volume	ft^2/ ft^3	0.3844	0.3845	0.4165	0.4191
Autothermal Reformer					
Flow rate	ft^3/hr	6,101,820	3,759,800	2,506,590	2,490,780
Volume	ft^3	10,554	7,114	5,922	5,956
Surface Area	ft^2	3,250	2,525	2,290	2,342
Surface/Volume	ft^2/ ft^3	0.3079	0.3549	0.3866	0.3932

Table 21. Comparison of Key parameters when relieving

Parameters	Unit	Case 1	Case 2	Case 3	Case 4
Pre-reformer					
Required relieving rate	lb/hr	76,620	74,320	66,020	67,730
Selected orifice size	in^2	6.380	6.380	4.340	4.340
Rated relieving rate	lb/hr	112,400	112,200	75,290	75,180
Autothermal Reformer					
Required relieving rate	lb/hr	338.9	265.8	232.2	233.5
Selected orifice size	in^2	$3.078*10^{-2}$	$2.792*10^{-2}$	$2.511*10^{-2}$	$2.335*10^{-2}$

In the **Table 22**, only information of pre-reformer and ATR are shown as the representatives of syngas production system. The size of corresponding piping and equipment are also reduced with the less S/C ratio. Therefore, from the reforming system point of view, more benefits can be gained in the loss of containment. However, only steam contents decrease at the similar amounts of carbon contents. When the containment is released to the atmosphere, it is estimated to present similar consequence between operating cases in the toxic and jet fire scenario.

Additionally, an internal explosion is avoided due to enough inert gas above CO_2 and N_2 of 25 vol. % with negligible O_2 in the system.

Table 22. Heat loss to the surroundings of the different Operating options

Temperature	**Heat Loss considered**	**Insulation considered**	**Case 1**	**Case 2**	**Case 3**	**Case 4**
Pre-reformer						
$T_{equilibrium}$	No	-	669.4	669.9	679.3	680.6
$\Delta T_{equilinrium}$	Yes	Yes	-0.2	-0.2	-0.1	-0.2
	Yes	No	-1.1	-1.1	-1.0	-1.0
Autothermal Reformer						
$T_{equilibrium}$	No	-	1938	1942	1953	1952
$\Delta T_{equilinrium}$	Yes	Yes	-1	0	-1	-1
	Yes	No	-3	-2	-3	-3

Notes:

1. Ambient temperature:32°F

With the lower system volume, the less loss of containment is shown. However, as the system volume decreases, the ratio of surface to volume increases (shown in **Table 20**). It causes more heat loss to the surroundings. The amounts of heat loss from the system to surroundings are estimated, which is shown in **Table 22**. The results show the heat loss of pre-reformer and ATR at the ambient temperatures and with a different application of external insulation with lower S/C ratio. The temperature differences between cases are 1 °F or below with the application of insulation; however, without insulation, the temperature difference is about 3°F. Despite the higher surface area to volume caused by the smaller volume of the system, heat loss to the surroundings has not critical impact on the adiabatic equilibrium. It can be negligible when we considering the external insulation for both reformers. Equipment and piping must be having insulation due to: (1) to maintain the performance of adiabatic reaction in the both reformers, 2) to protect personals from the hot surface of the equipment, and (3) to conserve the heat in the system.

6.4 Environmental Sustainability Analysis

Table 23 shows CO2 emissions as well as the contribution of emission sources. From the results, the total amounts of CO_2 emission of case 3 are less than other cases. This is because of (1) reduced fuel gas usage by the reduced heating duty and (2) no additional combustion of natural gas with self-sufficient heating (internal heating ratio =1).

Table 23. CO_2 emissions of different Operating options

Parameter		**Unit**	**Case 1**	**Case 2**	**Case 3**	**Case 4**
Total		lbmole/hr	25,168 (100%)	19,624 (100%)	16,395 (100%)	23,267 (100%)
Process			6,581 (26.1 %)	5,620 (28.6%)	5,960 (36.4 %)	5,953 (25.6%)
Combustion	**NG**		11,221 (44.6 %)	3,760 (19.2%)	0 (0%)	0 (0%)
	Tailgas		7,365 (29.3%)	10,244 (52.2 %)	10,435 (63.6%)	9,801 (42.1%)
	Excess gas (Note 1)		0	0	0	7,513 (32.3%)
CO_2/Heat Duty		lbmole /MMBtu	8.01	7.71	8.56	8.14

Notes:

1. Excessive fuel gas is used as a heating source for generating power.

It clearly indicates that CO_2 emissions from the combustion for generating heat or power occupy a large proportion (60~70%) of the total emission. CO_2 emission can be significantly reduced by energy integration of heating and cooling duty.

The amount of inherently generated CO_2 by the reforming reaction decreases by reducing the S/C ratio. However, since about 36~38% of generated CO_2 is recycled to ATR to meet the syngas ratio 2:1, the ratio of recycling in case 1 and 2 is bigger than that of the reduction of CO_2 emission benefits from reduced S/C ratio in case 3 and 4.

Natural gas is more sustainable fuel than fuel gas. The LHV of the fuel gas is about 50% of natural gas, while carbon contents including CO of the fuel gas are about 58~76% of natural gas. CO_2 emissions from the fuel gas burning are higher than that of natural gas for the same heating duty. The ratio of CO_2 to heat duty also explains that utilizing as much natural gas as possible is recommended to decrease the CO_2 emission from the combustion.

For case 4, the biggest amount of CO_2 is generated among four cases. Higher tailgas is recycled to fuel gas system, compared with the heating demand. Excessive tailgas is be used for power generation or purge gas to flare header.

For the carbon efficiency (showin in **Table 13**), the carbon efficiency of case 3 is slightly higher than other cases. Self-sufficiency in heating energy offsets the disadvantage from lower carbon conversion in ATR.

6.5 Integrated Insights for Decision Making

Based on the results obtained, the following observations and recommendations are drawn. These address the economy, safety, and environment sustainability implications to provide multi-objective insights case for the decision makers.

1) Utilizing tailgas and off-gas as alternative carbon sources to natural gas is beneficial to economic achievement. From the operating cost point of view, by utilizing tailgas and off-gas instead of natural gas, costs for fresh feed source and heating source are saved. To maximize the effectiveness, it is recommended to

split the recycled tailgas and send to the ATR and the FT reactor respectively considering tailgas composition and to utilize tailgas as much as possible as a feed to the reformer to bring added value to the maximum.

2) Consuming tailgas as a feed instead of natural gas is beneficial to environmental sustainability achievement. CO_2 emission rate significantly decreases by reducing or eliminating the burning off the light-ends during the normal operation. From the carbon efficiency and energy usage points of view, fresh natural gas is saved as feed. However, utilizing fuel gas (a part of tailgas, and off-gas) as an alternative fuel for firing equipment to generate heat energy is not beneficial to environmental sustainability achievement. The heating value of fuel gas is only 50-60% of natural gas, while the carbon contents including CO in the fuel gas is more than 60% of natural gas.

   At the same heating duty, more CO_2 is generated by combusting fuel gas than natural gas.

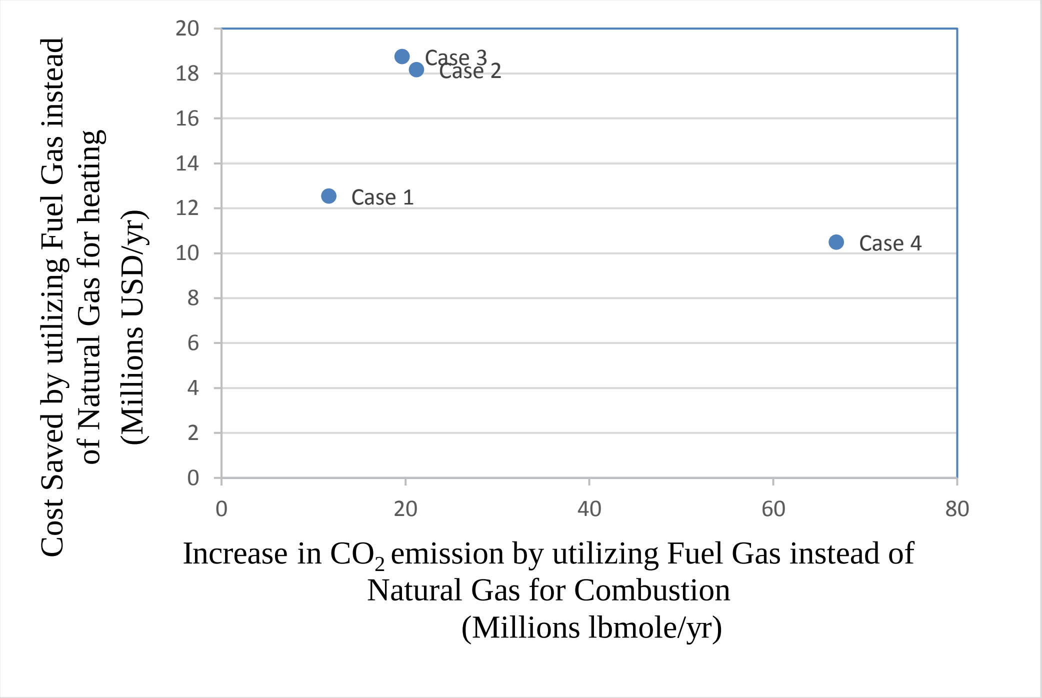

Figure 11. Cost saving versus CO_2 emission by utilizing Fuel gas for Heating

The economy and sustainability analysis provide **Figure 11** for cost saved versus an increase in CO_2 emission by utilizing fuel gas instead of natural as for generating heat energy of each operating case. This figure shows the trade-off between the conflicting objectives and provides an optimal operating case for the decision maker. In the figure, case 1 is located in the left-most point, which implies that the lowest increase in CO_2 can be obtained and Case 3 is in the right-most point that the highest cost saving by utilization of fuel gas instead of natural gas. The optimal point depends on the objective by the decision maker. When the carbon tax imposed to CO_2 emission is less than the difference of cost saving between case 1 and 3, case 3 is an optimal point in economic view. On the other hands, when the carbon tax is higher than the difference between case 1 and 3, case 1 is an optimal point in both sustainability and economy.

To maximize the effectiveness in sustainability, it is recommended controlling the tailgas recycling ratio for the internal heating ratio to be one (1) to optimize the CO_2 emission rate from the combustion. It is also recommended to utilize heat integration technique to reduce heating and cooling energy and reduce the CO_2 emission from the heat generation by the firing equipment. According to the results of this study, more than 60% of CO_2 is produced from the combustion of carbon sources to generate heat energy. This technique seems to be an effective way to reduce CO_2 emission as well as to reduce the operating cost.

3) Utilizing tailgas and off-gas as alternative carbon sources to natural gas is not beneficial to inherent safety. From the fire and explosion hazard point of view, the individual risk of natural gas is lower than that of fuel gas. Moreover, both individual risks are higher than acceptance risk criteria (10^{-5} per year, ALARP) [47]. From the toxic hazards point of view, CO in the fuel gas has high toxicity to human health. To reduce the frequency of leak from the pipe, regular and systematic maintenance is required to check the erosion inside of the pipe. To reduce the leak by internal corrosion, sufficient corrosion allowance to avoid any corrosion during normal operation is required for designing material thickness.

Higher rated design and maintenance enable to utilize fuel gas instead of natural gas by reducing the frequency of leak or failure in the pipe and equipment. Proper detection systems are needed to identify any leaks and to alert for the need to evacuate in case of leakage or rupture of equipment or piping.

4) Reducing the S/C ratio is beneficial to economic achievement. From the operating cost point of view, by reducing the required heat duty, costs for fresh feed source and heating source is saved, even though lower CH_4 conversion offsets the benefits from the reduced steam rate. From the capital cost point of view, the reduced flow rate to ATR contributes to reduction of the number of ATR trains in syngas production section and to the reduction of capital cost.
5) Reducing the S/C ratio is beneficial to sustainability achievement. In a CO_2 generation from the process, there is no remarkable difference between operating cases. Even though CO_2 recycling offsets higher CO_2 generation from the process inherently in S/C ratio of 0.6, the amount of generated CO_2 from the reaction decreases by reducing the S/C ratio. On the other hands, the amount from the combustion to produce heat decreases significantly because of reduced heat duty. The reduce heat duty contribute to increasing in carbon efficiency by reducing the required fresh natural gas for heating.
6) Reducing the S/C ratio is beneficial to inherent safety in terms of reduced loss of containment while maintaining the efficiency of the adiabatic reforming reaction. From the system volume point of view, by reducing the steam portion occupying in the system, the required volume of equipment decrease significantly. This implies that in the case of exposing to external fire, the less heat is absorbed by the surface wall of equipment and piping and the less amount of containment in the system is lost to the outside of the system, such as atmosphere when they are ruptured or relieved to flare system to avoid rupture of equipment.
7) To maximize the effectiveness of the reduced S/C ratio while avoiding any carbon formation during reforming process, C_2+ contents should be minimized. To minimize the risk of carbon formation, existing plants have the system to remove

longer hydrocarbon before recycling to ATR. Instead of higher S/C ratio, eliminating or reducing longer hydrocarbon in the feed to ATR is estimated more economical, sustainable, and safer way to maintain the process performance. By reducing S/C ratio and utilizing tailgas and off-gas as a feed and fuel, the economic, sustainable, and inherently safer operating options is obtained. According to the results of this study, case 3 is the optimal case among the operating options by multi-objective analysis.

7 CONCLUSIONS AND DISCUSSIONS

This work has assessed possible improvements to the GTL process in two areas: 1) tailgas recycling and 2) lower steam-to-carbon (S/C) ratio for auto-thermal reforming (ATR). Process simulation and published data were used to establish the base-case information and to evaluate the dependence of performance on several designs and operating degrees of freedom. Performance has been assessed in terms of cost, inherent safety, and environmental sustainability.

Care should also be given to reducing carbon deposition. Carbon deposition is not formed by just one factor. It is a very complex phenomenon which depends on catalysis, S/C ratio, operating conditions, heat transfer, and mechanical design. To avoid carbon deposition in the reformer, mechanical design including the burners should be improved in conjunction with proper usage of S/C ratio, catalyst, and operating conditions.

Employment of energy integration technique is recommended to reduce heating and cooling energy and reduce the CO_2 emission from the heat generation by the firing equipment. According to the results of this study, 60~80% of CO_2 is produced from the combustion of carbon sources to generate heat energy. This technique seems to be an effective way to reduce CO_2 emission as well as to reduce the operating cost.

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APPENDIX A. PROCESS FLOW DIAGRAM FOR THE GTL PROCESS