DEVELOPMENT OF OPTIMAL GAS-TO-LIQUIDS (GTL) PLANT USING STEAM/CO_2 REFORMING FOR SYNTHESIS GAS PRODUCTION

BY

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CERTIFICATION

This is to certify that this work "Development of Optimal Gas-to-Liquids (GTL) Plant Using Steam/CO_2 for Synthesis Gas Reforming" was carried out by **I EKWUEME, STANLEY TOOCHUKWU (20164023478)** in partial fulfilment for the award of the degree of M.Eng in Petroleum Engineering in the Department of Petroleum Engineering of the Federal University of Technology, Owerri.

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DEDICATION

This work is dedicated to the Almighty God for his love, Strength and insights and to my parents who have endured many things that I may progress and to my late brother Chinaza, rest in the Peace of the Lord

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ABSTRACT

This research work is on method for optimisation of GTL plant using Steam/CO_2 reforming for syngas generation. Extensive modeling of GTL plant has been done. Two cases were considered during the simulation of the GTL plant. The first case being the base case was the use of oxygen gas as the feed reactant gas using an auto-thermal reformer for the production of synthesis gas. The alternative case which is the proposed method in this work uses CO_2 in lieu of oxygen for the production of synthesis gas. CO_2 method was chosen because of its cheap availability and the ability to be recycled from purge gas and reused reducing pollution. Honeywell's Unisim software was used for the simulation and the Peng-Robinson equation of state was chosen as the fluid property package. The simulation was done unit by unit and integration of all units was made. The synthesis gas unit was simulated in Unisim as a conversion type reactor using two separate reactors while three equilibrium reactors were used to control the water gas shift reaction to maintain favourable H_2/CO ratio. The FT reactor was modeled as a multi-tubular bed reactor and simulated as a plug flow reactor (PFR) in Unisim using heterogeneous catalytic reaction type. Technical and economic performances were analyzed for both methods. The technical analyses revealed that the proposed steam/CO_2 method gave a H_2/CO ratio of 2.17 compared to 2.21 obtained for the autothermal reformer (ATR). Furthermore the carbon efficiency of the two methods revealed 77.68% and 92.17% for base case and the proposed method respectively making the proposed method more efficient. The liquid yield shows that the proposed method has a liquid yield of 5730b/d over the 5430b/d obtained from the base case representing an increase in product yield of 5.5%. The economic analyses show a quicker pay-out time of 4.9 years from the proposed model as against 5.9 years from the base case. Using the proposed method gave an annual cashflow increase of 20.9% and NPV increase of 59.7% at 10% discount rates. Thus the proposed method is more profitable in terms of NPV. This project will be suitable for application in the Niger Delta stranded and remote gas locations which are known for gas flaring leading to environmental pollution.

Keywords: Autothermal reforming, Fischer-Tropsch, Gas-to-Liquids, Steam/CO_2 reforming, Synthesis gas

CHAPTER ONE

INTRODUCTION

1.1 Background

Natural gas has been recognized as the cleanest fossil fuel. In the recent transition to alternative energy, natural gas stands as the bridge fuel between fossil fuel energy and alternative energy sources. This reason of course is due to its abundance in nature and less pollution characteristics when burnt as compared to crude oil making it an environmentally friendly fuel.

The vast oil fields of the world have been noted to produce associated natural gas. Utilizing these gases was problematic because of immaturity of gas projects. Traditionally, these gases where utilized onsite where they are re-injected into the reservoir to maintain reservoir pressure or when the associated gas was available in large quantity to attract a ready market, pipelines were constructed and the gas was processed to pipeline quality gas and sold. In most cases the volume of the gas and/or the non-existent of ready market makes construction of pipeline economically prohibitive. Since storage of the gas is an issue in the field, operators resorted to flare the gas which the claim was for safety reasons as it helped reduce pressure build up in the storage tanks and allow the industry to shift focus to oil which usually were the main target. Gas Flaring poses great financial and environmental implications and as such many nations are seeking for technologies to utilize the otherwise flared gas (Chabrelie and Rojey, 2010).

The technologies available for monetization of natural gas are Liquefied natural gas (LNG), compressed natural gas (CNG), Gas to wire (GTW), Gas to hydrates (GTH), Gas to liquids (GTL), and natural gas liquids (NGL) extraction.

Each of them has its conditions for economic viability and areas of applicability. GTL can offer adequate monetization of small associated gas volumes in scattered locations in the Niger Delta. (Spath and Dayton, 2003). Initially GTL was viewed as a capital-intensive project requiring huge capital expenses and availability of large volume of gas for economic viability. Because of these constraints only very few large scale commercial plant are operational. The only plant in Nigeria is the Escravos GTL facility in Escravos Delta state. The project cost more than 5 billion dollars for its construction and expected to run at a capacity of 34000b/d of product fuels like diesel, gasoline etc. Economies of scale has made available smaller plants for improve utilization of associated stranded gases. GTL products have two basic economic advantages, the first is that its transport cost is much less than that of natural gas from which it was made, because due to its volume, natural gas presents high capital cost and require specific assets like pipelines and cryogenic vessels for their transportation. The other advantage of GTL is that its products present important environmental advantages over traditional products from crude oil refineries as they are derived from cleaner fuels i.e. natural gas. (Enyi, Nagid and Nasr, 2011)

Aside the advantages, GTL has two major setbacks, firstly, it is capital intensive and require huge CAPEX and OPEX. One of the principal threats to GTL technology is the huge capital cost for startup. For large plants, capital cost range from \$25000 PBLD (Per barrel Liquid a Day) to \$80000 PBLD. Smaller plants have reduced total cost but also have less capacity which makes its capital cost per barrel basis as high as \$80000 PBLD to \$100000 PBLD. Much research and development are needed to lower the cost and improve on the efficiency of the system. Furthermore, conventional GTL technologies especially Fischer-Tropsch synthesis are net generators of CO_2. The intensity of the CO_2 generated depends on age and size of the plant. The

CO_2 generated comes from the reactions in the FT reactor and the reformer and the combustion of natural gas as fuel in the furnaces.

In optimizing GTL plants, the optimsation step must address these problems. Thus, GTL optimsation is geared towards the following objectives.

1. Development of a GTL system that requires less capital and operating cost.
2. Development of an optimal catalysts to achieve higher conversion performance from gas to liquid both in the reformer and the FT reactor.
3. Development of an optimal GTL system for higher energy efficiency and performance.

Research has shown that among the various steps present in the GTL system, the syngas generation step is the most capital intensive. This is because of its high energy consumption, cost of construction and complexity of configuration as an additional unit. In traditional GTL syngas generation, autothermal reforming has been proven and selected as the best for syngas generation in terms of efficiency and economy. Thus, many commercial GTL plants utilize this method for syngas generation. Because it requires oxygen as its feedstock, there is need for external supply of oxygen. This is gotten from separating oxygen from air through the use of an air separation unit (ASU) configured with the system (Bello, Joel and Ikiensikimema, 2012). The volume of oxygen required is dependent on the capacity of the plant. For commercial plants large volume of oxygen is usually required and these significantly results to high capital cost of the syngas process which adds to the overall capital cost of the GTL system. For some plants, syngas generation takes about 40% of the capital cost of the GTL system.

In optimizing the plant, it is necessary to provide an alternative approach in the autothermal reforming unit that will reduce the volume of oxygen intake or replace the oxygen fuel with some other fuel that is cheap and readily available. A new method is provided in this work. The method uses CO_2 instead of O_2 for the autothermal reforming. Thus, the CO_2 in the raw natural gas is utilized. This method reduces the capital cost of the syngas generation and the overall capital cost of the GTL plant is reduced due to the following reasons (Suehiro, 2005)

1. No need for use of the ASU for O_2 generation
2. No need for use of CO_2 removal unit in the treatment plant
3. No need for use of H_2 conditioning unit for syngas, because syngas generated using CO_2 instead of O_2 is pure.

1.2 Statement of Problem

Two major setbacks recognized in most traditional GTL technologies include:

1. GTL systems are very capital intensive and require huge capital cost for initiation and operation.
2. Conventional GTL technologies using steam methane reformer or autothermal reformers are net generators of CO_2 which causes severe environmental pollution
3. The required H_2/CO ratio for optimal Fisher Tropsch Liquid reaction is 2. This conversion ratio has to be provided by the synthesis gas reformer. If this ratio is not provided or maintained by the synthesis gas reformer then the reaction in the FT unit for liquid transport fuel will not be optimal and efficiency of the unit will not be maximized.

An optimsation procedure is such that will address these problems. One of the contributors to the huge capital cost of GTL plants comes from the syngas generation stage. This utilizes air separation unit for the recovery of pure oxygen from air. This unit contribute to the overall cost intensiveness of the syngas generation stage making it the most expensive stage in the GTL operation. The high capital cost of this stage also translates to the overall capital intensiveness of the GTL system.

A new approach that will eliminate the ASU will greatly reduce the capital cost of the project. Thus, the use of CO_2 instead of oxygen for autothermal reforming in the production of syngas will not only eliminate the need for ASU but will also eliminate the need for separation of CO_2 from the inlet gas as the CO_2 can now take part in the reaction process rather than seen as an impurity and removed. The result of this is reduced system cost and reduction in carbon dioxide generation in the reaction process as the CO_2 is recycled and utilized in the reformer technology. Furthermore, the use of carbon dioxide enhanced autothermal reforming yields more of the desire GTL products at increased efficiency of plant.

1.3 Objectives of Study

The main objective of this work is to develop optimal GTL plant that favours the production of longer chain hydrocarbon liquids by use of steam/CO_2 reforming technique for synthesis gas production.

Other specific objectives include:

1. The development of GTL configuration reduction with less capital and operating cost by using CO_2/steam reforming process.
2. The development of a GTL plant with less carbon dioxide emission characteristics by a method of CO_2 flue-gas reuse.
3. The development of an optimal GTL plant with higher energy efficiency and technical performance details using Honeywell Unisim software.

4. To develop GTL systems that will be economical to use by investors in gas monetization in Nigeria.
5. Evaluation of the Economics of the proposed CO_2 reductive synthesis gas reforming alternative.

1.4 Scope of Study

This work centres on the optimsation of GTL plant. The optimsation approach employs the use of a new reactant, CO_2 instead of O_2 for the production of synthesis gas in the reformer section. The plants make use of compositional CO_2 in the natural gas feedstream and more volume of CO_2 can be gotten onsite from the hydrogenation plant. The work compares technically and economically the performance of the traditional GTL system that uses O_2 recovered from the ASU (Air Separation Unit) and our new system that employs CO_2 instead of oxygen. the comparative analysis of the two scenarios are in terms of capital cost, operating cost, performance, product yield, product purity, plant reaction pollution characteristics and economic parametres such as the NPV, DCF-ROR, and POT.

Honeywell’s Unisim software shall be used to model the plant while the MATLAB software shall be used in the optimization and programming in writing executable scripts and programs that would handle tedious calculations.

1.5 Significance of Study

This work shall provide the knowledge needed in the development of an optimal GTL technology that would require less capital and operating cost. Also, the knowledge gain from this work will aid in the reduction of the CO_2 emission notable with most GTL technologies. Furthermore, the knowledge of the improvements in plant design gained in this work will not only increase the efficiency and product yield of the GTL system but will encourage larger investors participation in the associated gas monetization using GTL. This is because much of the setbacks and limitations accrued with the GTL technology have been addressed. We shall publish technical papers stating the plant configuration and flowsheet of the Honeywell Unisim simulation of the GTL process for the various steps of the GTL operations which will include both the technical and economic considerations. The papers that will be published will be useful to investors and engineers in the area of gas-to-liquids and gas processing projects.

CHAPTER TWO

LITERATURE REVIEW

2.1 Natural Gas

Natural gas is a naturally occurring hydrocarbon gas mixture that consist mainly of methane, and also varying compositions of other higher alkanes, and oftentimes a small proportion of carbon dioxide, nitrogen, hydrogen sulfide, or helium. Natural gas is formed partly from decomposed plant and animal matter was made to undergo intense heat and pressure under the surface of the Earth over millions of years. The plants obtain and store energy in the form of chemical bonds.

Natural gas belongs to a fuel source known as fossil fuel. As an energy source it is utilized for cooking, heating, and generation of electricity. It is also used in vehicular transport as fuels for vehicles and also as a chemical feedstock in the manufacture of varieties of petrochemical and chemical products including plastics.

In the early days of oil exploration, natural gas recovered during oil production, could not be profitably sold, it was simply flared or vented. When flaring or venting was not the case, the gas was often times re-injected into the formation for enhanced oil recovery either for pressure maintenance or miscible/immiscible flooding. The Conservation, re-injection, or flaring of natural gas in associated with oil mainly depends on its proximity to markets (pipelines), and regulatory restrictions.

Because of the emergence of gas utilization technologies, natural gas is now in high demands and the government of many nations has promulgated laws that seek to eradicate gas flaring. Aside the use of natural gas for power generation by transporting it through large pipeline to power production destinations, natural gas has other end uses which include conversion to liquefied natural gas (LNG), and conversion into liquids by means of gas-to-liquids technology (GTL). Gas-to-liquids technology has the potential to convert natural gas into liquids like gasoline, diesel or jet fuel. Many gas-to-liquids technologies have been developed, they include; Fischer–Tropsch (FT), methanol to gasoline (MTG) and syngas to gasoline plus (STG+). Fischer-Trospch (FT) produces a synthetic crude that can be further refined into finished products like gasoline, kerosene etc, while MTG has the potential to produce synthetic gasoline from natural gas. STG+ can directly produce drop-in gasoline, diesel, jet fuel and aromatic chemicals from natural gas through a single-loop process (Anyasse and Anyasse, 2016).

Natural gas can come as "associated" (found in oil fields), or "non-associated" (isolated in natural gas fields), and is also found in coal beds (as coalbed methane). Natural gas sometimes has a significant amount of ethane, propane, butane, and pentane. These are heavier hydrocarbons that are separated or removed for commercial purpose before the resulting dry gas which is mostly methane is sold as a consumer fuel or chemical plant feedstock. The non-hydrocarbons constituents such as carbon dioxide, nitrogen, helium, and hydrogen sulfide must also be removed before the natural gas can be transported.

2.2 Associated Gas

Associated petroleum gas (APG), or associated gas, is a form of natural gas which is found in contact with oil, either dissolved in the oil or as a free "gas cap" above the oil in the reservoir (Roland, 2010). Historically, this type of gas was released as a waste product from the petroleum extraction industry. It may be a stranded gas reserve due to the remote location of the oil field, either at sea or on land, this gas is simply burnt off in gas flares. When this occurs, the gas is referred to as flare gas. Considering the fate of natural gas associated to oil reservoirs which are often flared, thus wasting a limited natural resource as well as affecting the environment, new policies have been implemented. A growing consideration concerns CO_2 emission. Initial measures consist in avoiding flaring in particular in the case of associated gas.

Natural gas after processing can be utilized in many ways: sold as sales gas by including it in the natural gas distribution network, for generation of electricity onsite through gas-to-wire technologies, for enhanced oil recovery by reinjection of the gas into the reservoir, conversion to liquids through GTL in production of synthetic liquid fuels and as petrochemical feedstock in the petrochemical industry.

When no infrastructure for transmission and distribution is available, then the associated gas has few utilization outlets. This includes a re-injection of the gas and gas flaring (which is not a preferred option due to resource conservation and greenhouse gas issue). Where there is availability of transport network and market potentials, the gas can be processed with the extraction of heavier fractions as natural gas liquids (NGLs). In situations where injection for EOR is not favourable, then a new capital intensive project will be considered, this can be LNG or GTL process schemes.

2.3 Stranded Gases

A stranded gas reserve is a natural gas field that remains unusable after being discovered due to physical or economic reasons. Stranded in this sense means that the gas cannot be brought to the market and as such left in the areas where they are produced. A good percentage of natural gas reserve is stranded in deep offshore locations, in difficult and remote areas or produced as associated gas. It is difficult to bring these stranded gases to the market especially when construction of pipelines in such circumstances is not economically viable. Thus, the resource availability to end users is hindered by costs of production and transportation which may exceed the sales cost of the gas. Because of this, it is required that technical options are developed to reduce the costs by providing new outlet for the natural gas. (Chabrelie and Rojev, 2010).

1. Economically stranded gas

Natural gas can be economically stranded for one of two reasons:

1. The resource may be too remote from a market for natural gas, making construction of a pipeline excessively expensive.
2. The resource may be in a region where demand for gas is saturated, and the cost of exporting gas beyond this region is excessive. Such a reserve is likely to be exploited in the future when existing sources begin to diminish.

2. Physically stranded gas

A gas field that is too deep to drill for, or is beneath an obstruction, may be considered physically stranded. Developments and innovations in drilling technology provides possibilities and ways to exploit this resource

2.3.1 Modes of Occurrence of Stranded Gases

1. Deep offshore locations

One of the forms of stranded gases is the deep offshore gas present in deep waters and arctic zones. This constitute over half of the world’s proven reserve. The potential depth of deep-water hydrocarbon development is enormous. This resource is made stranded owing to difficulty in laying pipelines in undersea, deep waters or distance to gas gathering facilities in the location.

2. Marginal Fields

Marginal fields also present sources of stranded gases. These gases come from oil reservoirs considered marginal in production i.e. to say the economic life of the field has been drastically reduced. Owing to this, the operating companies may become disinterested in developing the gas resource since they may be marginal. This depends on the Gas-oil-ratio (GOR) of the reservoir, the reservoir and well operating conditions.

Gases from marginal fields come from oil reservoir that has been considered marginal in production. For this reason, the operating companies may not be interested in developing the gas since they too may be marginal depending on the GOR of the reservoir, reservoir and well operating conditions (Chabrelie and Rojev, 2010).

3. Remote Locations

These are gases found in areas that are not accessible because of environmental or topographical limitations or due to distance from markets. These gases are referred to as remote gases and their remoteness makes them stranded. For example, some of the fields in Africa is remote to markets in Europe. The remoteness of a gas resource is evaluated with key concern in transportation costs and the potential cost reduction. The presence of innovative technology will highly influence the monetization of such resource.

2.4 State of Associated Gas in Nigeria

Nigeria is a country with vast quantities of gas reserves. Vast proportion of the Nigeria gas utilised is those that come as associated gas. The Niger Delta oil is considered as foamy because it contains significant proportion of gas in association with it. In the past, this gas has proved difficult to harness when exploration activities targeted oil production. These associated gases were seen as nuisance and bye product of oil production. Owing to this the earlier fields developed were without infrastructures to harness the associated gas produced with the oil, hence the gas was subjected to flaring.

The chief reason why Nigeria gas is not utilised or harness is because they are considered as stranded. As earlier stated, the principal reasons why gases are considered stranded are (Onwukwe and Duru, 2015)

1. The field is remote.
2. The field is located in deepwater.
3. The field is marginal that is to say the field is too small to justify a gas pipeline for long term production.

Other reasons may include

i. Inadequate pressure to transmit associated gas at surface facility thereby requiring booster stations.
ii. Lack of application of adequate technology.
iii. Weak legislation by the government to stop gas flaring.

Owing to the above reasons much of the associated gas was flared. The country loses estimated annual revenue of $2.5billion to gas flaring with an estimate of about 850bcf of natural gas being flared annually (Lean, 2008). The recognition of this economic loss has instigated the government into setting strategies of exploiting the abundant natural gas resources to enhance economic development. First the government promulgated the associated gas re-injection act and the associated gas re-injection (amendment) in 2004. This mandated the oil producing companies to produce detail account of the use of their associated gas utilization strategy. This was with the vision of eradicating gas flaring and encouraging gas re-injection in the fields. Unfortunately, the target was never achieved as the operating companies preferred to pay the penalty and continue in flaring gas than developing gas utilization projects for the associated gas. Thus, the vision of eradication of gas flaring was not achieved by 2008.

2.5 The Nigeria Natural Gas Industry

Apart from oil, Nigeria has the largest reserves of natural gas in Africa. Even with this, Nigeria has limited infrastructural capacity to develop her natural gas resource. The Natural gas in Nigeria is located in relatively simple geological structures along the country's coastal Niger River Delta and the offshore blocks. Other prospective hydrocarbon bearing basins include the Benin basin, Anambra basin, Benue trough, etc. But these are yet to be fully exploited (World Energy, 2004). Associated natural gas production is mostly flared but the development of regional pipelines; the expansion of liquefied natural gas (LNG) infrastructure and policies to eradicate gas flaring are expected to fast-track growth in the sector.

Figure 2.1 shows the countries that has the highest volume of proven non-associated gas. Russia has the largest volume of non-associated gas followed by Iran. Nigeria occupies the 8th position in the ranking of countries that has the largest proven non-associated gas in the world.

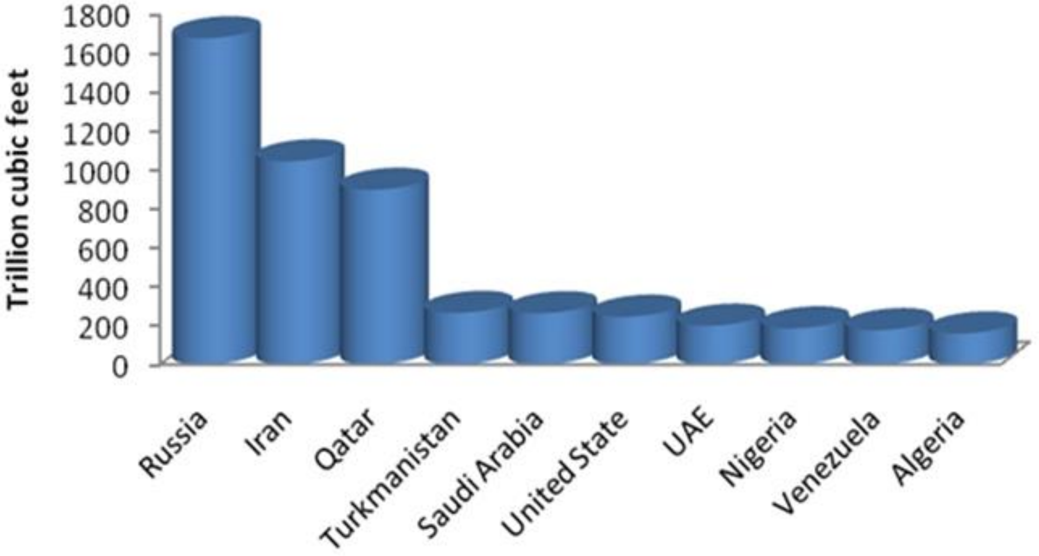


Figure 2.1: Top Proven Non-Associated Gas Reserve Holder Agboola *et al* (2011)

2.6 Gas Flaring

Because the associated gas was not harnessed, the resultant act is to flare the gas.

Gas flaring refers to burning of associated natural gas during the production of oil. This means of gas disposal by flaring takes place in all the states that comprise the Niger Delta area and as a result has been blamed for varied environmental, health and resource management problems. World Bank (2009) estimated that 100 billion $m^3$of associated gas are flared or vented on a worldwide basis annually, while Africa contributes 37% of this volume (EIA, 2009).

World Bank in 2009 estimated that Nigeria flares about 75% of her total gas production, which amounts to 70 metric tonnes (Mt) of carbon dioxide emission. In line with this, Nigeria contributes a measurable percentage of the world´s total emissions of greenhouse gases (GHGs). Much of this gas is released as methane because of low efficiency or effectiveness. Methane has high global warming potentials. All the major oil companies in Nigeria, principally the Shell petroleum development company (SPDC), and American oil companies (Chevron and Exxon Mobil) contribute to gas flaring.

Nigeria flares 17.2 billion m^3 of natural gas per year in conjunction with the exploration of crude oil in the Niger Delta (GGFR, 2002). This high level of gas flaring is enough for one quarter of the current power consumption of the African continent (GGFR, 2002). The NNPC Gas Production Report of 2016 showed that a total of 112.1 BSCF of gas was flared in the first half of the year which is a loss of about $336.33 million, an equivalent of N105 Billion. This problem was caused by many oil companies which have been in operation for many years. The economic and environmental implications of this extent of gas flaring is enormous, aside being a potential waste of monetisable resource, it pollutes the underlying ecosystem.

Aside the financial quantification of loss from gas flaring, gas flaring possesses great environmental implications. It is known to be a major contributor of greenhouse gases that generally lead to greenhouse effects. Gas flaring has been blamed for a variety of illnesses in host communities such as asthma, cancer, bronchitis, painful breathing etc. flared gas has been the contributor of acid rain that damage trees and rooftops of houses in host communities and environs.

The GGFR in 2007 funded a study on gas flaring. The aim was to encourage developing policies and regulations on gas flaring and utilization. The study suggests that there are four major factors that hinder energy producers from capturing and utilizing flared gas, they are:

1) Lack of infrastructure such as gas processing plants and pipelines needed for transport

2) Lack of policy frameworks that provide sustained incentives for producers to better utilize flared gas,

3) Large volumes of flared gas come from small fields in less populated and remote areas far from major local energy markets which make pipeline connection costs excessively high,

4) Low prices of natural gas, propane and butane extracted from flared gas.

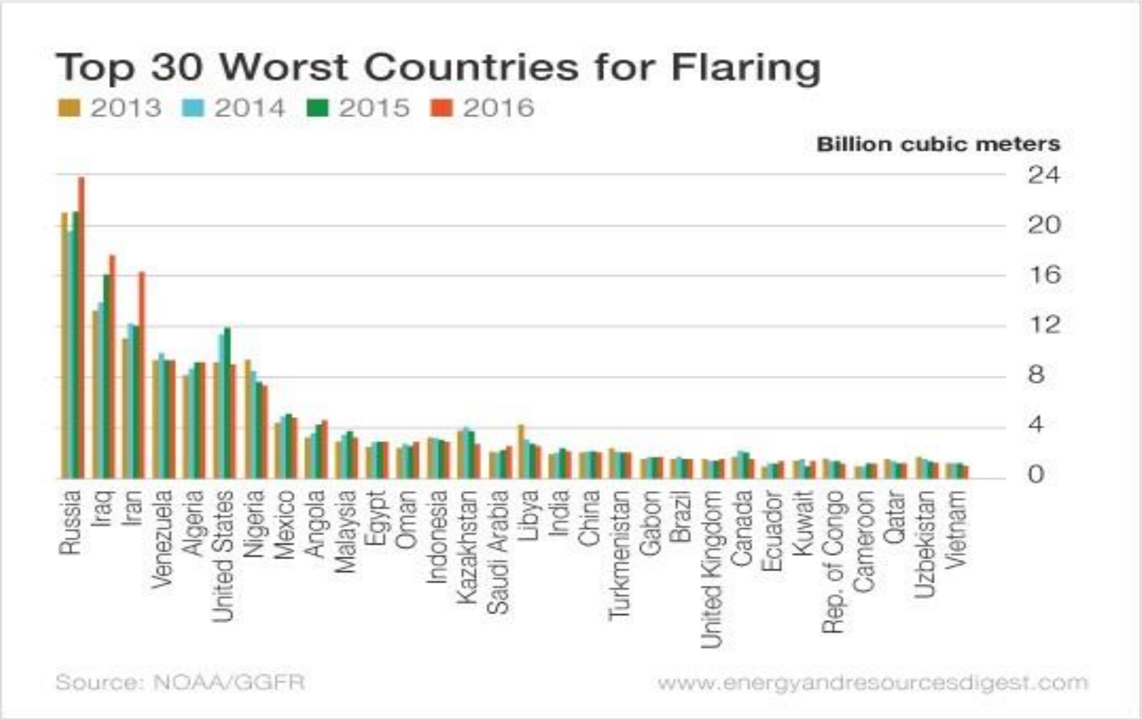


Figure 2.2: Gas production, utilization and flared since 1990 -2006 ***(Agboola et al, 2011)***

2.7 Forms of Stranded Gas Conversions

Summarized in the figure 2.3 below are the methods to convert natural gas from their stranded locations.

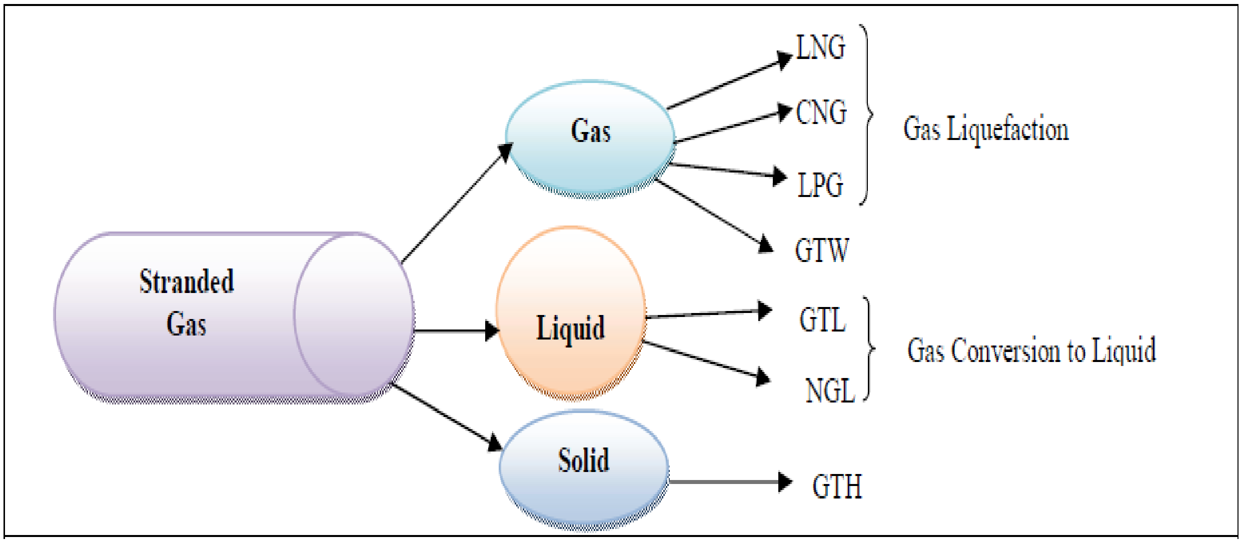


Figure 2.3: Forms of Qualitative conversion of natural gas. (Ekejiuba, 2017)

2.7.1 Gas Liquefaction

This exists originally in gaseous forms. Gas conversion by this means is with the sole intent of getting the gas to reach end user destinations. The gas is liquefied by a physical process and allowed to be in the liquid state until it reaches the end user location before the gas is converted back to gas phase before it can be used. Gas-to-wire is a means of utilizing the gas for electricity production onsite before part or all of it can be sent to the national grid. This enables the gas to be made useful because of its electrical value.

2.7.2 Conversion to Liquids

These methods employ technologies used to convert the gas to liquids such as GTL technologies and NGL processing plants. These conversion options are usually monetization options for the gas as the gas is sold and monetized while as liquids.

2.7.3 Conversion to Solids

This technology although relatively new harnesses the characteristics of Hydrate formation and occurrence to useful benefits. Natural gas is converted to hydrates by altering the temperature and pressure conditions. This enables very large volume of natural gas to be reduced to very small volume or lump mass of hydrate. This technology is new and may have the potential to replace LNG and CNG due to its less maintenance requirements. The hydrates formed are kept in special trucks while they are transported to enable the gas to remain in solid state till user destination is reached. The gas in solid state must be regasified before it can be utilized. Figure 2.4 shows the four basic routes that stranded gas could be put to transportation.

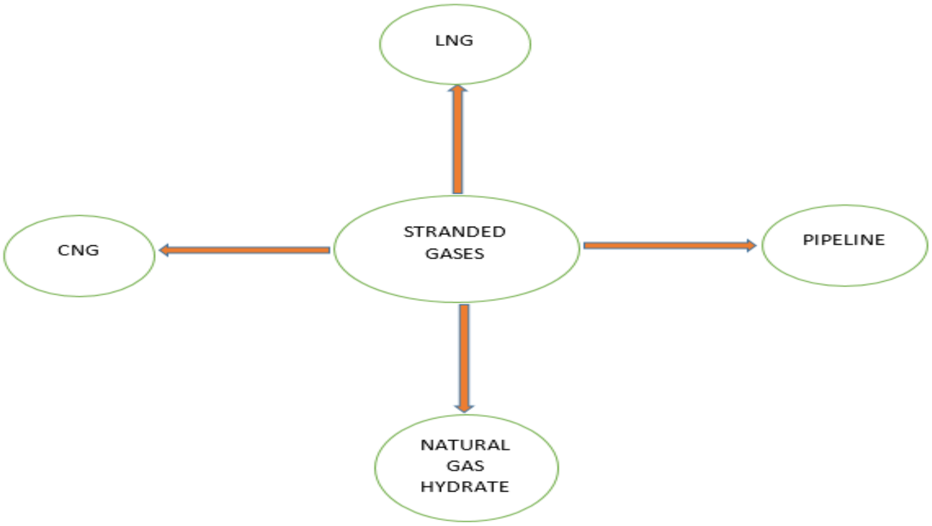


Figure 2.4: Different route for stranded gas transportation (Ekejiuba, 2017)

2.8Gas Monetization Technologies

Several gas monetization technologies exist that could be used to extinguish flares in Nigeria. Some of the most promising technologies are briefly discussed below.

2.8.1 Gas-to-Wire

Presently, much of natural gas transported is used for electricity generation at the final destination. Through gas-to-wire, GTW, generation of electricity can be done anywhere, particularly at or near the reservoir source and transported by cable to the required destination(s). For instance, offshore or isolated gas could be used to fuel and offshore power plant which would generate electricity for sale onshore or to other offshore customers. The challenges of GTW includes the high cost of installing power lines, significant energy losses from cables along the distance transmission lines and large volume of gas needed for power generation (Kanshio and Agogo, 2017).

2.8.2 Natural Gas Liquids (NGL) Extraction

Associated gas comprises methane and heavier hydrocarbon molecules commonly referred to as natural gas liquids (NGL). NGL comprises ethane, propane, butane and other heavier hydrocarbons. These heavier gases are dissolved in or volatilized from petroleum due to the changing pressure in the presence of crude oil exploration. Recovery of NGL from wet natural gas will upgrade the quality of commodity natural gas while heavier hydrocarbons recovered which are of higher value than methane and are sold.

2.8.3 Liquefied Natural Gas (LNG)

Liquefied natural gas (LNG) is natural gas that has been cooled to the point that it condenses to a liquid, this transformation occurs at a temperature of approximately -256^{o}F (-162^{o}C) and at atmospheric pressure. The technology aids the monetisation of natural gas resource especially where for technological or political reasons, gas transportation is less attractive. Therefore, LNG technology makes natural gas available throughout the world. Conventional LNG plants require large feed gas volumes in the range 450-600MMscfd or 3.8-5.5mtpa (metric ton per annum) per LNG train. Therefore, substantial investment in upstream gas gathering will be required to develop small gas reserve into onshore LNG. These factors limit the prospects of developing remote stranded gas via conventional LNG (Kanshio and Agogo, 2017).

2.8.4 Compressed Natural Gas (CNG)

These are gases transported in containers at high pressures, typically 1800 psig for a rich gas (significant amounts of ethane, propane, etc.) to roughly 3600 psig for a lean gas (mainly methane).

CNG can be a fossil fuel substitute for (petrol), diesel or propane fuel. This is made by compressing natural gas mainly methane to less than 1% of the volume it occupies at standard atmospheric pressure. It is stored and distributed in hard containers at a pressure of 200-248 bar (2900-3600psi) usually in cylindrical or spherical shapes. Its combustion produces gases with lower pollution and greenhouse gases than other conventional fuels. (Osokogwu, Ademujimi, and Ajienka, 2011)

CNG is used in some countries for vehicular transport as an alternative to conventional fuels (gasoline or diesel). However, the time to fill a tank with 3000 psig gas can be slow and frustrating. The filling stations can be supplied by pipeline gas but the compressors needed to get the gas to 3000 psig. The thermodynamics of gas compression (heat generation), and gas expansion (significant cooling), have to be considered in any gas processing operation and appropriate heat exchangers used, which adds significant costs.

2.8.5 Natural Gas to Hydrates (NGH)

Natural gas can be transported by conversion to solid form by means of natural gas to hydrates. Ordinarily, natural gas hydrates refers to crystalline compounds that are composed of water molecules and light molecules such as methane, ethane, propane, isobutane, nitrogen, carbon dioxide etc. Natural gas can be effectively and efficiently stored as gas hydrate. This is made possible through proper study and understanding of the processes involved to convert the gas to hydrate and the processes required to prevent the hydrate from dissociating. The storage of natural gas as hydrates will require the synthesis of the hydrate and its regasification. This process is beneficial because the density of natural gas hydrates reduces the space requirements for the storage of natural gas. These hydrates either as solids or slurries are transported easily using trucks to user destination where the hydrates are regasified and made ready for use.

The major driver for natural gas hydrate is simplicity, economics, safety and can readily be practice even in changing market conditions such as contractual agreements because the trucks are mobile. There are basically three approaches to this operation to make it an economical process:

1) First, large quantities of gas hydrates is formed to avoid high pressure recompression on recycle.

2) The conversion of the gas and water to hydrate in order to reduce the amount of water transported.

3) The transportation of gas hydrates to locations with small amount of refrigeration and dissociation units needed for the whole operation.

2.8.6 Gas-to-Liquids (GTL)

GTL is a catalytic process which involves the chemical conversion of natural gas (primarily methane) into liquid hydrocarbons. It is one of the appropriate options in utilization of natural gas. The main products include naphtha, diesel, gasoline, jet fuels, white oils, waxes, methanol, DME etc. they produce premium quality liquid fuels that burns cleaner than ones obtained from crude oil fractions. GTL technologies can be in large scale or in small scale (mini GTL).

Figure 2.5 shows the general overview of ways that stranded gas could be utilized. This depends mainly on its capacity (volume) and distance to user destination. One must consider the capacity and volume of the gas in choosing the best means of monetization or utilization of the gas.

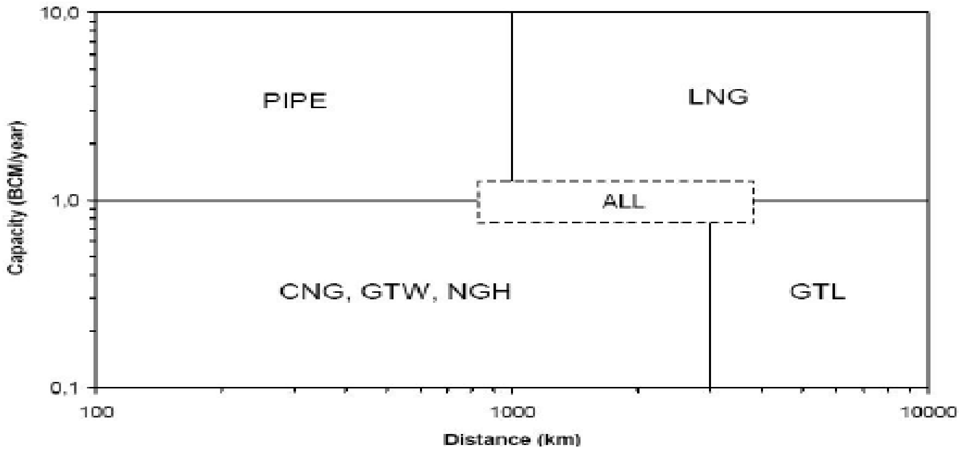


Figure 2.5: The capacity distance diagram (Onwukwe and Duru, 2015)

2.9 Factors Affecting Gas Monetization Options

The two main parametres to be considered in gas monetization are the quantity of gas available and the distance to the final market (Chabrelie and Rojev, 2010).

1. For quantities of gas large enough, pipeline or LNG transportation remain the most competitive options. By reducing the transportation cost, technical innovation can contribute to widen significantly the conditions for which these options are economically acceptable, which means increasing the maximum distance or reducing the minimum capacity for which a new project will be considered feasible.
2. For large distances and mid-to-large quantities of gas, GTL conversion appears a potential attractive option, especially if pipeline or LNG transport is not feasible due to distance.
3. For small quantities of gas, reinjection is the option to choose if no market exists at a short distance. But other options available to capture the gas are GTW, CNG, and NGH.

2.10 Gas-to-Liquids Technology

In general, the term gas-to-liquid (GTL) refers to a small number of technologies designed to convert natural gas or other gaseous hydrocarbons such as gasified coal, gasified biomass into longer-chain hydrocarbon liquid synthetic fuels (such as diesel, gasoline, naphtha, methanol, Di-methyl ether etc.) either via direct conversion using non-catalytic processes that convert methane to methanol in a one step or indirect conversion via syngas as an intermediate, such as Fischer-Tropsch method, Mobil process, and the syngas to gasoline plus (STG+) process (Anyasse and Anyasse, 2016) as alternatives to the traditional refining of crude and other natural gas commercialization routes such as liquefied natural gas (LNG), liquefied petroleum gas (LPG). From these two main paths are available for GTL. They are

1. The direct conversion means
2. The indirect conversion means

The direct conversion means uses catalysts to convert the methane to methanol. It is a one-step means and mostly used in the production of methanol and dimethyl ether. The indirect means uses technologies that convert the natural gas to syngas, an intermediate conversion product before the catalytic synthesis of the syngas into liquids using known technologies such as the Fischer Tropsch technology or the Mobil technology. Figure 2.6 show the different routes for indirect conversion of gas to liquid products via Gas-to-liquids technology. The three main indirect conversion means are Fisher-Tropsch, the Methanol and the Dimethyl ether (DME).

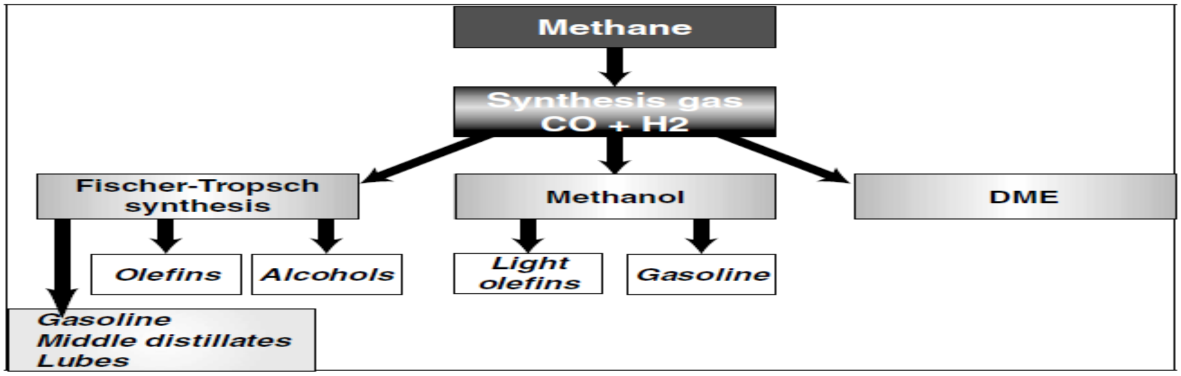


Figure 2.6: Different route for indirect conversion means (Chabrelie and Rojey, 2010)

Figure 2.7 gives a more detailed classification of GTL conversion routes. While indirect route requires first to convert the gas to synthesis gas, the direct routes does not need intermediate conversion to synthesis gas before the conversion to finished products. Direct routes are the production of hydrogen and methanol.

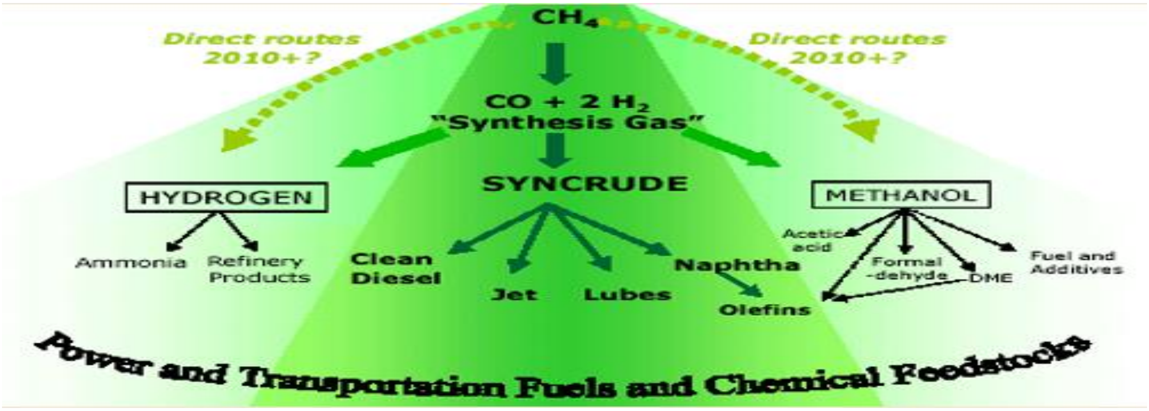


Figure 2.7: Classification of GTL routes (Ekejiuba, 2017)

2.11GTL Technology Processes

There are four basic steps in the Fisher-Tropsch GTL plant processes. These are

1. The feed gas pre-treatment
2. The synthesis gas production

3. The Fischer Tropsch reaction
4. The product upgrading

2.11.1 The Pretreatment of the Feed Gas

The associated gas coming from oil wells after separation contains impurities and liquid condensable liquids that must be removed before the resulting gas is ready for use in the GTL plant. Usually the kind of processing and degree of purity depends on the nature of the natural gas and the degree of primary oil field separation and field processing of the gas if there was any. Sometimes the gas coming from the field may not require much treatment and processing before they can be used in the GTL plant. The reason for treatment is to remove contaminants in the gas that would pose problems for the GTL plant. The gaseous contaminant in natural gas is Sulphur compounds like H_2S and mercaptans, CO_2 and Nitrogen.

The presence of H_2S in the gas makes the gas sour. Both CO_2 and H_2S are called acid gases and are the major constituent of gaseous impurities in the gas. The pretreatment of the flare gas involves removal of the acid gases. This is called sweetening of the gas.

The process selected for sweetening a sour gas depends on the general conditions:

1. H_2S and mercaptan concentration in the sour gas, and sales gas H_2S and total sulfur limits
2. maximum design flow rate
3. raw gas inlet pressure
4. requirement for sulfur recovery
5. acceptable method of waste products disposal

The most important operation in the pretreatment is the desulphurization of the gas. In some operations depending on the choice of technology, CO_2 may be allowed in the gas stream. The sulphur content in the gas stream should never exceed 1ppm. For this to occur process temperature should be around 400^{o}C.

Depending on the degree of liquid hydrocarbon content of the natural gas, it may be required to recover free liquid hydrocarbons in the gas stream as NGLs. Large volumes of heavier hydrocarbons lead to formation of olefins which is undesirable. The remaining liquid hydrocarbons which proved difficult to recover are taking care of in the pre-reformer section of the syngas generation unit.

2.11.2 The Synthesis Gas Production

After the treatment of the natural gas and the removal of free hydrocarbon liquids as NGLs, the next step in the GTL process is the conversion of the pre-treated natural gas to synthesis gas (syngas). This entails the conversion of natural gas into a mixture of hydrogen and carbon monoxide known as synthesis gas. This step contributes the largest capital expense in the GTL process. In some plants, the syngas production step contributes over 50% of the overall capital cost of a GTL plant (Asberg-Petersen and Christensen, 2002). For this reason, there is a great economic importance in the choice of the right type of technology to be utilized in the syngas production to minimize the cost associated with it. Thus, a lot of extensive research is ongoing in this area aimed at optimizing this part of GTL. This has yielded a wide range of optional technologies available for utilization in syngas production.

1. Pre-Reforming

Pre-reforming is part of the syngas production unit. Not all the heavier hydrocarbons were recovered in the NGL recovery from the natural gas feed. Thus, ethane plus fractions are still present in the natural gas in gaseous phase with methane. The presence of this heavier hydrocarbon in the methane may lead to the production of olefins during the syngas production process. To avoid this, a pre-reformer is applied as a first step in the production of syngas (Panhi, 2012). This has shown to increase the capacity of the plant by 10-20% and hence make the plant more economically feasible.

A pre-reformer is a catalytic fixed bed reactor operating adiabatically at about 500^{o}C. In this temperature range higher hydrocarbons are converted to methane and CO_2 according to the reaction. (Panahi, 2010)

$$C_nH_{2n+2} + \frac{1}{2}(n-1)H_2O \rightarrow \frac{1}{4}(3n+1)CH_4 + \frac{1}{4}(n-1)CO_2 \qquad 2.1$$

The reaction can also be controlled to produce syngas according to the reaction below

$$C_nH_m + nH_2O \rightarrow \left(n + \frac{m}{2}\right)H_2 + nCO \qquad \text{For n} \geq 2 \qquad 2.2$$

One important advantage of including the pre-reformer in the syngas production unit is that it reduces the chance of carbon deposition later in the process. With higher temperature levels the probability of carbon formation will increase. (Guettel, 2008)

There are several processes and technologies for the main syngas production. The basic ones are

1. the steam methane reforming (SMR)
2. the partial oxidation reforming (POX)
3. the autothermal reforming (ATR)

2. Steam Methane Reforming (SMR)

This involves the reaction of steam with methane over a fixed be of Nickel based catalysts. The reaction takes place at a high temperature (over 750^{o}C). The main reactions equations occurring here are the steam methane reforming and the water gas shift reaction. The main principle of the technology is the catalytic endothermic conversion of steam and methane to hydrogen and carbon monoxide (Wilhelm, Simbeck, Karp and Dickenson, 2001). Because the reaction is endothermic, energy has to be supplied into the system. The energy needed here is supplied by the combustion of fuel (usually natural gas) outside of the reformer tubes. There is also a possibility of replacing some of the entering steam with CO_2. This replacement depends on the desired ratio of H_2/CO for downstream process. The equation of reaction of steam with methane is given below (Christiansen and Rostrup-Nielsen, 2011)

$$CH_4 + H_2O \ \rightarrow CO + 3H_2 \Delta H = 206KJ/mol \qquad 2.3$$

The water gas shift reaction is given as

$$CO + 3H_2 \ \rightarrow \ 3H_2 + CO_2 \Delta H = -41KJ/mol \qquad 2.\ 4$$

A major challenge of this technology is providing sufficient heat into the reaction system to maintain the require reaction temperature. This requires large capital investment. Also, a substantial amount of excess steam is required to prevent coking of the reactor tubes typically 2.5: 1 in terms of molar steam to carbon ratio. Another drawback of the steam methane reforming is that the H_2/CO ratio produced. The theoretical H_2/CO ratio is 3: 1 but the actual ratio is 5:1 (75% H_2, 15% CO and 10% CO_2) (Al-Saadoon, 2007). The ratio is much higher than the required 2:1 ratio required for the downstream Fischer Tropsch system unit. Also, SMRs are very large in size and may not be suitable where sizing and compactness of the plant is a factor to consider such as in modular GTL units.

The advantage of this process is that it does not require oxygen and there is no need for the air separation unit. The SMR is more commonly used in hydrogen gas production.

Figure 2.8 illustrates a top-fired steam methane reformer equipped with its feedstock purification processes. Hydrocarbon feed gas enters from the bottom of the tower and goes to a purification unit where acid gases and other impurities are removed. The resulting treated gas then goes to the steam unit where steam reacts with the gas at high temperatures to form synthesis gas. The synthesis gas is a mixture of hydrogen and carbon monoxide.

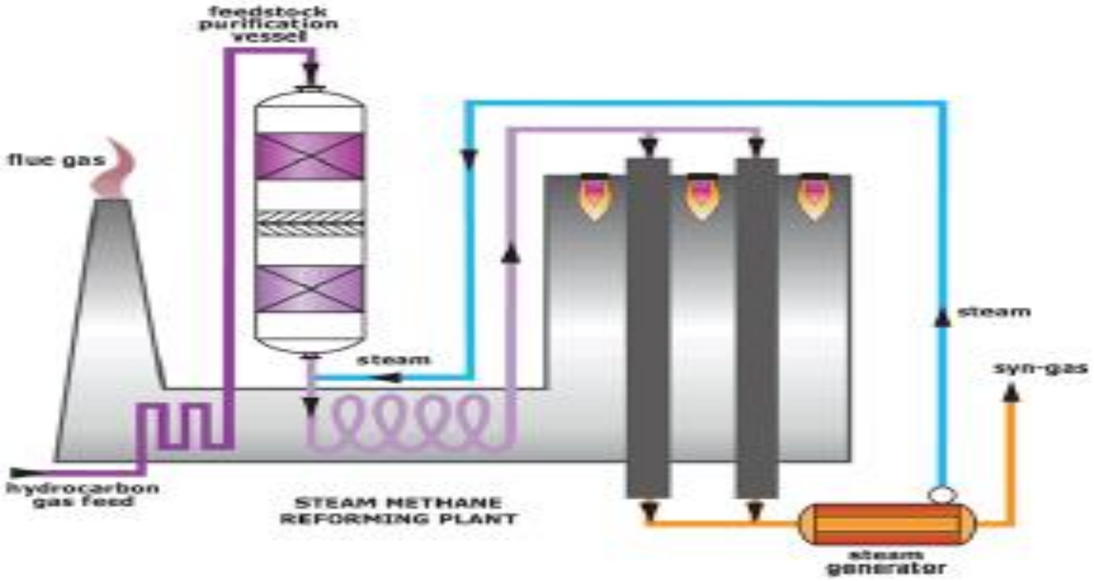


Figure 2.8: A top-fired steam methane reformer including the feedstock purification process (Rafiee and Hillestad, 2012)

3. Partial Oxidation Reforming (POX)

This is an exothermic, non-catalytic reforming process for the production of syngas (below (Christiansen and Rostrup-Nielsen, 2011)**.** As a consequence of operating without a catalyst, the operating temperature is very high at about 1200^{o}C to 1400^{o}C (Anton, 2001). Methane and oxygen are needed as the feedstream fuels, steam is not needed. POX produces a H_2/CO ratio that is theoretically 2:1, but the actual H_2/CO ratio is 1.8 (62% H_2, 35% CO and 3% CO_2) (Gaffney, Cline and Assocs, 2001). It requires high volume of oxygen which makes it expensive. The POX equation of reaction is given below.

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \Delta H = -36KJ/mol \qquad 2.5$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \Delta H = -803KJ/mol \qquad 2.6$$

The second equation is the reaction of methane with more of the oxygen to produce carbondioxide and water. This must be checkmated. Figure 2.9 below is an illustration of partial oxidation system for synthesis gas production. The figure shows the inlet points where natural gas and oxygen are fed into the units and an outlet point where the synthesis gas formed in the process is collected after production in the unit.

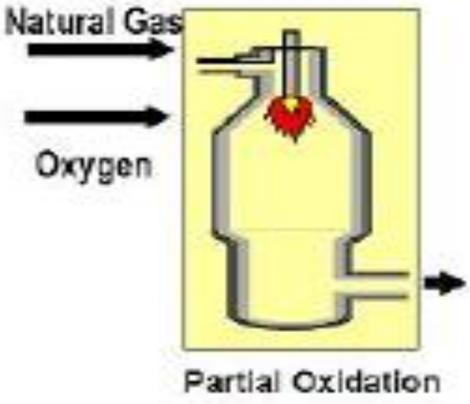


Figure 2.9: Partial oxidation reforming (Rafiee and Hillestad, 2012)

4. Autothermal Reforming (ATR)

This is the most promising technology of the three mentioned in terms of efficiency and economy. It combines some of the best features of steam methane reforming and partial oxidation reforming. (Hao, 2008). An ATR consists of a burner, a combustion chamber and a catalyst bed located inside a refractory steel vessel. Methane, steam and oxygen are injected into the combustion zone where the partial and complete oxidation of methane occurs at 1900^0C. Unconverted methane continues through the reactor end and enters the reforming zone where catalytic reforming takes place. A water shift gas may form in the catalytic zone of the reformer (Christiansen and Rostrup-Nielsen, 2011). Equation 2.5 and 2.6 are applicable

From equation 2.5 $CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \Delta H = -36KJ/mol$

From equation 2.6 $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \Delta H = -803KJ/mol$

From equation 2.3 $CH_4 + H_2O \rightarrow CO + 3H_2 \Delta H = 206KJ/mol$

A water gas shift reaction may also be seen in the process as shown in equation 2.4

$$CO + 3H_2 \rightarrow 3H_2 + CO_2 \Delta H = -41KJ/mol$$

The general stoichiometric equation for the autothermal reforming is given below

$3CH_4 + H_2O \rightarrow 3CO + 7H_2$ 2.7

Figure 2.10 is an illustration of autothermal reforming process. The autothermal reformer requires three feedstocks which are natural gas, steam and oxygen. The oxygen is produced in the air separation unit which may be part of the autothermal reformer system or externally designed.

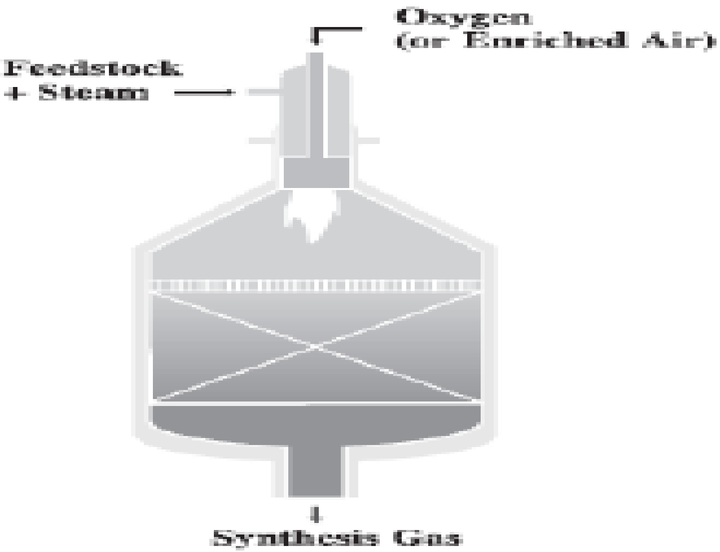


Figure 2.10: Autothermal reforming (Asberg-Petersen *et al*, 2003)

ATR does not require external heating source. The heat is generated from the POX. But it requires an air separation unit. It is more compact, simpler and more efficient than steam reforming and is proposed for mega GTL projects (Christensen and Primdahl, 1994). Figure 2.11is an overview of various reforming technologies available and their corresponding H_2/CO ratios for both naphtha and natural gas. From the figure autothermal reforming (ATR) has the most favourable range of H_2/CO ratio.

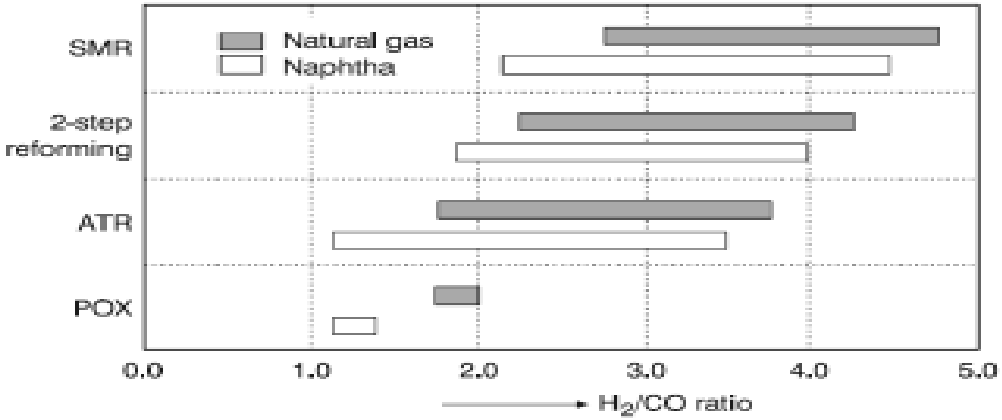


Figure 2.11: Overview of the various reforming technologies and their corresponding H_2/CO ratio for both naphtha and natural gas (Wilhem et al, 2001).

The theoretical H_2/CO ratio for ATR is 2.3 from the generation equation of reaction (i.e. $3CH_4 + H_2O \rightarrow 3CO + 7H_2$) but the theoretical H_2/CO ratio is 2.0 (64% H_2, 32% CO, and 4%CO_2.) (Gaffney, cline and Assocs, 2001).

Table 2.1: Table of advantages and disadvantages of the various syngas production technologies.

S/N	PARAMETER	SMR		POX		ATR	
		ADVANTAGES	DISADVANTAGES	ADVANTAGES	DISADVANTAGES	ADVANTAGES	DISADVANTAGES
1	units in operation	High			Low		Low
2	operating temperature		Low	High		Medium	
3	H2/CO ratio		High		Low	Favourable	
4	Feedstock requirement		Limited (CH4)	Unlimited			Limited (CH4)
5	Oxygen requirement	No			Yes		Yes
6	Steam requirement		Yes	No			Yes
7	External heat requirement		Yes	No		No	
8	Catalyst Requirement		Yes	No			Yes
9	CO2 production		High	Low		Low	
10	CO2 recycling		Yes	No or Low		No or Low	
11	Sulhur tolerance		None	Yes			None
12	Methane Slippage		High	Low		Low	
13	operational difficulty (start/stop)		High	Medium		Low	
14	Coking	No			Yes		Yes

Conventional GTL technologies especially Fischer-Tropsch synthesis are net generators of CO_2. The intensity of the CO_2 generated depends on age and size of the plant. The CO_2 generated comes from the reactions in the FT reactor and the reformer and the combustion of natural gas as fuel in the furnaces. There is need to reduce the CO_2 emissions from GTL plants. To address the emissions from the reformer section newer technologies have to be devised to handle the CO_2 and convert it to use in the process mechanism. One of such method is the development of technologies that will utilize CO_2 in the reforming reactions as one of the reactant species. This method has been tested and proven and there are two ways CO_2 can be utilized in the reformer section; they are dry reforming of methane wherein CO_2 and methane are the only reactant species and Bi-reforming of methane wherein CO_2, steam and methane are chosen as the reactant species.

5. Dry Reforming of Methane (Dry CO_2 Reforming)

The dry reforming of methane produces synthesis gas from carbon dioxide and methane (CH_4). The dry reforming produces synthesis gas with H_2/CO ratio equal to 1, much lower than that of the synthesis gas produced by the steam reforming. It also appears that the amount of heat to be supplied is much greater than that required for steam reforming. The advantage is that the CO_2 present in the natural gas need not to be separated. Furthermore, the technologies help to reduce the amount of CO_2 in the effluent by recycling the effluent CO_2 for use as one of the reactants thereby drastically reducing the volume of pollution since most of the gaseous by products are CO_2.

The equation of reaction for dry reforming of methane is given below

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H_{298} = 247KJ/mol \qquad 2.8$$

6. Bi-Reforming of Methane (Steam/CO_2 Reforming)

This is also called steam/CO_2 reforming. Steam, CO_2 and methane are the reactants. This is more favourable to FT reactors because the H_2/CO ratio is two. Steam/CO_2 reforming consists of three equilibrium reaction given below.

From equation 2.3 $CH_4 + H_2O \rightarrow CO + 3H_2 \Delta H = 206 KJ/mol$

From equation 2.4 $CO + H_2O \rightarrow CO_2 + H_2O \Delta H = -41.6 KJ/mol$

According to equation 2.8: $CH_4 + CO_2 \rightarrow 2CO + 2H_2$ $\Delta H_{298} = 247$KJ/mol

The general stoichiometric equation for steam/CO2 reforming is given below

$$CH_4 + CO + H_2O \rightarrow 4CO + 8H_2 \Delta H = 220 KJ/mol \qquad 2.9$$

For the bi-reforming of methane its main advantage over dry reforming of methane is the stoichiometric H_2/CO ratio of 2. This is a more favourable syngas composition for most downstream operations, such as conversion to liquid fuels via Fischer- Tropsch synthesis (FTS). This ratio can also be easily varied by adjusting the inlet composition of the feed gases with respect to CO_2.

2.11.3 Fischer-Tropsch Reaction

The conversion of produced syngas (CO and H_2) to liquid hydrocarbons takes place in the Fischer Tropsch reactor. The reaction process is a chained growth reaction on carbon monoxide and hydrogen on the surface of a heterogeneous catalyst (Patel, 2005). The process proceeds by addition of methane group to the chains. This is known as methanation. The length of the hydrocarbon chain is determined by the Anderson-Schulz-Flory distribution in 1978. There may be some formation of methane in the process which is undesirable and must be controlled. The reaction equation is given below (Panahi, 2005).

$$nCO + 2nH_2O \rightarrow n(-CH_2-) + nH_2O \qquad 2.10$$

The methane formation equation is

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad 2.11$$

The methane formation must be prevented by adjustment of parametres to favour the production of the longer chain hydrocarbon. This is achieved by the catalyst used in the FTS unit.

The main attribute needed for the reactor is effective heat removal and temperature control, as Fischer Tropsch reactions are highly exothermic. High temperature may deter the vessel material, deactivate the catalysts and favour the production of methane over long chain hydrocarbon which is undesirable. Fischer Tropsch reactions can be run at either high temperature or low temperature. The high temperature HTFT reaction is at about 300-350^{o}C while the low temperature LTFT reactions are at about 200-240^{0}C. The two processes result in different products and also use different types of reactions. The high temperature Fischer Tropsch (FT) reaction are suited for the production of light hydrocarbon ends such as gasoline and olefins while the low temperature FT reactions are suited for the production of heavier products such as wax (Dry, 2002)

There are three basic types of technology for fisher Tropsch reactions. These are

1. The tubular bed reactors
2. The fluidizes bed reactors (both fixed fluidized bed and circulating fluidized bed reactors)
3. The slurry phase or slurry bubble column reactors.

For the HTFT reaction, there will be only two phases present in the reactor because of the high temperature, i.e. syngas and solid catalyst. The two main technology for the HTFT reaction are the fixed and the circulating fluidized bed reactors. In the LTFT process, liquid is present due to low temperature giving rise to three phases being present in the reactor. The multi tubular bed reactor has been more in use for the LTFT process. But recently the slurry phase or slurry bubble column reactors are gaining attention in the LTFT process (Jager, 2003)

2.11.4 Fischer-Tropsch Catalysts

For Fischer-Trospch process, the metals in group VIII B of the periodic table are considered to be suitable for use as catalysts (Guettel, 2008). This includes Iron, Cobalt, Nickel and Ruthenium. However, the two most common in use are the iron and cobalt. Nickel produces much methane and ruthenium is very expensive to be applied industrially.

Although cobalt catalyst is more expensive than iron, they have a longer lifetime than the iron catalyst, the replacement for cobalt and iron catalyst are at about 5 years and 6 months respectively. Cobalt is about 1000 times costlier than scrap iron when compared (Dry, 2002). Iron catalysts are considered to have water gas shift activity for the Fischer Tropsch reactions while cobalt does not. Thus, for iron catalysts more hydrogen will be produced at the expense of the carbon monoxide. The water produced in the FT reaction however inhibits iron catalyst kinetically and hence cobalt has higher activity and is considered the preferred choice when high conversion per pass is required. For LTFT both iron and cobalt are used industrially but for HTFT process only iron catalysts are applied. This is because excess amount of methane is produced in the HTFT process when cobalt is used as catalyst.

Koo (Koo, Roh, Seo, Yu and Yoon, 2008a; Koo, Roh, Seo, Yu, and Yoon, 2008b) listed the criteria for choosing F-T catalyst considering the molecular adsorption and formation effect to overcome the disadvantages listed above. They also introduce an effective and stable nano-sized catalyst for the F-T reaction. It also tells the way to adjusting the usage ratio other than controlling the feed steam to gas ratio, by looking into the agglomeration, dispersion and activity of the different types of catalyst. To increase the economic use cycle of the catalyst, recycling the catalyst is a mandatory way.

Brumby, Verhelst, and Cheret. (2005) discusses some of the challenges and the economic concerns when considering catalyst recycling strategy. In their paper the demand, supply and prices of the most used catalysts for the oil refining process were given. To facilitate economically valid recycling process, they combined recycling of the base metal with the recycling of the precious metal, weighing two potential methods: precipitation or pyrometallurgical method.

The following are factors associated with lowering activity for F-T catalyst (Steynberg and Dry, 2004)

1. Fouling in catalyst pores will bring diffusion problems for catalyst.
2. Elemental carbon depositing on the surface of catalyst, will cause less contacting area for catalyst and reactant.
3. Poisons from feed gas in the form of H2S or sulphur compounds will cause the Catalyst less active.
4. Due to hydrothermal sintering, catalyst will be less active.
5. Due to oxidation, the catalyst metal will become inactive crystals.

In the presence of cobalt catalyst, heat removal is a serious issue to consider. If the heat exchange is not effective enough, large amount of methane will be produced. Heat removal is also important for both catalysts since improper temperatures will result in formation of light hydrocarbons and coke that may lead to deactivation of active sites on catalysts (Steynberg and Dry, 2004).

2.11.5 Product Selectivity

Carbon distribution in the Fischer-Tropsch synthesis is determined by the probability of chain growth on the catalyst, also called the α-value. The product distribution is often explained by a statistical distribution called Anderson, Schultz and Flory (ASF), given by:

$$w_n = n(1-\alpha)^2\alpha^{n-1} \qquad 2.12$$

Where n is the number of carbon atoms, and w_n is the weight fraction of a component with length n, αindicates the probability of another chain propagation step and consequently

1-αindicates the probability for chain termination. Chain length of hydrocarbons depends on the nature of the catalyst and the chosen process conditions. If longer chains are desired, it is beneficial to decrease the H_2/CO ratio and the temperature while increasing the pressure level. (Chorkendorff and Niemantsverdriet, 2007). Table 2.2 gives the common available catalyst used for Fisher-Tropsch reactions and their α values.

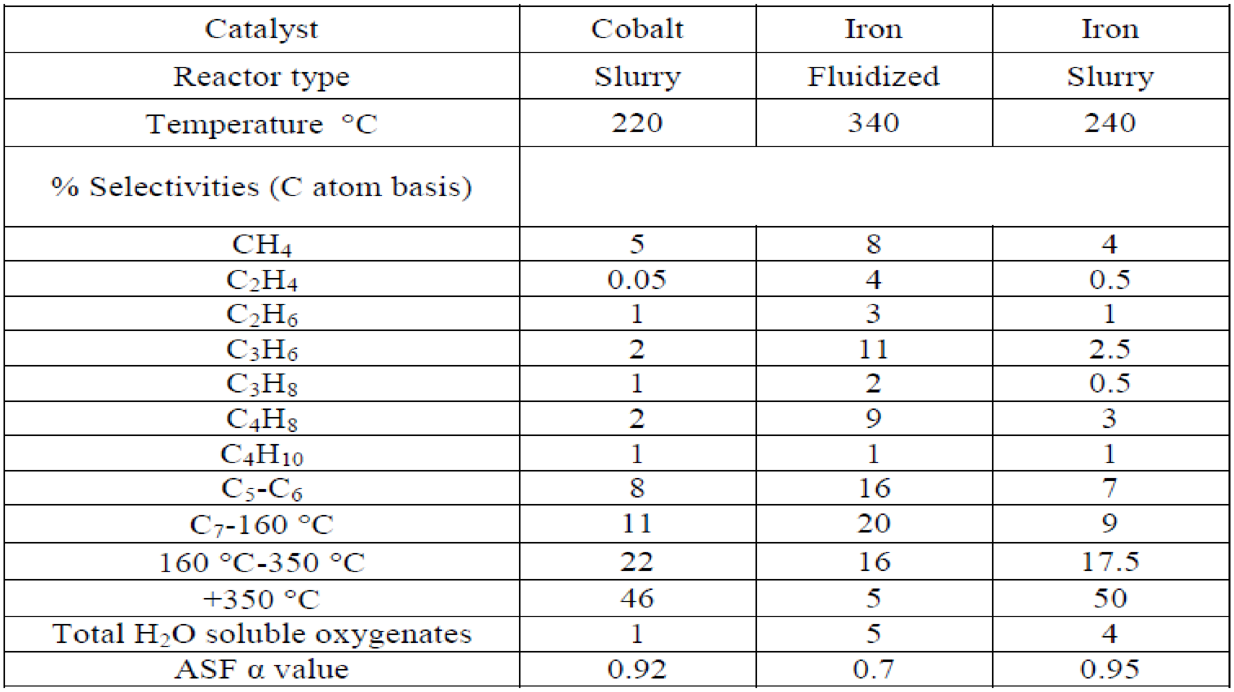
Table 2.2: Common F-T catalyst and their α values

CATALYST	α	MAIN PRODUCT
Nickel	low	Methane
Iron	0.65-0.70	Gasoline
Cobalt	0.75-0.85	Waxes

In practice it has been difficult to explain the complex kinetic behaviour that occur here. There are some deviations from the ASF distribution. One major deviation is related to the production of methane and ethane. The actual methane production is usually higher than that predicted by the ASF distribution while the ethane produced are considerably lower than that predicted by the ASF.

Table 2.3 shows various catalyst uses in different Fisher-Trospch product distribution

Table 2.3. Example of a pilot F-T product distribution (Steynberg and Dry, 2004)



Catalyst	Cobalt	Iron	Iron
Reactor type	Slurry	Fluidized	Slurry
Temperature °C	220	340	240
% Selectivities (C atom basis)			
CH_4	5	8	4
C_2H_4	0.05	4	0.5
C_2H_6	1	3	1
C_3H_6	2	11	2.5
C_3H_8	1	2	0.5
C_4H_8	2	9	3
C_4H_{10}	1	1	1
C_5-C_6	8	16	7
C_7-160 °C	11	20	9
160 °C-350 °C	22	16	17.5
+350 °C	46	5	50
Total H_2O soluble oxygenates	1	5	4
ASF α value	0.92	0.7	0.95

2.11.6 Product Upgrading

The product upgrading decides the composition of the final product pool. The main processes are the cracking of the long chain hydrocarbons into desired products such as naphtha, diesel, gasoline, kerosene etc. some of the methods in the product upgrading are:

i. Hydrocracking

ii. Hydrotreating

iii. Hydroisomerization

iv. Separation

Separation is typically the way to tackle the products with many phases. Pressure requirements should be met to facilitate the atmospheric storage. First, light gases are separated. Oxygenated compounds are usually removed from the liquid for the ease of later processing. Then, through fractionation and extractive distillation olefins could be removed from the straight liquid products. They are either oligomerised, alkylated or hydroformylated to produce desired products or blended with other liquid products for the mixing use. The other products are generally converted into naphtha and diesel by the means of hydrogenation step and fractionated. The naphtha can be further processed to gasoline. For LTFT processes with cobalt catalyst only hydro-processing and separation are employed since the olefin content is low (Steynberg and Dry, 2004; Perry and Green, 1984; Maiti, et al., 2001).

Usually, the produced diesel is blended with special chemicals to enhance stability. At the same time, other methods may be used to improve properties such as lubricity. Chemical conversion is one method involving hydro-isomerization, in which straight chain hydrocarbons are changed to branched ones for improving cold flow properties (Maiti, et al., 2004). While long chain hydrocarbons have two ways to go. One is hydrocracked to further provide naphtha. Alternative one is hydro-processed to high quality lubricant base oils. To get further cuts or fractions, vacuum or short path distillation is used to produce special demanded wax or products (Steynberg and Dry, 2004).

In light of the increasing demand for diesel for transportation and industrial uses, producing diesel mainly from GTL process is a good choice, especially this diesel is very low in sulfur content. Thus, wax could be cracked with certain selectivity to diesel with the help of special catalysts, and produced naphtha is another resort to get diesel through various processes.

2.11.7 Hydrogen Plant

A hydrogen plant is necessary for a refining plant to function. This hydrogen amount will be used for both sulfur removal and upgrading of the hydrocarbon products. Older hydrogen plants consist of a steam methane reformer (SMR) that converts the hydrocarbon feed to a syngas mixture. The combination of a high temperature converter (HTSC) and low temperature shift converter (LTSC) shifts the CO to hydrogen. The produced amount is subsequently sent to a CO_2 removal unit followed by a methanation step which converts the remaining CO and CO_2 to methane and water. With this configuration a product gas contains normally 95 to 97% hydrogen.

In recent years large technology enhancements have been made in the field of hydrogen purification. The CO_2 removal unit and methanation step are now replaced by a pressure swing adsorption unit. This change together with other design and technology improvements has resulted in a product stream with purity of typically 99.99 %, of hydrogen. The absorption unit operates with rapid cycles due to isothermal operation, reducing vessel size and lowering capital cost for the unit. The absorbent is regenerated by reducing pressure inside the vessel as indicated by the name of the unit. An industrial size PSA normally requires 4 to 12 absorbent vessels in combination to process the required amount.

2.12Review of Works on GTL Optimizations

Lu (Lu and Lee, 2007) has shown that the feed gas composition to the F-T synthesis plays a major role in determining the chain length and the hydrocarbon product distribution. Several studies that utilized data collected from pilot plant, lab experiment, and semi-simulation looked at influence of syngas composition on product yields, energy efficiency, and carbon utilization (Suehiro, et al., 2004; Keshav and Basu, 2007). They suggested by later recycling process to adjust H_2/CO ratio, the carbon efficiency for the process will increase to 50% based on the case in that paper. CO_2 function was also examined and only a diluting role was found under current commercial slurry phase F-T process.

Another paper indicates (Iandoli and Kjelstrup, 2007) that heat and power exergy is related in some way to operation cost. It's better to fully utilize the heat and find a balance between power consumption and work produced. Simulation work has been done based on slurry phase process using cobalt based catalyst focusing on the efficiency of both HTFT and LTFT. Air separation unit is indicated to be a major power consumption unit and heat released from F-T reactor can be a supplement to it. By controlling CO_2 content waste exergy will be adjusted.

Issues with reactor modeling have been addressed by some researchers (Hao, 2008; Khoshnoodi, 1997; Levenspiel, 2002; Sehabiague, et al, 2008). Using a rigorous calculation of vapor-liquid equilibrium Quasi-steady-state model was proposed to be suitable to the transient simulation considering two chain propagation mechanisms (Ahon, et al., 2005; Wang, 2004; Zhang and Zhu, 2000). Results showed that the hydrocarbon product distribution could be explained by including both olefin readsorption and the propagation mechanisms. Process simulation analysis has been conducted on the once-through concept and recycle model to investigate the carbon efficiency and the selectivity towards $C5^+$. Other simulation comparisons have been tested to evaluate different property method applicable in the process (e.g., Ahon, et al., 2005; Hao, et al., 2008; Wang, 2004; Zhang and Zhu, 2000).

A new GTL process is proposed (Jaramillo, 2007; Larsson, 2007; Suehiro, et al., 2004) to be candidate in natural gas utilization mainly focusing on reducing greenhouse gas emissions although GTL is quite low in other emission discharges. Energy system aspects of this process are summarized with an attempt to get an overview of the pathway, figuring out the economic issues with the emissions.

A full product life cycle assessment was conducted on GTL process by three joint companies (Five Winds International Inc., 2004). Result showed that waste released from GTL is dramatically reduced compared with other diesel production processes. By constructing a model to research economy influence, they concluded that GTL industry will bring significant benefits to government and society, conceiving a very promising industry in market. Figure 2.12 illustrates the percentage CO_2 produced from each unit of the GTL plant. It can be observed that most of the CO_2 is produced in the Reformer unit

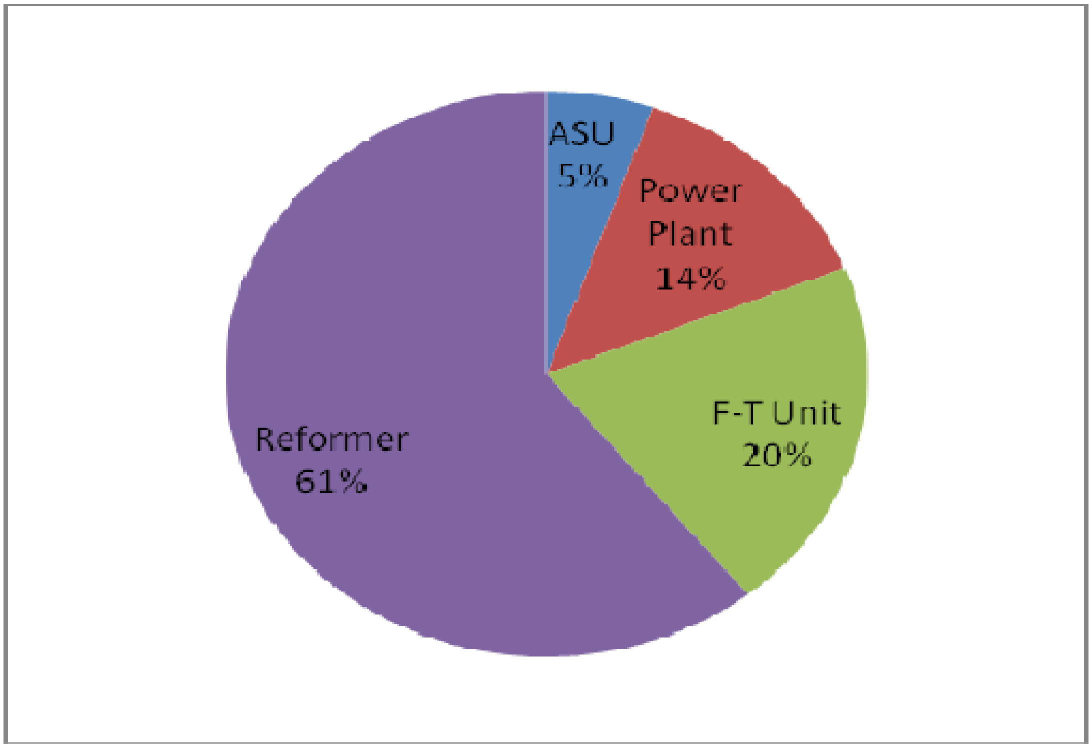


Figure 2.12: CO_2 from each unit (Iandoli and Kjelstrup, 2007)

2.13 Large Scale GTL and Small Scale GTL Plants

GTL can come in large scale plants and in small or mini plants

2.13.1 Large Scale GTL Plants

Since conventional FT reactors are designed to work on a large scale, traditional GTL plants are built to process substantial amounts of gas. These plants require large capital investment, and they are only economically viable for plants producing approximately 30 thousand barrels per day (Mbpd) or more of liquid fuel.

The cost and capacity constraints explain why only few GTL plants are operating commercially today: the Bintulu plant in Malaysia, the Mossel Bay plant in South Africa, and the Oryx and Pearl plants in Qatar.All operate on a vast scale. The Pearl plant, for example, cost approximately $18 billion to $19 billion to build. With a design capacity of 140,000 bpd of GTL product and 120,000 bpd of associated condensate and liquid petroleum gas (LPG), Pearl is expected to produce about 3 billion bbls of oil-equivalent (boe) fuel over its lifetime. Only 6% of the world's known gas fields are large enough to sustain GTL plants on these scales, and the majority of potential undiscovered gas finds are thought to contain less than 1 trillion cubic feet (Tcf) of gas—an amount too small to make conventional GTL plants economic (World Energy Outlook, 2011)

A large-scale GTL plant can convert 300 million metric standard cubic feet per day (mmscfd) of gas to 30,000 bpd of diesel or gasoline, while a methanol plant produces about 2500 tonnes per day (tpd) of methanol from 75 mmscfd of gas. By taking advantage of new technologies, such as microchannel reactors, to shrink the FT and SMR hardware, GTL plants can be scaled down to provide a cost-effective way to take advantage of smaller gas resources (see sidebar). GTL plants based on the use of micro-channel FT reactors can be operated on a distributed basis, with smaller plants located near gas resources and potential markets.

2.13.2 Small Scale GTL (Mini GTL) Plants

Small scale or mini GTL is a GTL technology that operates in smaller volumes. They convert smaller volumes of natural gas feedstock into liquid petroleum products. They are useful in areas of stranded gas or remote areas where there is no pipeline facility to channel the gas to a central processing or larger GTL facility (White, 2012).

In large GTL facility, the gas supply comes from long pipeline that must supply adequate volumes of gas to the facility. The Escravos pipeline for example receives it gas supply from the Escravos gas pipeline. The EGP is a huge pipeline that carries natural gases from several field locations. These field locations have central gas gathering systems for collection of the gas and major field processing activities. But in a areas so remote or in deepwater locations where there is no central gas gathering system on site it may be economically justifiable to build gas gathering facility and pipeline system on site considering the volume of the AG and the nature of the region, for such the use of small scale or mini GTL technologies proffers the solution of monetising the gas (White, 2012).

Smaller, modular GTL plants are suitable for use in remote locations. In contrast to conventional GTL plants, they are designed for the economical processing of smaller amounts of gas ranging from 100 million cubic meters (MMcm) to 1,500 MMcm, and they can produce 1,000 bpd–15,000 bpd of liquid fuels. Their modular structure makes microchannel reactor systems very flexible. The plants can be scaled to match the size of the resource, expanded as necessary, and potentially integrated with existing facilities on refinery sites (World Energy Outlook, 2011).

Smaller-scale GTL operations also pose a lower risk to producers. Since the plants are smaller, construction costs are reduced; and, since the plants are modular, investment can be phased. The construction time is short, at 18–24 months. In addition, because the modules and reactors are designed only once and then manufactured many times, much of the plant can be standardized and shop-fabricated in skid-mounted modules. This reduces the cost and risk associated with building plants in remote locations. In addition, the components can be designed to use standard, off-the-shelf equipment, so there is less strain on supply chains, and the need for onsite construction work is reduced.

Smaller-scale GTL plants open GTL to the broader market by reducing the entry price and significantly increasing the number of locations where GTL technology can be installed. This flexibility offers great potential for monetizing resources like shale gas and stranded gas, which can be located far from existing pipeline infrastructure and markets. Smaller-scale GTL processes also offer the potential to expand refinery capacity and to produce hydrocarbon-based feedstocks from gas. Additionally, they improve profitability by unlocking gas resources that would otherwise be wasted, thereby capturing value from the gas-to-oil spread, widening access to global markets and taking advantage of existing infrastructure.

2.13.3 How is Mini GTL Different from Large-scale GTL?

The world’s first large GTL plant was commercialized by Shell in Bintulu, Malaysia in 1993. Large-scale GTL comes with the complexities of massive and expensive facilities, which may not be economically feasible in areas where output of the gas is less than or equal to 25 MMscfd. Moreover, large GTL projects can lead to delay in the project start-up, as the complexity involved in project execution is similar to that in any other big refinery or petrochemical project.

Mini GTL plants are compact and modularized, which are useful in unlocking opportunities that were previously uneconomic. Small-scale GTL can be modularized to specific sites and a wide range of products can be obtained that are of the same quality and grade as those obtained from conventional large-scale GTL plants.

Apart from providing a host of value-added products, mini GTL has many advantages over large-scale GTL projects. These include modularization of equipment, which helps in the installation of units in remote or challenging locations. This is possible because the reactor's size is smaller and lighter than that in conventional technology and 70% of the plant can be factor-built before installation. Due to modularization, the plant can be built faster, with reduced delays that could lead to cost overruns.

There are a number of companies investing heavily in the development of mini GTL technologies. Although the basis for mini GTL is the Fisher Tropsch (FT) process, there are 12 companies that have developed innovative technologies and are about to commercialize them in the market. These 12 companies are classified based on the overall technical remaining risk and the time required to commercialize the technologies. CompactGTL, Velocys, Oberon, Fuels, and GasTechno were the ones with the lowest overall remaining risk and the closest to the commercialization of their respective projects.

Three companies—CompactGTL, Velosys, and GasTechno—are leading the mini GTL market and are competing head-to-head in commercializing their respective technologies.

Compact GTL's new onshore plant designs have been developed by incorporating conventional reforming and modular FT processes. CompactGTL's first demonstration plant in Brazil was approved by Petrobras; it operated stably throughout 2012 (White, 2012).Velosys has its own patented micro-channel reactor FT technology, which provides maximum conversion of gas to liquid by consuming less catalyst. Velosys has made significant progress in commercializing its technology is last 2 years. The company has 5 projects in the pipeline; yet, when it comes to risk, the micro-channel reactor is on the higher side when compared to conventional reactors.

GasTechno has been promoting its early adoption program since 2012. The first pilot plant was installed in 2012 in an oil and gas field in Michigan and it was successfully able to convert C1-C6 hydrocarbon from a flare to alcohols and aldehydes. However, the major concerns with GasTechno's technology were the limited availability of long-term plant performance data, lack of selectivity of the process, and economic viability. GasTechno offers low-capital expenditure (CAPEX) plants for very small gas volumes, which is not readily addressed by other technologies (World Energy, 2012).

2.13.4 Economic Benefits of Mini GTL

Economy plays a significant role in deciding the future of any new technology; same is the case with mini GTL. As mini GTL is deployed in places where gases with limited output is involved, economics of scale remains the deciding factor for the profitability of the project. The example of GasTechno can be taken to understand the economics of a mini GTL plant. The GasTechno Plant can be scaled down to 1 mmscfd and the mini GTL plant can be scaled down even further, to 200 metric standard cubic feet per day (mscfd). In this case, the final processing of the raw products has to be performed at the central processing facility.

Although the economics of the mini GTL is positive, the need for a central processing facility slightly decreases the internal rate of return (IRR), thereby reducing the earnings before interest, taxes, depreciation, and amortization (EBITDA). By scaling up the plant to 5 mmscfd, the economics can be significantly increased. Though mini GTL can be an innovative technology to monetize the stranded gas, it will be economically profitable only when the available gas for input is more than 5 MMscfd.

2.14 Economics of GTL Plant

In considering economics of GTL plant, factors relating to the project economics are of interest. The factors affecting the viability of GTL are summarized below.

1. Capital expenditures
2. Operating expenditures
3. Crude oil price
4. Natural gas price

2.14.1 Capital expenditure (CAPEX)

The capital expenditure (CAPEX) is the most significant factor affecting the viability of any GTL product. The early capital cost of plants was so high and it made the project comparatively expensive and economically not viable. But recent advances in GTL technology, particularly the use of better catalyst have been responsible for the significant drop in cost and increased viability and outlook for GTL projects.

The CAPEX of GTL is often expressed in barrel-liquid-per-day basis. From literature the current capital cost for large scale GTL plants for economic viability to be achieved is estimated to be $20,000 to $40,000 PBLD. The CAPEX depends on many factors such as

1. The type of technology used
2. Geographical location of the facility
3. Product/workup slate
4. Economies of scale
5. Learning curve cost improvement

6. Local infrastructure availability

The CAPEX may include the cost of pretreatment and the cost of air separation unit. Below is a rundown of typical contributory component of CAPEX.

1. Gas plant (pretreatment and processing)
2. Synthesis unit including air separation unit
3. Fischer-Tropsch unit
4. Product upgrading unit
5. Other processing unit
6. Utilities
7. Offsites

Oxygen generation is a significant portion of syngas generation and thereby a CAPEX, and is important to explore for purposes of cost reduction. Geographic location of the proposed facility also weighs heavily on the CAPEX.

2.14.2 Operating Expenditure (OPEX)

This comprises the Feedstock OPEX and the non-feedstock OPEX, the feedstock OPEX is the most important part of the operating expenditure. The feedstock OPEX is the price of the natural gas.

1. The non-feedstock OPEX

The non-feedstock annual OPEX for large projects have been estimated to be between 5 to 7% of CAPEX. The non-feedstock OPEX comprises

1. Operation and maintenance cost
2. Overhead cost
3. Environmental compliance

4. Payroll

The non-feedstock OPEX for most GTL plant is estimated to be between 5 to 7% of the CAPEX. For this work 5% non-feedstock OPEX shall be used.

2. Natural gas price (Feedstock cost)

Natural gas prices are key factor in the viability of a GTL project. The price of gas utilized as feedstock by GTL is usually negotiated between the host nation and the investor with little reference to market prices. Studies have shown that for a GTL project to be viable, the price of gas must not exceed $0.5/MMBTU. IOCs who have partnered with producing nations on GTL projects may obtain preferential gas prices for their GTL facility. In some cases, because the feedstock is flared gas it can be given at no cost initially for a contract agreement to investors on agreement with host government in bid to develop the resource, monetize the gas and stop gas flaring in the country.

2.14.3 Crude Oil Price

Refined crude oil products provide the target products for GTL products. The prices of refined crude oil products are to a large extent determined by the prevailing crude oil prices. This implies that the price of oil (both crude and its refined products) is important in considering the viability of GTL. For the viability of GTL, crude oil prices must continue to remain at a very high level. This is because the price of crude oil products determines the price of GTL products. In literature it is estimated that a crude oil price of $25/bbl would be favourable to the viability of a GTL(World Energy Outlook, 2011).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

The section describes the materials used in this research work. The work is purely a simulation work. The materials used in this work comprise the computer software packages that are used to perform the modeling and simulations. Two software were used in this work. Honeywell's Unisim software and MATLAB. Unisim is utilized for the GTL plant design and process operation while MATLAB is used for the economics analyses

3.1.1 Unisim Software

Honeywell Unisim R380 was used for the GTL plant process design and simulation. Unisim is an interactive modeling tool that helps engineers to create steady state and dynamic models for plant, design, monitoring of plant performance, operational improvement and troubleshooting. It is widely used in process simulation jobs for oil, gas, chemicals, energy, power etc. simulations. Unisim is essentially impressive in design and optimisation applications helps in the determination of workflow, equipment needs and implementation requirements for a given process to be deployed. With these software users can design plant process thereby improving profitability, performance and efficiency at greatly reduced operational costs.

3.1.2 MATLAB software

MATLAB which stands for Matrix Laboratory is software developed by MathWorks. MATLAB is a numerical computing environment that allows users to work with data in form of matrices, functions, algorithms and creation of user interfaces. It is the top programming language dedicated to mathematical and technical computing. Typical utilization of MATLAB includes Math and computation, Algorithm development, Modeling, simulation, and prototyping, Data analysis, exploration, and visualization, Scientific and engineering graphics, Application development, including Graphical User Interface building.

3.2 Methods

The methods comprise the modeling and simulation. These comprise the simulation of the GTL plant process for the production of GTL products and the economics analyses of the processes**.** For the GTL plant system simulation, two cases are be considered, the base case and the alternative case. The base case is the design of GTL plant with conventional ATR synthesis gas unit while the alternative case the design of an optimal GTL synthesis gas unit using steam/CO2 as inlet feed reactants. In the plant simulation, the technical performance of each of the cases is considered. Afterwards, economic analyses of the GTL project is done to ascertain the economic viability of the projects and the cases considered.

For these work the factor that determines distinction of the operations of each case is the choice of technology and approach for the production of the synthesis gas. Thus, of the primary stages in the GTL process, the synthesis gas stage defines and distinguishes the base case from the alternative case. The present work’s main cases considered is summarized below.

3.2.1 Base case method

The base case for this work is the design of a GTL process plant and its operation for the production of premium GTL Transport fuel using Autothermal reforming method as the method for the synthesis gas production. The synthesis gas here is the precursor to the actual Fischer Tropsch reaction. The Autothermal reformer (ATR) uses oxygen from air separation unit (ASU) as one of the reactants. Other reactants include steam and the pre-treated natural gas.

3.2.2 Alternative case method

For the alternative case, a process plant that would minimize cost and enhance performance and less pollution was designed. In this work, a method that was CO_2 reductive was proposed, this method utilized the inherent CO_2 in the natural gas, consumed the CO_2 that was produced in the reaction phases and also used the CO_2 that was in the effluent stream of the GTL plant for the production of synthesis gas in the syngas unit using steam/CO_2 reforming technology. Furthermore, $CO_2$was supplied externally from the market to get the required amount necessary for the synthesis gas production.

3.2.3 Description of Processes and Consideration of the GTL Plant

The processes involved in GTL plants operations are divided into four main units given below

1. The natural gas pre-treatment units
2. The synthesis gas unit
3. The Fisher Tropsch unit
4. The product upgrading unit

These four main units in the GTL plants have their peculiar operation, processes, considerations and objectives. A full GTL plant process is an integration of these units and processes for a common goal. Each unit is peculiar and distinct from the other and is important to the overall integrated steam.

1. The Natural Gas Pre-Treatment Unit

This unit sees that the natural gas from the flare point is pre-treated to remove impurities or reduce them to acceptable levels for the actual GTL process. The actual GTL plant operations begin from the synthesis gas unit. For this work the choice of pre-treatment varies for each case considered. Because of the different principles involved in the reforming of the two cases considered, their pre-treatment also differs. This difference affects the choice of their technologies and process applications. For optimal treating-complex design, process selection for the individual units must be made on the basis of an integrated approach that considers interactions between units

For the ATR reformer, the aim of the pretreatment is to remove all impurities or at least reduce it to a level that can be tolerated by the catalyst and equipment in the subsequent syngas units. For these the acid gases, Nitrogen, Mercaptans and other impurities are removed from the natural gas. Many approaches to achieve this exist but the selected approach for this work is use of amine systems to sweeten the sour flare gas. Figure 3.1 gives a schematic description of the process used for the acid gas removal from the raw flare gas for the ATR syngas process method.

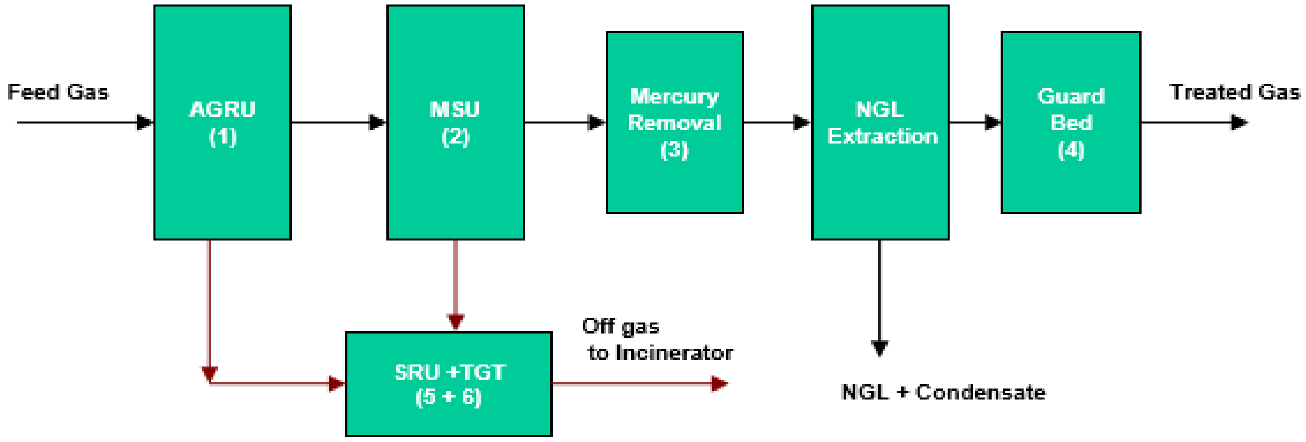


Figure 3.1: Typical Block Flow Scheme of Sour Natural Gas Treating Unit

The acid gas removal unit (AGRU) removes H_2S and some of the mercaptans. The molecular sieve unit MSU removes the bulk of the mercaptans and dries the gas to specification for the NGL recovery unit. Mercury is removed prior to NGL extraction. The final step being the guard bed ensures that stringent sulphur component specification of the downstream process is met.

Although for GTL processes do not require full removal of the acid gases, a level can be tolerated. CO_2 of 0.5-1% mole of CO_2 can be tolerated while the specification of sulphur level must be less than 0.1 ppm weight.

The steam/CO_2 reforming for the alternative method requires a new method for the pretreatment of the raw flare gas other than the one suggested above. This is because the CO_2 in the natural gas will not be removed so that it can take part in the reaction. For this only the H_2S and the other sulphur components needs be removed. Thus, the pre-treatment for the steam/CO_2 method is mainly a desulphurization of the raw flare natural gas. We proposed a method to achieve the desulphurization which consist of passing the raw natural gas feed at about 300 to 400^oC over cobalt molybdenum catalyst in the presence of hydrogen to convert the organic sulphur containing compounds to hydrogen sulphide according to equation 3.1

$$NG + S + H_2 \rightarrow H_2S + NG \qquad 3.1$$

This is then followed by adsorption of the hydrogen sulphide on zinc oxide in a guard chamber to form zinc sulphide according to the reaction below in equation 3.2. This reaction reduces the sulphur level in the natural gas to less than 0.1 ppm wt. which is the level that can be tolerated by downstream GTL equipment.

$$NG + H_2S + ZnO \rightarrow ZnS + H_2O + NG \qquad 3.2$$

The pretreated natural gas either in the base case or in the alternative case is feed to the synthesis gas unit. The pretreated natural gas composition is given in the table 3.1 below:

Table 3.1: Mole Composition of the Raw Natural Gas from the Flare Stack

Component	Mole Composition (Mol %)
Methane	80.15
Ethane	5.13
Propane	3.75
N-butane	2.54
I-pentane	1.58
N-pentane	1.24
Hexane	0.76
Nitrogen	1.24
CO_2	1.88
Hydrogen sulphide	1.73
Total	100

Table 3.2 gives the composition of the feed gas after the pretreatment has been done.

Table 3.2: Mole Composition of Natural Gas after Pretreatment and Processing (Pre-Reformer Feed Composition)

Composition	Mole Fraction %
Methane	95.5
Ethane	3
Propane	0.5
N-Butane	0.4
I-Butane	0.2
Nitrogen	0.4
Total	100

When the raw natural gas has undergone pretreatment and desulphurization, then three main steps remain available for the conversion of the gas to liquids

2. The Synthesis Gas Unit.

The synthesis gas unit includes the following sub-sections, a pre-reformer, heating unit, and a reformer (ATR for base case and steam/CO_2 reformer for alternative case):

(1) The pre-reformer cracks heavier hydrocarbons in the pre-treated natural gas stream before being sent to the reformer. Here all hydrocarbons heavier than methane are converted according to equation 3.3. In addition, the methanation and shift reactions (equations 3.4 and 3.5) are assumed to be in equilibrium.

$$for\ n \geq 2, C_nH_m + H_2O \rightarrow \left(n + \frac{m}{2}\right) H_2 + nCO \tag{3.3}$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \tag{3.4}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{3.5}$$

The exit temperature of the adiabatic pre-reformer will depend on the inlet composition and temperature. The exit temperature is between 212 and 572^oF lower than the desired ATR inlet temperature, which means that a fired heater is needed.

(2) The heating unit supplies the required energy for

  a. Preheating Fresh natural gas and Recycle hydrocarbons from FT reactor, i.e. the pre-reformer feed to 851^oF

  b. Superheated process steam (pre-reformer feed) and superheated steam for driving the turbines of compressor in the oxygen plant and the much smaller recycled tail gas compressor.

  c. Preheating the outlet gas from the pre-reformer to 948.15^oF (optimized value)

  d. Preheating oxygen or CO_2 as the case may be to 473.15^oF

The required fuel for the fired heater is supplied by the combustible components in the purge stream plus some fresh natural gas. An efficiency of 98% is assumed for the combustion of fuels.

(3) The reformer converts methane in the stream from the heating unit to syngas by reacting it with steam and oxygen/CO_2. It is modeled as an adiabatic equilibrium reactor

For the base case ATR, the following reactions are seen:

Oxidation of Methane: $CH_4 + 1.5O_2 \leftrightarrow CO + 2H_2O$ 3.6

Steam Reforming of Methane: $CH_4 + H_2O \leftrightarrow CO + 3H_2$ 3.7

Water Shift reaction: $CO + H_2O \leftrightarrow CO_2 + H_2$ 3.6 3.8

The oxygen is supplied by the air separation unit (ASU) and is blown into the ATR. For GTL applications with a cobalt-based Fischer-Tropsch reactor, a typical H_2 to CO ratio in the fresh syngas is about 2, but the exact value will be obtained as a part of the optimization of the process.

The hot syngas leaving the ATR is cooled to ambient temperature for water removal before going to the CO_2 capture unit.

For the steam/CO_2 method the following reaction is seen in the reformer

Steam Reforming of Methane $CH_4 + H_2O \rightarrow CO + 3H_2$

Dry Reforming of Methane $CH_4 + CO_2 \rightarrow 2CO + 2H_2$

Water Shift reaction $CO + H_2O \leftrightarrow CO_2 + H_2$ 3.9

Note that large amounts of water are produced in the subsequent FT reactor, so there is no strict limitation on the water content of cooled syngas, but it is removed for economic reasons to reduce the flow to the FT reactor.

3. Fischer-Tropsch Unit.

The syngas is sent to the Fischer-Tropsch (FT) reactor where the highly exothermic FT reactions take place. The reactor is assumed isothermal with a temperature of 410°F. The reactions are typically written in the following form:

$$nCO + 2nH_2 \leftrightarrow (-CH_2-)_n + nH_2O \qquad 3.10$$

In addition, the production of methane is unavoidable

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \qquad 3.11$$

To simulate the reaction scheme, the reaction rates for CO consumption and CH_4 formation proposed by Iglesia et al (1997) together with the carbon mass balance as given by the ASF distribution model. The Iglesias's reaction rates on cobalt catalyst are valid at the following conditions

1. Temperature of 408°F to 4100°F
2. Pressure of 100 to 3000 kPa,
3. Synthesis gas ratio of H_2/CO = 1 to 10

The Iglesia's reaction rate on cobalt catalyst is for CO consumption and CH_4 formation are given below

$$r_{CH_4} = \frac{k_1 PH_2 PCO^{0.05}}{1 + (K_1 PCO)} \qquad 3.12$$

$$r_{CO} = \frac{k_2 PH_2{}^{0.6} PCO^{0.65}}{1 + (K_1 PCO)} \qquad 3.13$$

The values for A, E, n and the various component exponents of equations 3.12 and 3.13 for use in Unisim is given in table 3.3

Table 3.3: Parameters used for kinetic rate expression in Unisim for modeling of the FT reactions

Reactions	A	E	Exponent PH_2	Exponent PCO		n
				Numerator	Denominator	
r_{CH_4}						
k1	8.8*10-6	37326	1	0.05	-	-
K1	1.096*10-12	-68401.5	-	-	1	1
r_{CO}						
k2	1.6*10-5	37326	0.6	0.65	-	-
K2	1.096*10-12	-68401.5	-	-	1	1

The simulated reactor is a multi-tubular fixed bed (MTFB) reactor.

The Fischer-Tropsch synthesis was modeled as given by the ASF distribution. Only paraffins were considered in this work and, α was assumed to be 0.9. All of the components below carbon number 21 was modeled as individual units, while the components with carbon number from 21-30 was lumped in a component designated C_{21}^{+}. The stoichiometric coefficients were calculated from Equations given below

$$U = 3 - \alpha \qquad 3.14$$

$$r_{FT} = (1-\alpha)^2\alpha^{(i-1)} \qquad for\ C_i, i = 1 \dots\dots 20 \qquad 3.15$$

$$r_{FT} = (1-\alpha)\alpha^{(20)} \qquad for\ C_{21-\infty} \qquad 3.16$$

The overall FT reaction was modeled in Unisim as one reaction, and written as

$$CO + UH_2 \rightarrow r_{FT1}C_1 + r_{FT2}C_2 + - - - r_{FTN-1}C_{N-1} + r_{FTN,\infty}C_{N,\infty} + H_2O \qquad 3.17$$

$$X_{[N,\infty]} = N + \frac{\alpha}{1-\alpha} = 30$$

This means that $\mathrm{C}_{[\mathrm{N},\infty]} = \mathrm{C}_{30}$ represents $\sum_{\mathrm{N}=21}^{\infty} \mathrm{C}_{\mathrm{N}}$

Where

N=21

The direct equation of reaction used for the FT reaction in this work is given below.

$$\begin{aligned}\mathrm{CO} + 2.1\mathrm{H_2} \rightarrow\ & 0.01\mathrm{CH3} + 0.009\mathrm{C2H6} + 0.008\mathrm{C3H8} + 0.007\mathrm{C4H10} + 0.007\mathrm{C5H12} \\ & + 0.006\mathrm{C6H14} + 0.005\mathrm{C7H16} + 0.004\mathrm{C8H18} + 0.004\mathrm{C9H20} + 0.003\mathrm{C10H22} \\ & + 0.003\mathrm{C11H24} + 0.003\mathrm{C12H26} + 0.003\mathrm{C13H28} + 0.002\mathrm{C14H30} \\ & + 0.002\mathrm{C15H32} + 0.002\mathrm{C16H34} + 0.002\mathrm{C17H36} + 0.002\mathrm{C18H38} \\ & + 0.001\mathrm{C19H40} + 0.012\mathrm{C20H42} + \mathrm{C21} \\ & + \ \mathrm{H2O} \qquad 3.18\end{aligned}$$

3.2.4 Operational Constraints

The following constraints were considered for optimization:

(1) Molar ratio$H_2O/C \geq 0.3$ in feed to syngas unit. This is to avoid soot formation in the ATR.

(2) Reformer exit temperature is 1030^{o}C. This temperature is an average of some the reported operating outlet reformer temperatures by Haldor-Topsøe that ensures soot-free operation.

(3) Inlet temperature to the reformer 675^{o}C. This is a material constraint.

(4) The purge ratio is optimally around 2%, but for simulation purposes (to avoid convergence problem), it has bounded at a higher value (5% for α1 model and 3% for α2 and α3 models).

Soot forms as a result of incomplete combustion of methane or other hydrocarbon gases in the reactors. Soot are large mass of carbon deposited in the plant. Some of the reactions that causes carbon deposition are given below

Boudouard reaction: $2CO \rightleftharpoons CO_2 + C$ 3.19

CH_4 decomposition $CH_4 \rightleftharpoons C + 2H_2$ 3.20

CO reduction: $CO + H_2 \rightleftharpoons C + H_2O$ 3.21

Soot formation is a major problem in hydrocarbon reforming, this is because the carbon deposits on catalyst surface and blocks the active sites of the catalyst lading to catalyst deactivation or inefficient catalyst performance. Hence, a suitable catalyst for these reactions should be resistant to carbon formation, which may be achieved by enhancing the oxidation reactions. However, it is a more optimal operation to control carbon deposition. Oxidation reactions are given below

C oxidation: $C + \frac{1}{2}O_2 \rightleftharpoons CO$ (Incomplete) 3.22

C oxidation: $C + O_2 \rightleftharpoons CO_2$ (Complete) 3.23

3.2.5Simulation of the GTL Process Plant

The actual simulation process for this work is accomplished using Honeywell Unisim R380. The simulation is presented according to the case considered.

1. Plant Simulation for Base Case

The design specifications and requirements are discussed in the following sections on the basis of feed, product and operating conditions of the units.

The GTL plant was modelled in steady state condition using Honeywell's Unisim R380. In setting up the model, the fluid property package was chosen to be Peng-Robinson and all hydrocarbon components with C_4^+ were added as n-type hydrocarbons and $C_{21}\rightarrow\infty$ was modeled as C_{30} due to similarities in their properties. The reactions were added in sets for the three main units operations, Pre-reformer, ATR and FT-reactor respectively.

The simulation for the main GTL plant is described thus; first natural gas is heated from 104^{o}F to 850^{o}F by a heater. This is the common range for pre-reformer. The initial temperature of the steam was set at 485^{o}F. The heated natural gas and steam is sent to the pre-reformer. The pre-reformer was modeled as a conversion reaction while its water gas shift reaction was modeled as an equilibrium reactor. The pre-reformer temperature and pressure was set at 986^{o}F and 435 psia respectively. The outlet gas from the pre-reformer was sent to the ATR. The ATR was modeled as a conversion reactor while its water gas shift was modeled as equilibrium reaction in a distinct equilibrium reactor. Because of the exothermic nature of the ATR reaction, its upper temperature was set at a limit of 1886^{o}F in order to avoid soot formation.

A heat exchanger was connected downstream of the ATR to bring the temperature of the syngas down to 100.4^{o}F so that the steam generated in the ATR is converted to water that can be separated out before the FT-reaction, reducing the volume flow and hence the reactor size. However, 100.4^{o}F is a too low for the low temperature Fischer Tropsch (LTFT) process which runs at 392-464^{o}F and hence a heater was included in the model heating up the FTR inlet to 410^{o}F.

The FTR was modeled as a plug flow reactor (PFR) as this being the flow pattern that mostly resembles a multi tubular fixed bed (MTFB) reactor and a starting volume of 1000m^{3} was chosen. The FT reaction set was defined as kinetic and it included both the FT reaction and the methanation reaction. The stoichiometric coefficients for the FT reactions are modeled based on the ASF-distribution and the kinetics was implemented by the use of Iglesias rate of reactions.

The products of the MTFB reactor are gaseous and liquid products, gas and liquid products are separated inside the reactor by gravity- gas leaving at the top and liquid products trickling down and exiting the bottom. The gaseous products are cooled by heat exchanging with water to 100.4^{o}F (38^{o}C) before entering the 3-way separator together with the liquid products. This was done to separate out water that left the reactor as steam. This will eliminate unnecessary recycling and water being sent to product upgrading.

In the 3-way separator more water is separated out, liquid products are sent to upgrading unit and the remaining gases is split in a purge and a recycle stream.

Table 3.4 shows the input conditions for the base case. It gives the temperature, pressure and molar flow of the reactants.

Table 3.4: Base case input conditions for natural gas, steam and oxygen

Input	Temperature (^oF)	Pressure(Psia)	Molar Flow (Kmol/hr)
Natural Gas	850	435	2490 (50MMscfd)
Steam	485	590	9000
Oxygen	392	435	2500

The overall view of the GTL process schematics done on Unisim R380 software is given in the figure below.

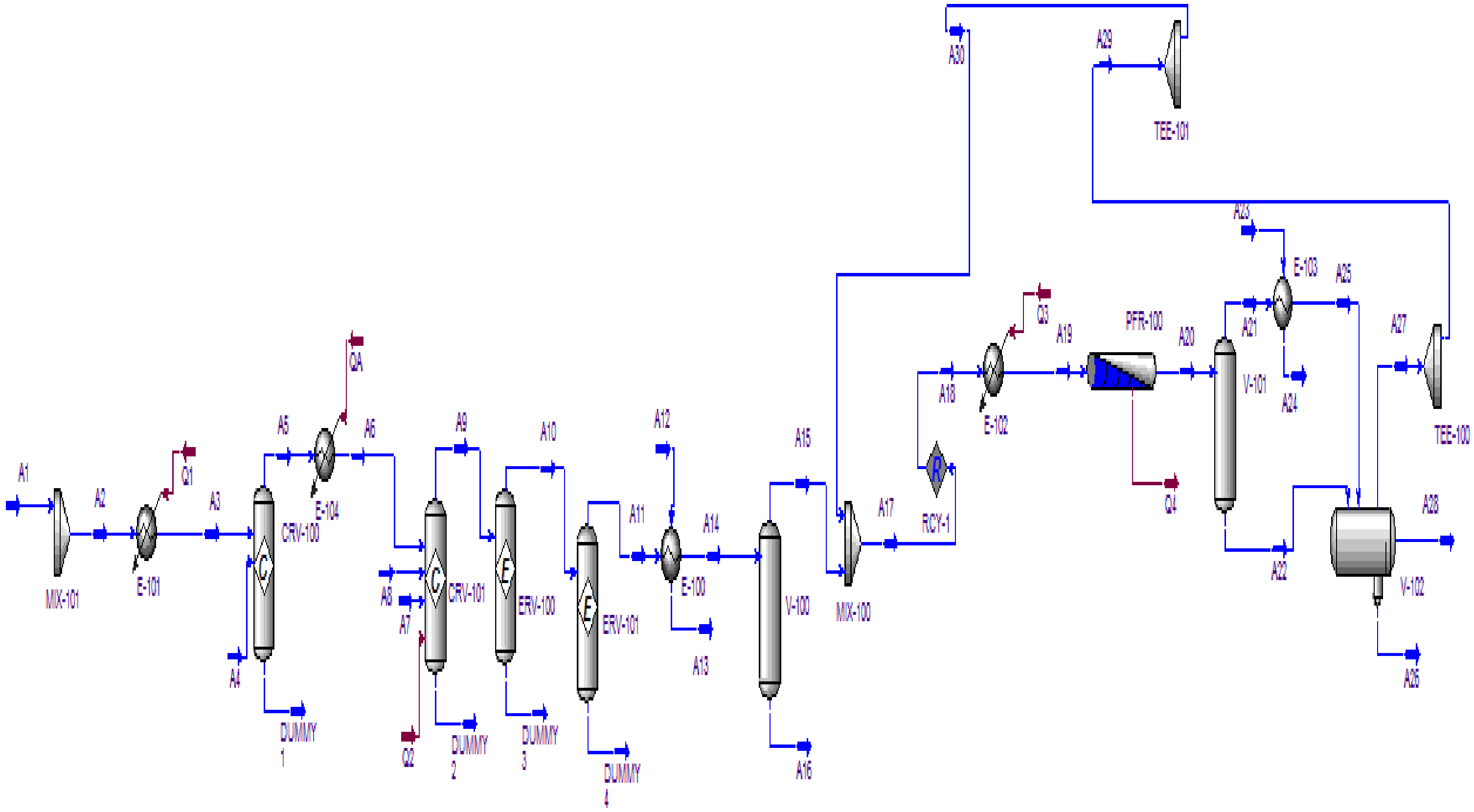


Figure 3.2: Complete process layout of the GTL plant design in Unisim

From figure 3.2, it can be that the first two conversion reactors modeled the pre-reformer and ATR reformer respectively while the last two equilibrium reactors modeled the water gas shift reaction from the pre-reformer and the reformer respectively.

The synthesis gas unit is very important to the operation because it is the deciding factor in the success of the FT reaction. The equilibrium reactors in the synthesis gas unit is necessary to achieve favourable H_2/CO ratio consequent for the FT unit. Figure 3.3 below shows a distinct layout of the simulated synthesis gas unit.

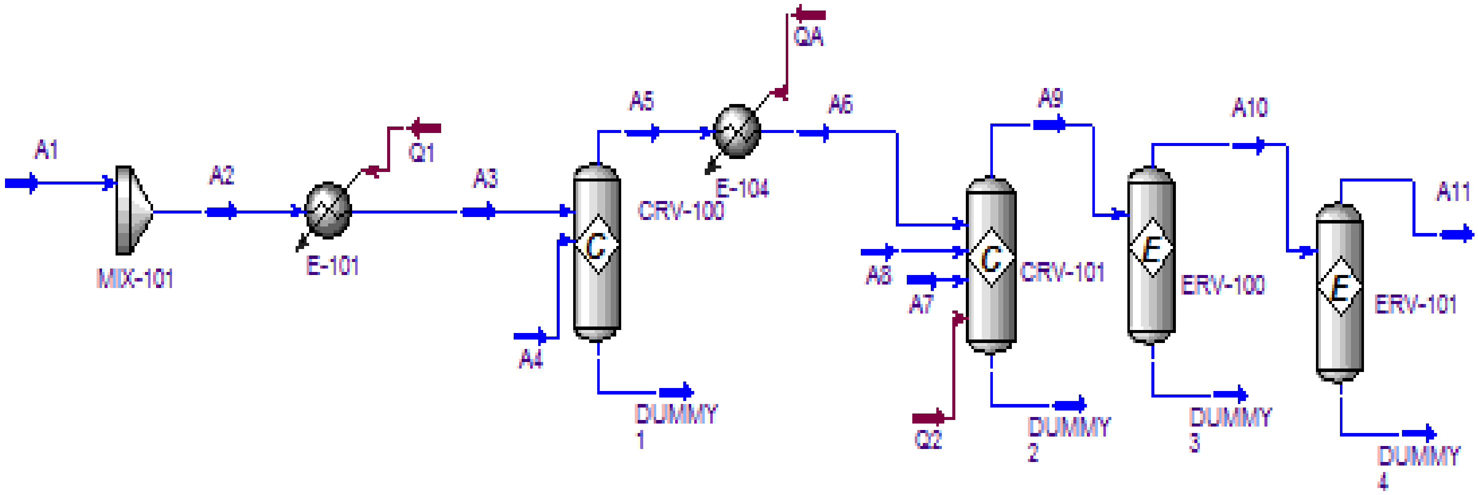
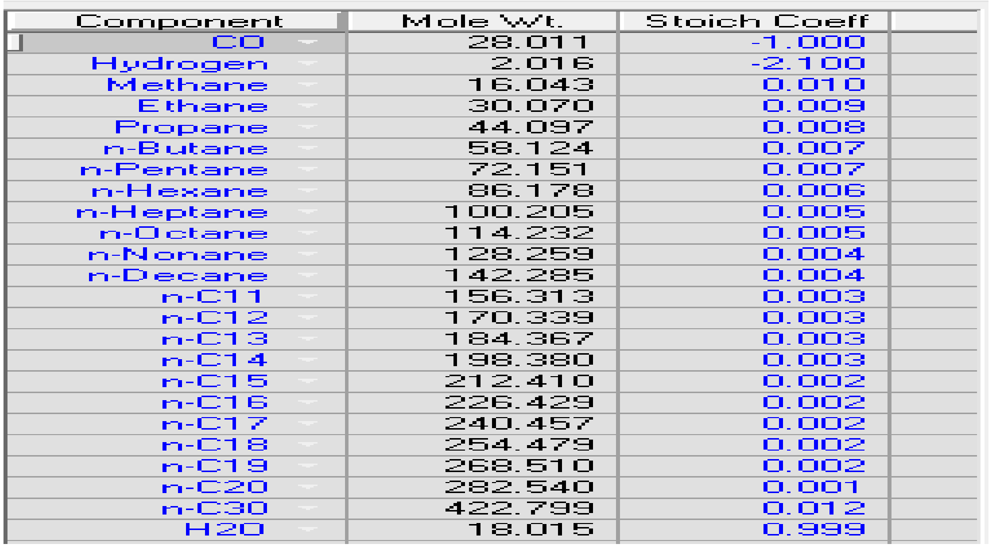


Figure 3.3: The Unisim simulated synthesis gas unit of the GTL process for base case.

The Fischer Tropsch reaction stage is done with a Plug flow reactor (PFR). The reaction is typical of the heterogeneous catalytic reactor. The plug flow reactor used for the Fischer Tropsch unit requires the stoichiometry of the reaction. Equation 3.9 and 3.10 govern the reaction for the Fisher Tropsch reaction. The reaction stoichiometry is governed by equation 3.11, 3.12 and 3.13. The stoichiometric coefficient for the plug flow reactor in the FT unit is gotten as

Table 3.5: FT reaction stoichiometry in the PFR



Component	Mole Wt.	Stoich Coeff
CO	28.011	-1.000
Hydrogen	2.016	-2.100
Methane	16.043	0.010
Ethane	30.070	0.009
Propane	44.097	0.008
n-Butane	58.124	0.007
n-Pentane	72.151	0.007
n-Hexane	86.178	0.006
n-Heptane	100.205	0.005
n-Octane	114.232	0.005
n-Nonane	128.259	0.004
n-Decane	142.285	0.004
n-C11	156.313	0.003
n-C12	170.339	0.003
n-C13	184.367	0.003
n-C14	198.380	0.003
n-C15	212.410	0.002
n-C16	226.429	0.002
n-C17	240.457	0.002
n-C18	254.479	0.002
n-C19	268.510	0.002
n-C20	282.540	0.001
n-C30	422.799	0.012
H2O	18.015	0.999

The figure 3.4 below is the Unisim simulation view for the Fischer Tropsch simulation using Plug flow reactor

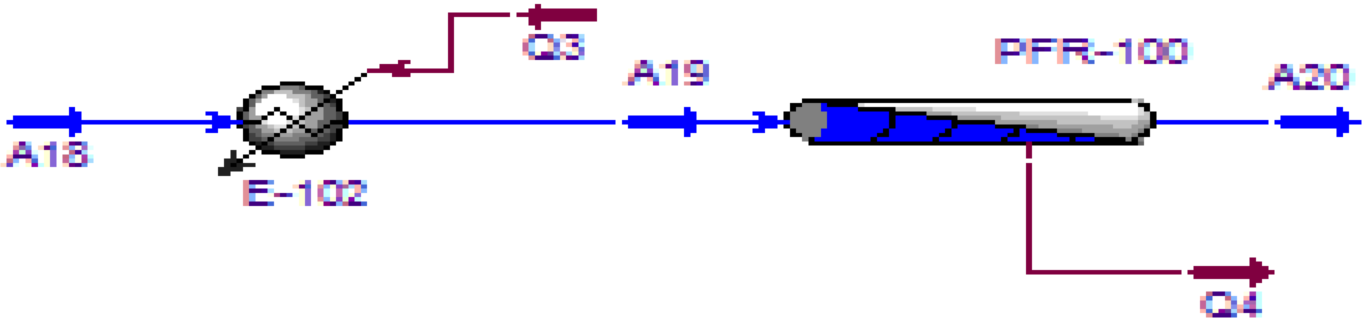


Figure 3.4: FT reaction process view in Unisim

2. Case 2: Simulation using Steam/CO_2 Reforming Method

For the pre-reformer unit the desulphurized natural gas is pre-heated to 851°F just as in the case of the ATR. The heated gas is sent to the pre-reformer. Steam enters the pre-reformer at 410°F. The pre-reformer just as in the case of the ATR was modeled as a conversion reactor while the water gas shift reaction was modeled as an equilibrium reaction.

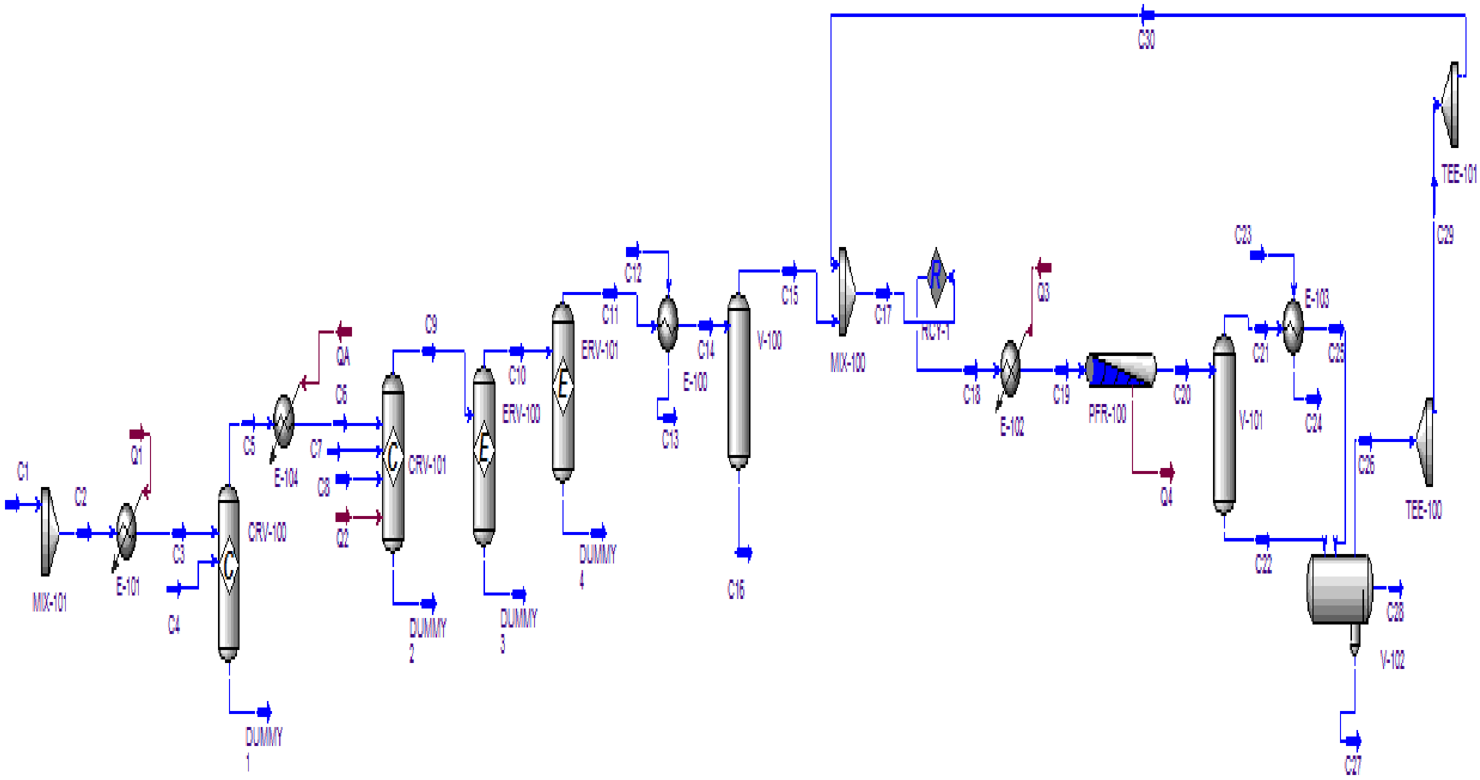


Figure 3.5: The Unisim simulation of the steam/CO_2 showing the synthesis gas and FT stages.

The synthesis gas unit was fed with hot CO_2 instead of Oxygen as in case 1. The simulation of the synthesis gas unit is given below.

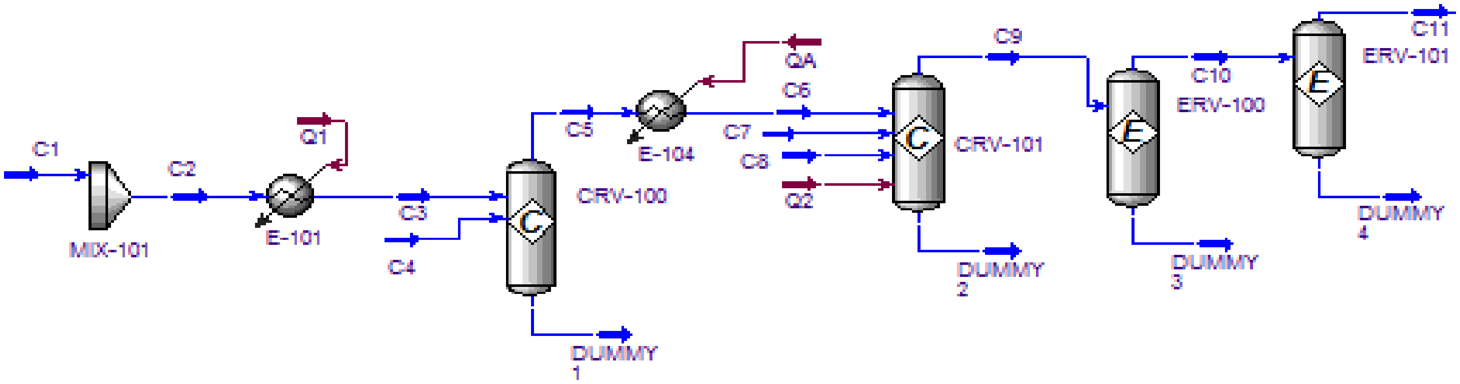


Figure 3.6: The Unisim simulation process view for the steam/CO_2 synthesis gas unit

3.2.6 Economic Model Development

Every project must have economic justification. This section covers the development of the economic model for the GTL plant

1. Evaluation of sources of project cost

The several sources of the project cost are given and discussed below

1. Capital investment

The capital investment (CAPEX) for GTL plant comes from various units and represents the largest economic expenditure of the GTL plant. The capital investment for a GTL plants includes the following:

i. **The cost of the equipment (Ce):** These include all the equipment to be used in the GTL facility and include individual equipment from all the units in the GTL process plant. The various units start from the gas pre-treatment stage down to the product work-up. But in most GTL operations the pre-treatment stage is not usually part of the main GTL process operation, this is because the treatment of the gas is sub-contracted out to companies and treated gas is delivered on purchase to the GTL operators. Although in some situation, the operators may wish to accomplish the pre-treatment of the natural gas onsite as part of the GTL operation especially in large commercial plants.

ii. **The installation cost (Ci):** this includes the cost of installing the various equipment onsite.

iii. The sum of the total equipment cost and installation cost is called the inside battery limit cost (ISBL)

iv. The outside battery limit cost (OSBL): this includes other cost such as the engineering and design, offsites, contingents.

v. The working capital (Wc): The working capital is additional money needed in order to run the plant until the plant starts to earn income. The working capital is returned at the end of the project time. For petrochemical industries the working capital is typically 15% of fixed capital investment

ISBL = $C_e + C_i$ 3.24

Total fixed cost (T_{fc}) = $ISBL + OSBL$ 3.25

Total investment cost = $T_{fc} + W_c$ 3.26

Total investment cost (CAPEX) = $C_e + C_i + OSBL + W_c$ 3.27

2. Installation cost

The installation cost comprises the following operations

1. Piping
2. Electrical
3. Equipment erection
4. Instrumentation and control
5. Civil works
6. Structures and building
7. Lagging and paint

2. The Operating/Production Cost Estimation

These are costs which are dependent on production, such as electricity and operators. For the purpose of this work the natural gas cost is excluded from the operating cost. This is done for easy evaluation of the sensitivity of the project economics to changing natural gas price since the operating cost (OPEX) is given as a percentage of the CAPEX

3. Estimation of CAPEX

To address the plant capacity, economies of scale relate the CAPEX to the plant capacity and may be expressed according to the equations below (AL-Saadoon, 2005)

$$Cost\ Ratio = (Capacity\ Ratio)^Y \qquad 3.28$$

$$Cost = Base\ Cost * \left[\frac{Capacity}{Base\ capacity}\right]^Y \qquad 3.29$$

$$Cost = constant * (Capacity)^Y \qquad 3.30$$

Where Y reflects the degree to which a particular facility benefits from economies of scale. A value of 1.0 implies the facility does not benefit from economies of scale. For example, the construction of parallel trains (instead of larger ones) would yield Y values approaching 1.0. Y values for refining and petrochemical plant are typically 0.5 to 0.88. The value for GTL plant is estimated at 0.66.

3.2.7 Investment Decision Parameters

The following economic appraisal techniques shall be considered

1. The Payout time (POT)
2. The internal rate of return (IRR)
3. The net cash flow
4. The net present value.

1. Cash Flow/NCR

This shows the total cash outlay of a project. It shows the difference between the revenue received and cash disbursed over a given period of time. It is sometimes called the net cash returns of the investments.

The cash flow is calculated from the formula given below:

$$C_f = \{(R_a - A_{toc} - d_a) * (1 - F_{it})\} + d_a \qquad 3.31$$

Where

C_f= cashflow/NCR

R_a =Annual Revenue in dollars

A_{toc} =Annual total production cost

d_a= Annual depreciation

F_{it}= fractional income tax

The taxable income (T_{in}) is given by

$$(T_{in}) = R_a - A_{toc} - d_a \qquad 3.32$$

The fractional income tax is the amount of money spent as tax divided by the taxable income. It is expressed in percentage and may be converted to decimals.

The depreciation used here is the straight-line depreciation method and is given by

$$Depreciation = \frac{\text{Equipment cost} - \text{Salvage value}}{\text{Life period of Equipment}} \qquad 3.33$$

The total annual operating cost is the total cost per year of the non-feedstock cost and the natural gas price.

2. Payout Time (POT)

The undiscounted POT is the period of time it takes the undiscounted cashflow to pay back the undiscounted investment cost. At this time the revenue is zero, meaning that the undiscounted cashflow is equal to undiscounted investment. Mathematically the pay-out time is calculated as

$$POT = \frac{Capital\ cost}{casshflow/NCR} \qquad 3.34$$

3. The Discounted Cashflow Rate of Return (DCF-ROR)

This is the discount rate at which the net present value is equal to zero.

4. Net Present Value (NPV)

Is the difference between the sum of the discounted cashflow and the investment cost. If the value of the NPV is positive, then the project is viable, while if it is negative, the project is not viable. The following is the formula for calculating NPV

$$NPV = \sum_{t=1}^{T} \frac{C_t}{(1+r)^t} - C_0 \qquad 3.35$$

Where:

C_t = net cash inflow during the period t

C_o= total initial investment costs

r = discount rate, and

t = number of time periods

3.2.8 Project Case Study

The case study here describes the location under investigation. For this project we are looking at the conversion and monetisation of the flare natural gas at Egbema production sites. This region has been heavily impacted by gas flaring. The construction of GTL facility in this area is expected to convert the flare gases into premium quality transport fuels like diesel, gasoline and kerosene for home usage. The GTL products are to be mostly utilized in the nearby Owerri, the capital city of the state while surplus is sold to Port Harcourt and Onitsha, the adjoining cities. Literature reveals that more than 50MMscfd of gas is flared from this region (Osujieke et al., 2018; Nwagbara et al., 2020). This volume becomes our target volume for monetisation. We employ mini modular technology because of the relatively small volume of the gas and to ensure project optimisation and private investor partnership. The project is expected to yield 5000b/d of GTL liquid fuels, this is the plant capacity.

To determine the capital cost of this 5000b/d plant we make comparison with existing mini GTL facilities currently in operation in other areas. For this project analyses we make use of the capital cost of CompactGTL facility at Kazakhstan. This facility has a capacity of 2500b/d of GTL liquid products with an overall capital cost of US$275MM. from these we can calculate the capital cost of our proposed GTL plant using equation 3.26 which is given below:

$$Cost = Base\ Cost * \left[\frac{Capacity}{Base\ capacity}\right]^{Y}$$

Where the Base cost is the cost of CompactGTL which is US$275MM and base capacity is 2500b/d while the capacity for our proposed plant is 5000b/d. Y is taken to be 0.66. From the calculation the total capital cost of our proposed plant is US$434,522,721 which is approximated to be US$434.5MM. The capital cost calculated includes all the units which also comprise the ASU plant for generation of oxygen. But since this plant will be operated by independent licensed operators and oxygen sold to the GTL operators, we shall exclude the cost of ASU plant from the capital investment cost (CAPEX) of the GTL plant.

From literature conventional ATR plants with ASU has its ASU contributing about 20% of the total investment cost (CAPEX) of the overall process plant. If we subtract 20% from the estimated cost of the GTL, then the new GTL CAPEX without ASU plant will be US$347,618,177, approximately US$347.6MM. Thus, the capital cost of the ATR configuration for use in this work is US$347.6MM

3.2.9 Project Economics and Economic Parameters

Every project although technically proven must be economically justifiable. In view of this we determine the economic viability of the project. We determine the economics for each case considered and compare them to ascertain the method which saves cost and with higher energy efficiency. The economic parametres for the project is given below.

i. Plant capacity is 5430b/d for ATR GTL plant and 5730b/d for steam/CO_2 GTL plant from natural gas inlet flowrate of 50MMscfd
ii. Capital cost is US$347.6MM (ASU excluded)
iii. Feedstock cost is $2.5/MMBTU since gas is flared gas
iv. OPEX is 5% of CAPEX (excluding natural gas price and cost of O_2 or CO_2)
v. Plant operational period of 25years
vi. 350 plant operational days per year
vii. Refined GTL product price of $100/bbl for diesel and kerosene, $90/bbl for gasoline.
viii. Straight line depreciation method
ix. Salvage value of zero
x. Income tax of 35% base case
xi. 100% owners’ equity

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1: Results

The analyses of results for the GTL simulation shall be done under the two cases considered, i.e. for the base case (ATR syngas reforming) process and for the alternative case (Steam/CO_2 reforming) process. Under each case we shall analyses both the technical performance analyses and the economic performance analyses of the project.

4.1.1: Technical Performance Analyses

In the technical performance analyses, we evaluate the parametres of the specific design and operation of the GTL project is discussed. The technical performance for each case shall be analyzed under the following heading

1. Plant component descriptions
2. H_2/CO ratio
3. Thermal and carbon efficiencies
4. Pollutants and emission characteristics
5. Steam generated
6. Molar/mass flow
7. Methane conversion/carbon conversion
8. Product Yield
9. CO_2production/emission
10. General performance indices

1. Technical Performance for Base Case GTL Plant Design Operation

The base case was designed in Unisim with O_2 as the reformer gas. The O_2 is gotten from the ASU. For most plants the ASU is part of the synthesis gas unit and operated as part of the GTL process configuration by the GTL operators onsite. But for the purpose of this work, for ease and simplicity technical and economic analyzed we assumed that the ASU was operated by a third-party operator with plant very close to the sight such that oxygen is supplied and sold onsite to the GTL operators in regular required volumes. These assumptionsmake it easy for the ATR reform to be compared to the steam/CO_2 reformer that uses steam and CO_2 since the CO_2 is also externally purchased and supplied onsite.

i. ATR Reformer Plant Stream Description

The various parametres and component streams specified by the alphanumeric codes in the GTL plant simulation flowchart is described in table 4.1. The various Unisim components used during the simulation are described below

1. **Mixer**: used to mix two or more coming in at different flowrate, pressure and temperature at equal proportions

2. **Heater**: To heat fluids and increase its temperature

3. **Pre-reformer**: a reactor that is used to convert heavier hydrocarbons in the natural gas to methane and synthesis gas

4. **Reformer**: This is a reactor where the methane is converted to synthesis gas

5.**Separator**: Vessel used to separate gas from liquid streams

6. **Recycler**: used to separate purge gas for purification

Plug flow reactor: A kind of reactor suitable for Fischer-Tropsch reaction for conversion of synthesis gas to syncrude

Heat Exchanger: A device used to transfer heat between two or more fluids. Usually used to transfer heat from hot streams to cold stream to lower the temperature of the hot stream.

Table 4.1: Plant stream Description for ATR Reforming of the GTL plant

STREAM	DESCRIPTION	TEMPERATURE (ºF)	PRESSURE(psi)	MOLAR FLOW (Kgmol/h)
A1	Natural gas	104	435	2490
A2	Mixed natural gas	104	435	2490
A3	Heated natural gas (pre-reformer inlet)	851	435	2490
A4	Steam	485.6	587	4500
A5	Pre-reformed gas	396.9	435	7400
A6	Reformer inlet gas	1247	435	7400
A7	Steam	485.6	435	90.35
A8	O_2	392	435	50.19
A9	Reformer outlet gas	1800	435	311.6
A10	First water gas shift gas (WGS gas)	1800	435	311.6
A11	Second WGS gas	1800	435	311.6
A12	Cold water	86	435	602.3
A13	Saturated steam	484.4	580	602.3
A14	Cooled synthesis gas	100.4	435	311.6
A15	Separator gas	100.4	435	93.8
A16	Separator liquid	100.4	435	217.8
A17	Recycle gas inlet	406.8	433	19000
A18	Recycle gas outlet	406.8	433	19000
A19	PFR inlet (FT outlet)	410	435	19000
A20	PFR outlet	410	434	19000
A21	Separated FT gas	410	434	7000
A22	Separated FT liquid	410	434	12000
A23	Cold water	104	435	803.1
A24	MPP saturated steam	122.2	434	803.1
A25	Cold FT gas	408.3	433	7000
A26	Separated FT heavy liquid	408.3	433	4500
A27	Flue gas	408.3	433	4000

A28	Separated FT light liquid	408.3	433	10500
A29	Mixed flue gas	408.3	433	4000
A30	Recycled flue gas	408.3	433	4000

1. **ATR Reformer H_2/CO Ratio:** the H_2/CO ratio is evaluated because of the downstream FT reactor. The best H_2/CO ratio for an efficient FT reaction is 2. For the ATR reforming the H_2/CO ratio is determined from the Unisim simulation after the second equilibrium reactor in stream A10 as 2.21. This value is nearly close to the optimal value of 2
2. **ATR Reformer Molar Flowrate**: molar flow of reactants in the GTL plants are necessary because low flowrate leads to incomplete combustion and presences of unreacted methane component in the downstream section of the reactor while too high flowrate is uneconomical considering the cost of the reactants and operating expenditures. The molar flowrate for oxygen in the reformer is90.35 MMscfd (4500Kgmol/hr). Oxygen inlet into the GTL plant was only throughthe reformer. Steam entered into the plant through the pre-reformer and the reformer. The molar flowrate of steam in the pre-reformer and reformer sections are50.19 MMscfd (2500Kgmol/hr) respectively. These values are ideal to maintain the required H_2/CO ratio of 2.21. Note that the molar flowrate of the Oxygen and steam was regularly adjusted before these values were reached to maintain the required H_2/CO ratio as stated.
3. **ATR Reformer Carbon and Thermal Efficiency**: in order to determine the efficiency of the GTL process we determine the carbon and thermal efficiencies of the units and the overall configuration. The carbon efficiency of the ATR reforming GTL plant 77.68%, while the thermal efficiency is 88%

4. **ATR Reformer Steam Carbon Ratio**: the carbon ratio is necessary to avoid carbon deposition in the reactor. The steam carbon ratio for the pre-reformer and the reformer section of the ATR synthesis gas plant is 0.58. This is higher than the boundary ratio of 0.3 needed to avoid coke formation in the reactors.
5. **ATR Reformer Methane Conversion/Carbon Conversion**: in syngas plants, the performance of the plant is also measured by the percentage and volume of unreacted methane at the exit of the reactors. An efficient GTL synthesis gas option is the configuration that achieves the best conversion of the methane into synthesis gas. The percentage conversion of methane is 76.06% while the percentage conversion of carbon is 71.09%. But some unreacted methane will still be seen at the exit of the reformers. For the ATR synthesis gas option, the unreacted methane produced at the end of the reforming is 11.43 MMscfd (23.94%) while the total unreacted carbon in the reformer exit stream is 15.24 MMscfd (28.91%).

6. **ATR Reformer CO_2 Production/Emission**: GTL plants are evaluated based on the volumes of pollutants generated. The pollutant in GTL operation are in the form of CO_2 gas generated. CO_2 generation in GTL plants can occur in units such as the reformer during synthesis gas production, in the FT reactor, in the product work up and in the process heating vessels. For this work we analyze the CO_2 production at the exit of the reformers to ascertain the emission characteristics of the selected reforming methods. For the ATR reformer, the percentage CO_2 of the gas stream at the exit of the reformer is 7.06% of the reformer exit stream corresponding to a molar volume of 22.02 MMscfd (1096.8 Kgmol/hr)

7. **ATR Reformer Product Yield**: the GTL simulation yield is summarized in the table below.

Table 4.2: GTL plant product yield for ATR syngas method

Component	Volume (bbls/d)
Gasoline	3025
Kerosene	1380
Diesel	1025
Total	5430

From the table above, the total volume of GTL products produced from the GTL operation is 5430b/d. for a rule of thumb the liquid product yield for GTL plant is 1 barrel for 10,000 scf of pre-treated natural gas feedstream. From this calculation our feedstream corresponds to a conventional production of 5000 b/d. but the ATR configuration gives 5430 b/d corresponding to 8.6% increase in product yield.

8. **ATR Reformer General performance indices**: for the GTL plant configuration with the ATR synthesis gas reformer, the general technical performance indices are given in the table below

Table 4.3: General technical performance parametres for ATR reforming method

PARAMETER	VALUE
H_2/CO ratio at FT inlet	2.21
O_2 molar flow at reformer inlet (MMscfd)	50.19
steam molar flow at pre-reformer inlet (MMscfd)	90.35
steam molar flow at reformer inlet (MMscfd)	90.35
Carbon efficiency (%)	77.68
Thermal efficiency (%)	65.16
steam/carbon ratio at the pre-reformer	0.58
steam/carbon ratio at the reformer	0.58
Methane conversion (%)	76.06
unreacted methane (MMscfd)	11.43
Unreacted methane (%)	23.94
unreacted carbon (MMscfd)	15.23
Unreacted carbon (%)	28.91
CO_2 emission (MMscfd)	22.02
Diesel production (b/d)	3025
Gasoline production (b/d)	1380
Kerosene production (b/d)	1025
Total Product Yield (b/d)	5430

2. Technical Performance for Steam/ CO_2Reforming GTLPlant

For the alternative GTL case, the synthesis gas unit was retrofitted to use steam and CO_2 as the reactants to convert the methane to synthesis gas. The CO_2 to be utilized comes from two major sources: from the CO_2 in the natural gas feedstream and externally purchased from CO_2 suppliers. The plant is designed to reuse CO_2 produced as effluent gas in several CO_2 production sites such as the reformer section, the FT section, the product work-up section and the fired heaters.

1. Steam/CO_2 Plant Stream Description

The various parametres and component streams specified by the alphanumeric codes in the steam/CO_2 GTL plant simulation flowchart is described below.

Table 4.4: Plant stream Description for Steam/CO_2 reforming of the GTL plant

Stream	Description	Temperature (^0F)	Pressure (psi)	Molar flow (Kgmol/h)
C1	Natural gas	104	435	50
C2	Mixed natural gas	104	435	50
C3	Heated natural gas (pre-reformer inlet)	851	435	50
C4	Steam	485.6	587	90.35
C5	Pre-reformed gas	396.86	435	148.6
C6	Reformer inlet gas	1247	435	148.6
C7	CO_2	485.6	435	90.35
C8	Steam	392	435	50.19
C9	Reformer outlet gas	258.8	435	223.8
C10	First water gas shift gas (WGS gas)	454.28	435	223.8
C11	Second WGS gas	454.28	435	223.8
C12	Cold water	86	580	100.4
C13	Saturated steam	401	580	100.4
C14	Cooled synthesis gas	100.4	435	223.8
C15	Separator gas	100.4	435	223.7
C16	Separator liquid	406.22	433	0.1317
C17	Recycle gas inlet	406.22	433	26220
C18	Recycle gas outlet	410	435	26220
C19	PFR inlet (FT outlet)	410	434	26220
C20	PFR outlet	410	434	26220
C21	Separated FT gas	410	434	26220
C22	Separated FT liquid	410	434	26220
C23	Cold water	104	435	803.1
C24	MPP saturated steam	446	434	803.1

C25	Cold FT gas	100.4	433	26220
C26	Separated FT heavy liquid	100.4	433	26220
C27	Flue gas	100.4	433	26220
C28	Separated FT light liquid	100.4	433	26220
C29	Mixed flue gas	100.4	433	26220
C30	Recycled flue gas	100.4	433	26220

2. **Steam/CO_2Reformer H_2/CO ratio:** for the alternative case, we investigate the H_2/CO ratio to see if it is within the range of that necessary for efficient FT reaction in the downstream section of the synthesis gas unit. Form the Unisim simulation database, the H_2/CO ratio for the steam/CO_2 synthesis gas configuration of the GTL plant is 2.17. This is good as it is very close to the optimal value of 2 specified for efficient FT reaction. Also, this value is better than that gotten foe ATR reforming which has a value of 2.21.

3. **Steam/CO_2Reformer Molar Flowrate:** components reacting with methane for the alternative case are steam and CO_2. The molar flowrate of steam and CO_2 must be greater than or equal to that theoretically calculated in the stoichiometric reaction to avoid carbon deposition. Carbon deposition is noted with reforming using CO_2. But the combined use of Steam and CO_2 in this work gives less tendency for carbon deposition as long as the flowrate of the reactants are well regulated. The molar flowrate for CO_2 is 90.35 MMscfd (4500kgmol/hr). The CO_2 enters at the reformer section of the synthesis gas unit. The steam enters the synthesis gas unit at the pre-reformer and at the reformer with molar flowrate of 50.19 MMscfd (2500MMscfd)respectively
4. **Steam/CO_2Reformer Carbon and Thermal Efficiency:** The carbon efficiency of the steam/CO_2 reforming is92.18% while the thermal efficiency is 91%. This value is greater than that gotten for the ATR reforming method.

5. **Steam/CO_2Reformer Steam/Carbon Ratio**: the steam carbon ratio for the steam/CO_2 reforming is 0.87. This is higher than that for the ATR because the feedstream carbondioxide added to the mole carbon ratio.
6. **Steam/CO_2 ReformerMethane Conversion/Carbon Conversion:** the methane conversion for the steam/CO_2 reforming of the GTL plant is 84% while the unreacted methane in the product stream is 7.64 MMscfd (16%). The carbon conversion is also 84 % while the unreacted carbon is 8.44 MMscfd (16.01%).
7. **Steam/CO_2 ReformerCO_2 Production/Emission:** the CO_2 content of the product stream corresponding to the pollution characteristics of the steam/CO_2 reforming is 5.04 MMscfd. This value will is much smaller than that for produced in the ATR reformer. Also, since the CO_2 produced at the outlet will be redirected to be re-used in the reformer section of the plant in the next cycle or step.
8. **Steam/CO_2 ReformerProduct Yield**: the GTL simulation product yield for Steam/CO_2 is summarized in the table below.

Table 4.5: GTL plant product yield for Steam/CO_2 syngas method

Component	Volume (b/d)
Gasoline	3120
Kerosene	1425
Diesel	1185
Total	5730

9. **Steam/CO_2 reformer General Performance Indices**: the table below gives the key performance indices of the steam/CO_2 reforming process for the alternative GTL plant process.

Table 4.6: General technical performance parametres for Steam/CO_2 reforming method

Parameter	**Value**
H_2/CO ratio at FT inlet	2.17
CO_2 molar flow at reformer inlet (MMscfd)	50.19
steam molar flow at pre-reformer inlet (MMscfd)	90.35
steam molar flow at reformer inlet (MMscfd)	90.35
Carbon efficiency (%)	92.17
Thermal efficiency (%)	68.76
steam/carbon ratio at the pre-reformer	0.58
steam/carbon ratio at the reformer	0.87
Methane conversion (%)	84
unreacted methane (MMscfd)	7.64
Unreacted methane (%)	16
unreacted carbon (MMscfd)	8.44
Unreacted carbon (%)	16.01
CO_2 emission (MMscfd)	5.04
Gasoline production (b/d)	3120
Kerosene production (b/d)	1425
Diesel production (b/d)	1185
Total Product Yield (b/d)	5730

3. Comparison of Technical Parameters between ATR and Steam/CO_2 Reformer GTL Configuration

Table 4.7 below summarizes the technical performance indices for the

Table 4.7: Comparison of general technical performance parametres for ATR reforming method and Steam/CO_2 reforming method

Parameter	**ATR value**	**Steam/CO_2 value**
H_2/CO ratio at FT inlet	2.21	2.17
O_2 molar flow at reformer inlet (MMscfd)	50.19	50.19
Steam molar flow at pre-reformer inlet (MMscfd)	90.35	90.35
Steam molar flow at reformer inlet (MMscfd)	90.35	90.35
Carbon efficiency (%)	77.68	92.17
Thermal efficiency (%)	65.16	68.76
Steam/carbon ratio at the pre-reformer	0.58	0.58
Steam/carbon ratio at the reformer	0.58	0.87
Methane conversion (%)	76.06	84
unreacted methane (MMscfd)	11.43	7.64
Unreacted methane (%)	23.94	16
Unreacted carbon (MMscfd)	15.23	8.44
Unreacted carbon (%)	28.91	16.01
CO_2 emission (MMscfd)	22.02	5.04
Diesel production (b/d)	3025	3120
Gasoline production (b/d)	1380	1425
Kerosene production (b/d)	1025	1185
Total Product Yield (b/d)	5430	5730

4.1.2 Model Validation

The proposed steam/CO_2 method used was validated with a similar operational pilot plant in Kazakhstan. The table below gives the result of the experimental process and the proposed method

Table 4.8: Model Validation

S/N	Parameter	Experimental (Kazakhstan)	Proposed method (Simulation)
1	H_2/CO ratio	2.14	2.17
2	Carbon Efficiency	92.58	92.17
3	Thermal Efficiency	69.37	68.76
4	Unreacted Carbon (%)	15.7	16.01
5	GTL Product Yield (bbls/MMscfd)	11.6	11.46

From table 4.8, it can be observed that the proposed model gives very close results with the experimental results in all the parameters considered. For the H_2/CO ratio, the proposed method gives a H_2/CO ratio of 2.17 while that of the experimental process was 2.14. The carbon efficiency for the experimental process and the proposed method are 92.58% and 92.17% respectively. The thermal efficiency of the experimental process and the proposed method are 69.37% and 68.76% respectively. The unreacted carbon in the process system are 15.7% for the experimental process and 16.01% for the proposed method.

The GTL product yield from the experimental process and the proposed method are 11.6 bbls/MMscfd and 11.46 bbls/MMscfd. The closeness of the results of the proposed method with the pilot test experiment conducted validates the proposed model developed

4.1.3: Presentation of Results for Economic Evaluation

Results of economic analyses will be presented based on the total barrels of liquid products produced. Each liquid product contributes to the revenue by multiplying its liquid yield by the unit cost of the product in barrels. The economic analyses shall be determined concurrently for both cases.

1. **Calculation of Revenue**

Revenue is calculated on annual basis. The annual revenue comprises the money accrued from the sales of the GTL product per year. The annual revenue calculation is presented in table 4.8 below.

Table 4.9: Revenue presentation for both cases of the GTL project

GTL PRODUCT	**MARKET PRICE (US$)/bbl**	**PRODUCTION CAPACITY (b/d)**		**TOTAL DAILY REVENUE (US$)**		**TOTAL ANNUAL REVENUE (US$)**	
		ATR	**STEAM/CO$_2$**	**ATR**	**STEAM/CO2**	**ATR**	**STEAM/CO$_2$**
GASOLINE	90	3025	3120	272250	280800	95287500	98280000
KEROSENE	100	1380	1425	138000	142500	48300000	49875000
DIESEL	100	1025	1185	102500	118500	35875000	41475000
TOTAL	-	5430	5730	512750	541800	**179462500**	**189630000**

From table 4.8 above, the annual revenue for ATR and steam/CO_2 reforming are US$179462500 and US$189630000 respectively. The revenue from the steam/CO_2 reforming of the GTL plant gave a 5.67% increase in revenue from that of the ATR.

2. Calculation of OPEX for the GTL Plant for Both Cases

The Operating expenses for the GTL project for both cases are presented in the table below. The total OPEX comprises the variable and fixed OPEX. The fixed OPEX are the cost accruing from the purchase of natural gas and oxygen while the variable OPEX comprises other operating expenses on production of GTL liquids other than the natural gas and oxygen purchase and supply expenses. The table below gives the result of the OPEX used in this work.

Table 4.10: Calculation of Total OPEX of the GTL project

Component	**Flowrate (MMscfd)**	**Cost per (Mscf)**	**Annual cost (US$)**	
			ATR	**STEAM/CO_2**
Natural gas	50	2.5	43750000	43750000
Oxygen	50.19	2	35133000	
CO_2	50.19	1.5		26349750
variable OPEX (5% of CAPEX)	-	-	17380908.85	17380908.85
Total OPEX	-	-	**78883000**	**70099750**

From table 4.9 above, the total OPEX for the ATR and the steam/CO_2 reforming GTL plants are US$78883000 and US$70099750 respectively. There was a reduction of 11.13% in the OPEX from the use steam/CO_2 reforming technique for the GTL plant.

3. Determination of the Economic Indicators for the GTL Project

The table below gives the economic indicators of the project. Comparison is made for both cases. The table for the spreadsheet calculation of these results is given at the appendix

Table 4.11: Presentation of Economic Indicators for the GTL project

ECONOMIC PARAMETRE	ATR	STEAM/CO_2	DIFFERENCE
ANNUAL CASHFLOW/NCR (US$)	58945738.7	71263726	20.9%
NPV (US$)	187434652	299245518	59.7%
DCF-ROR (%)	16.6	20.3	4.7
Pay-Out Time, POT (yrs)	5.9	4.9	1
P/$	3.24	4.13	0.89

From table 4.10 above, it is seen that using steam/CO_2 method for the reforming of the GTL improves the profitability in all the indices considered. There is a 59.7% difference in the NPV when steam/CO_2 method is chosen instead of the ATR for the GTL plant project. This amounts to a net profit of US$111810866 from the use of steam/CO_2 reforming method.

The DCF-ROR for the GTL project for US$2.5/Mscf natural gas price are 16.6% and 20.3% respectively while the Pay-out time are 5.9 years and 4.9 years for the ATR and steam/CO_2 reforming method respectively.The figure below gives the POT and the DCFROR for both cases considered

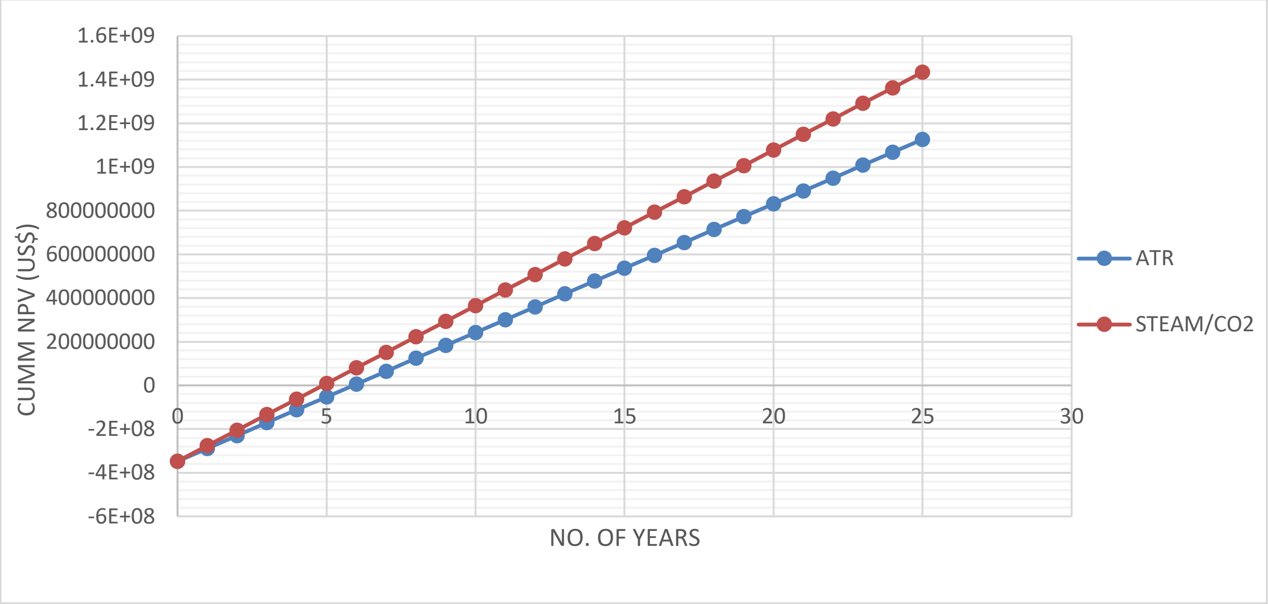


Figure 4.1: Figure showing Pay-Out Time for US$2.5/Mscf natural gas price for both cases of the GTL plant considered.

From figure 4.1, it is seen that using steam/CO_2 reforming gives a faster pay-out time than the ATR method for the synthesis gas production during GTL plant operation.

Figure 4.2: DCF-ROR for the project t natural gas price of US$2.5/Mscf

The discounted cashflow rate of return is the discount rate that will yield an NPV of zero. From the figure below, the DCF-ROR is 16.6% for ATR reforming GTL method and 20.3% for steam/CO_2 reforming GTL method. The DCF-ROR of 16.6% and 20.3% calculated shows that the project is economically viable for the two cases considered since the discount rates for most gas projects are not greater than 10%.

4.1.4Sensitivity Analyses

Sensitivity analyses is performed on both cases to ascertain the sensitiveness of economic variables on economic performance indices. This is done by changing some factors while others are kept constant to determine the baseline of profitably of the project under changing economic conditions in the future. The sensitivity of this work shall be conducted with changes in the following factors

1. Discount rates of 10%, 15% and 20% are used
2. Natural gas cost of US$2.5/Mscf and US$3/Mscf
3. Changes in non-feed stock OPEX of 5% and 6%
4. Changes in CAPEX of US$80,000 PBLD and US$100,000 PBLD

1. Sensitivity Analyses of the ATR Reformer GTL Plant

For the ATR reforming method, the total product yield is 5430b/d. The capital cost per barrel liquid a day (PBLD) is US$64018 PBLD. Thus, we evaluate the sensitivities for US$80,000PBLD and US$100,000PBLD. The table below gives the sensitivity analyses of the ATR reformer for natural gas price of US2.5/Mscf

Table 4.12: General economic indices for sensitivity analyses of ATR reformer GTL plant at natural gas price of US$2.5/Mscf

ATR: NG price US$2.5/Mscf	**CAPEX: $50,000/BLPD**		**CAPEX: $64,018/BLPD**		**CAPEX: $80,000/BLPD**	
	OPEX (% OF CAPEX)					
DISCOUNT RATES	**5%**	**6%**	**5%**	**6%**	**5%**	**6%**
10%	276334992	260316286	187434652	166924916	86079971	60450041
15%	118636769	107229162	33415866	18810004	-63743914	-81996085
20%	27106296	18375042	-55979005	-67158168	-150704000	-164674006
NCR	60353925	58589175	58945739	56686221	57340275	54516675
DCF-ROR	21.4	21.4	16.6	15.9	12.5	11.8
POT	4.63	4.63	5.9	6.13	7.58	7.97

From the table it is seen that the NPV decreases as the CAPEX is increased. The CAPEX is a factor that largely affects the NPV as shown in the figure 4.3 below

Figure 4.3: Graph of NPV vs. time for the ATR reforming at natural gas price of US$2.5/Mscf

Furthermore, we investigate the economic sensitivity of the project when the natural gas price increases from US$2.5/Mscf to US$3.0/Mscf. The table below gives the economic variables

Table 4.13: General economic indices for sensitivity analyses of ATR reformer GTL plant at natural gas price of US$3.0/Mscf

ATR: NG price US$3.0/Mscf	**CAPEX: $50,000/BLPD**		**CAPEX: $64,018/BLPD**		**CAPEX: $80,000/BLPD**	
	OPEX (% OF CAPEX)					
DISCOUNT RATES	**5%**	**6%**	**5%**	**6%**	**5%**	**6%**
10%	224709327	208690621	135808987	115299251	34454305	8824376
15%	81871921	70464314	-3348982	-17954844	-100508762	-118760933
20%	-1033105	-9764359	-84118406	-95297569	-178843401	-192813408
NCR	5466425	52901675	53258239	50998721	51652775	48829175
DCF-ROR	19.9	19.2	14.8	14.1	11	10.3
POT	4.97	5.13	6.53	6.8	8.41	4.97

If the cost of natural gas is increased, the profitability of the project reduces. An increase of natural gas price by US$0.5/Mscf gives a 0.36 year increase in pay-out time and a 1.5% decrease in the DCF-ROR for the ATR reforming of the GTL plant

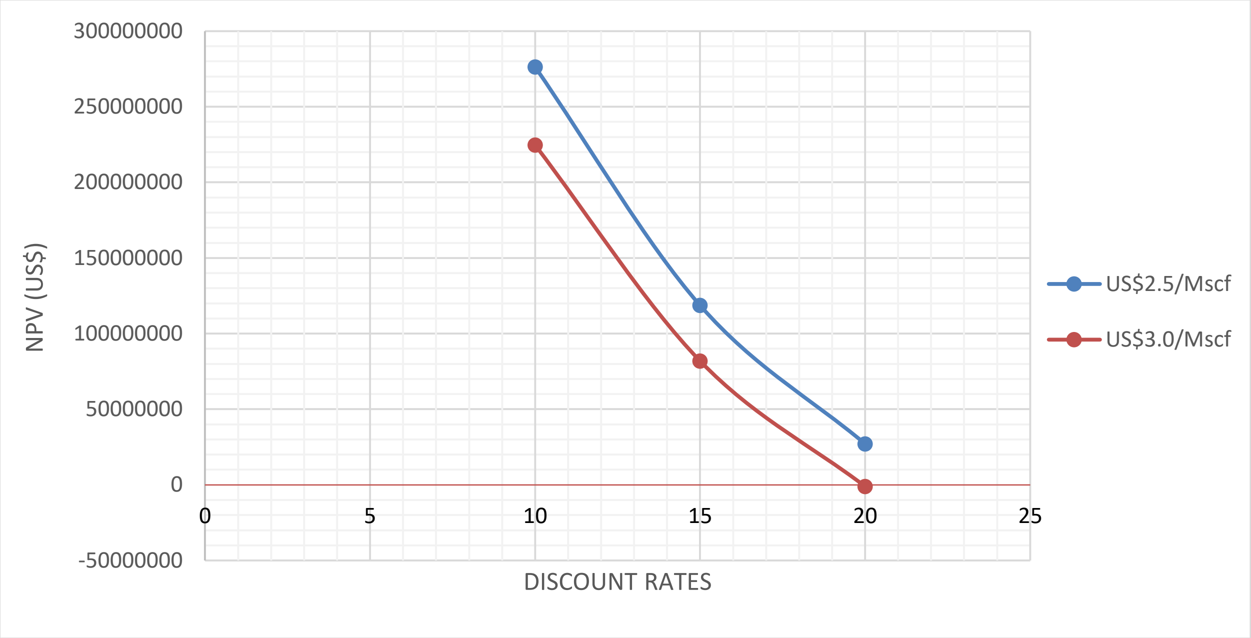


Figure 4.4: Graph of NPV vs. time for the ATR reforming at natural gas price of US$3.0/Mscf

2. Sensitivity for the Steam/CO_2 Reformer GTL Plant

Here we analyze the sensitivity of the economic variables on the economic performance of the GTL plant for the steam/CO_2 reformer. First, we evaluate for natural gas price of US$2.5/Mscf and then for natural gas price of US$3.0/Mscf. The table below gives the result.

Table 4.14: General Economic Indices for Sensitivity Analyses of ATR Reformer GTL Plant at Natural Gas Price of US$2.5/Mscf

Steam/CO$_2$: NG price US$2.5/Mscf	**CAPEX: $50,000/BLPD**		**CAPEX: $64,018/BLPD**		**CAPEX: $80,000/BLPD**	
	OPEX (% OF CAPEX)					
DISCOUNT RATES	**5%**	**6%**	**5%**	**6%**	**5%**	**6%**
10%	388145858	372127152	299245518	278735781	197890836	172260906
15%	198262077	186854470	113041174	98435312	15881394	-2370778
20%	88050611	79319357	4965310	-6213853	-89759685	-103729691
NCR	72671913	70907163	71263726	69004208	69658263	66834663
DCF-ROR	26.7	26	20.3	19.6	15.6	14.9
POT	3.74	3.83	4.9	5.04	6.24	6.5

The table 4.14 gives the economic performances indices for the steam/CO$_2$ reforming method of the GTL plant for natural gas price of US$2.5/Mscf. From the table it is seen that the steam/CO$_2$ reforming process shows better pay-out time and DCF-ROR than that of the ATR.

At 20% discount rates the project is profitable for CAPEX of US$50,000 PBLD and US$64,018 PBLD. The figure below illustrates the relationship of the NPV with the discount rates for steam/CO_2 reforming at natural gas price of US$2.5/Mscf.

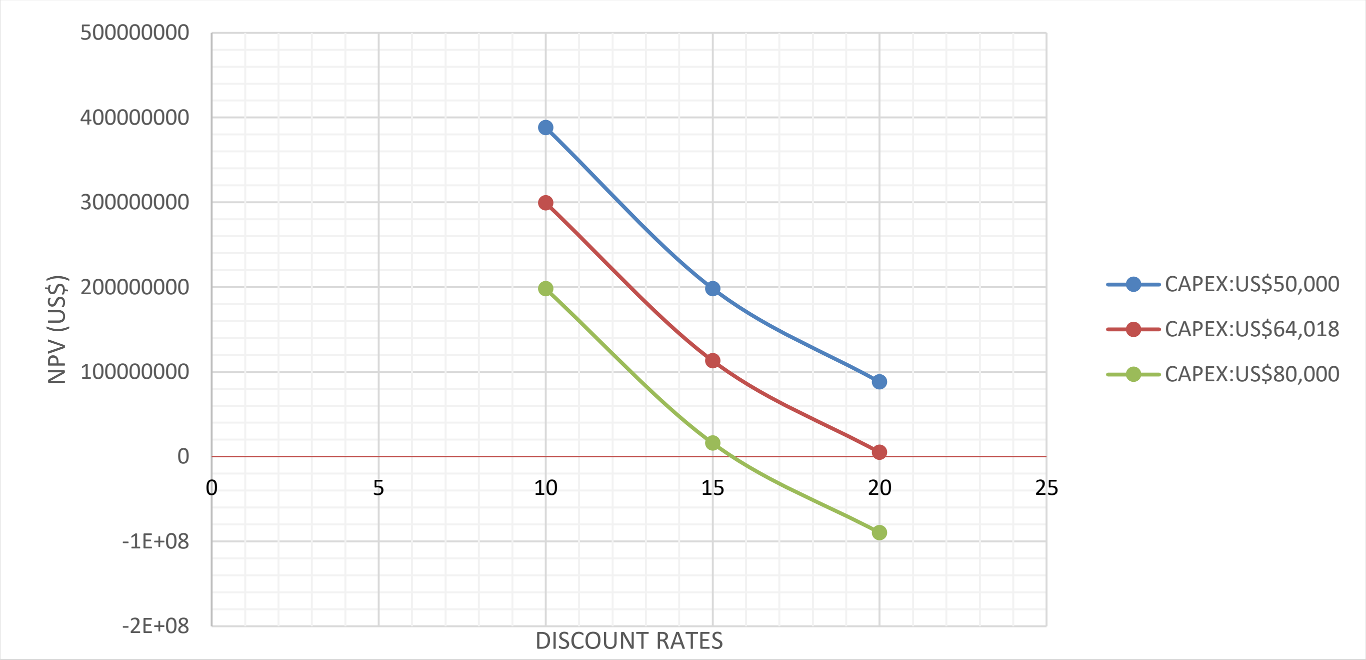


Figure 4.5: Graph of NPV vs. time for the steam/CO2 reforming at natural gas price of US$2.5/Mscf

For natural gas price of US$3.0/Mscf, the table below gives the effect of sensitivity on the economic performance of the project.

Table 4.15: General Economic Indices for Sensitivity Analyses of ATR Reformer GTL Plant at Natural Gas Price of US$2.5/Mscf

Steam/CO2: **NG price** **US$3.0/Mscf**	**CAPEX: $50,000/BLPD**		**CAPEX: $64,018/BLPD**		**CAPEX: $80,000/BLPD**	
	OPEX (% OF CAPEX)					
DISCOUNT RATES	**5%**	**6%**	**5%**	**6%**	**5%**	**6%**
10%	336520193	320501486	247619853	227110116	146265171	120635241
15%	161497229	150089622	76276326	61670464	-20883454	-39135625
20%	59911210	51179956	-23174091	-34353254	-117899086	-131869093
NCR	66984413	65219663	65576226	63316708	63970763	61147163
DCF-ROR	24.6	23.9	18.6	17.9	14.2	13.5
POT	4.05	4.16	5.3	5.49	6.79	7.1

Increasing the natural gas price increases the pay-out time by 0.21 years and reduces the DCF-ROR by 2.1% for the seam/CO_2 reforming method of the GTL plant operation. The figure 4.6 below illustrates the effect of natural gas price on NPV at various discount rates.

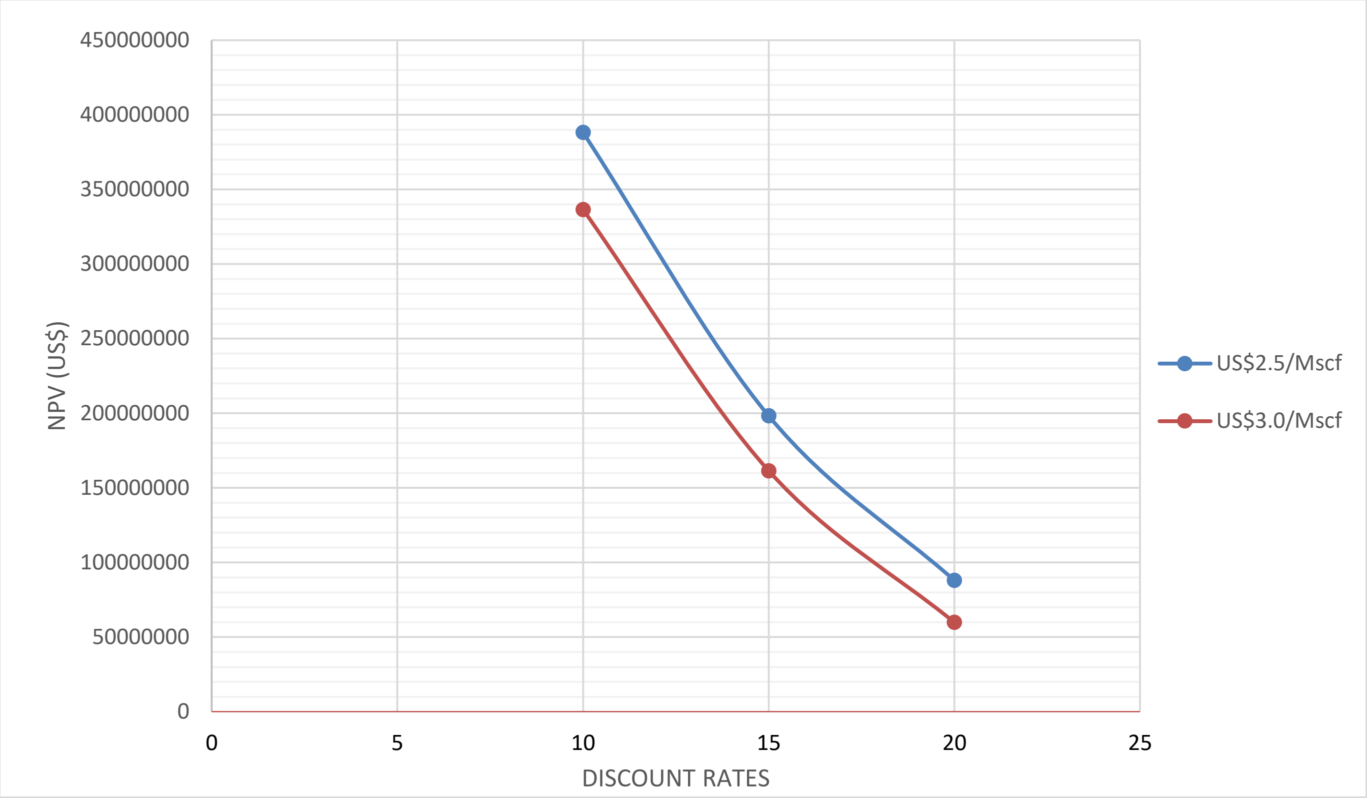


Figure 4.6: Graph of NPV vs. time for the steam/CO_2 reforming at natural gas price of US$3.0/Mscf

For the two natural gas prices of US$2.5/Mscf and US$3.0/Mscf considered for the steam/CO_2 GTL project, the project shows positive NPV for discount rates less than 20%.

4.2 Discussion of Results

Here discussions are made on the results presented both for the technical performance and the economic performance of the GTL plant in the two reforming methods considered.

4.2.1 Technical Performance Results

1. Steam/CO_2 reforming H_2/CO ratio of 2.17 is better than the H_2/CO ratio of 2.21 from the ATR. A better H_2/CO ratio favours the use of steam/CO_2 reforming than ATR reforming for the production of lighter end component (transport) liquids at the Fisher Tropsch plant.

The H_2/CO ratio synthesis gas reformer of the CompactGTL facility at Kazakhstan during its operation was found to be 2.14 which is very close to the value of 2.17 in the proposed method. The GTL operation at Kazakhstan gives us an experimental value to validate the accuracy of our GTL simulation using the Unisim simulation software. The error margin is 1.4% which is within acceptable limits for process plant operations.

2. Higher carbon and thermal efficiencies justify the use of steam/CO_2 reforming than the ATR. The difference in carbon and thermal efficiencies of the steam/CO_2 reforming andthe ATR reforming is 14.49% and 3.6% respectively. This shows that steam/CO_2 reforming is better than ATR reforming.
3. Lower pollution characteristics in terms of carbon emission is gotten from the use of steam/CO_2 reforming method than that of the ATR. This factor makes the use of steam/CO_2 reforming more environmentally friendly than the ATR method.
4. The product yield from the steam/CO_2 reforming is 5730b/d while that of the ATR method is 5430b/d representing a 5.5% increase in daily GTL liquid production. Thus, there is an increase in product yield from the alternative GTL method proposed in this work than the conventional method.

4.2.2 Economic Performance Results

1. The annual revenue generated from the steam/CO_2 method and the ATR methods are US$ 179462500 and US$189630000 respectively. Thus, the use of steam/CO_2 yielded higher annual revenue than the ATR. Thus, there was an increase of 5.67% from the use our proposed method.

2. Using our proposed method gives an annual cashflow increase of 20.9% and NPV increase of 59.7% at 10% discount rates. Thus, our proposed method is more profitable in terms of NPV.
3. Our proposed method gave faster pay-out time of 4.9 years as compared to that of 5.9 years for the base case. Furthermore, our proposed method gave a higher DCF-ROR than the base case for all sensitivities considered.
4. High CAPEX affects the profitability of the GTL project regardless of the method. But our proposed method shows higher profitability even at higher CAPEX than the base case.
5. Even at high discount rate of 20% our proposed method gives positive NPV for natural gas price of US$2.5/Mscf whereas the base case NPV become negative at these conditions.
6. Natural gas price greatly affects the profitability of the GTL project. A natural gas price difference of US$0.5/Mscf led to a 0.36 year increase in pay-out time and a 1.5% decrease in the DCF-ROR for the ATR reforming of the GTL plant, also 0.4 years increase in pay-out time and 1.7% decrease in DCF-ROR for the proposed steam/CO_2 reforming method.
7. The proposed method withstood the increase of natural gas price more than the base case.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Gas-to-liquids technology optimisation has been done using two methods: the base case method which uses autothermal reforming (ATR) method for the production of synthesis gas in the syngas unit and the proposed method which makes use of steam/CO_2 reforming for the production of synthesis gas. The base case method had utilized oxygen and steam as its feed reactant fuel while our proposed method had replaced oxygen use with carbon dioxide gas. Honeywell's Unisim simulation was performed for the two cases for using Peng Robinson fluid property package. A multi-tubular bed reactor was used for the Fischer Tropsch unit, this was simulated in Unisim as a Plug flow reactor and simulated as a heterogeneous reaction type following Iglesia reaction kinetics.

Technical performance and economic performance indices have been evaluated and compared for the two cases. The technical performance reveals that the proposed method is more technically justifiable for use in the GTL project than the base case ATR method in terms of carbon and thermal efficiency, pollution characteristics, H_2/CO ratio and product yield. Evaluation of the economic performance indices also reveals that the proposed method is more economically justified than the base case in terms of NCR, NPV, POT, DCF-ROR and P/$ for all economic conditions and sensitivities analyzed.

5.2 Recommendations

The following are recommendations from the work

i. Steam/CO_2 reformer method should be used for GTL technology operations for higher technical and economic performance especially for mini or small-scale plants.
ii. This method will be highly profitable when the GTL plant is in modular unit movable from one location to another.
iii. The scalability and movability of modular units will offer more cost reduction in both CAPEX and OPEX in the GTL operations.
iv. The work should be applied in the Niger Delta areas where there are many areas with large volumes of stranded gases that have been wasted due to flaring.
v. The government of Nigeria can partner with investors by providing enabling environment and providing fiscal policies that will favor the utilization of the vast stranded gases in the Niger Delta. These gases can be chemically converted to transportable liquids using GTL technologies and the techniques evaluated in this work. This will not only provide revenue and employment but will rid our environment of the huge environmental pollution emanating from varied flare sites in the Niger Delta region.

5.2.1 Further Research Areas

The following are further research areas associated with this research work

i. Determination of effect of catalyst activity on syncrude production in the Fischer-Trospch unit
ii. Evaluation of the effect of H_2/CO ratio on the product yield of GTL plant

iii. Optimization of Fischer-Tropsch unit using artificial neural Networks
iv. Investigation of the use of GTL waste heat in the production of electricity via GTL-electricity co-production.
v. Optimization of slurry-phase Fischer-Trospch synthesis using nano-sized catalyst

5.3 Contribution to Knowledge

1. Design and Retrofitting of a GTL plant with enhance technical performance indices using Honeywell Unisim software
2. Formulation of a GTL plant alternative for production of yield of premium GTL transport fuels with cleaner carbon footprint
3. Design of an alternative GTL plant system that has reduced capital and operating expenses
4. Design of GTL plant layout fitted with carbon dioxide capture and re-use mechanism for efficient utilization of flue gases from the GTL process plant.
5. Design of a modular GTL process scheme with less pollution and environmental impacts
6. Provision of GTL system with better incentives for individual/corporate investor participation through reduced capital and operating expenses and higher economic returns.

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NOMENCLATURE

APG: Associated Petroleum Gas

ASU: Anderson-Schultz-Floury

CAPEX: Capital Expenditure

CNG: Compressed Natural Gas

CO_2: Carbondioxide

DCF-ROR: Discounted Cashflow Rate of Return

EIA: Environmental Impact Analyses

GHGs: Greenhouse Gases

GTC: Gas-to-Chemicals

GtW: Gas-to-Wire

IOCs: International Oil Companies

ISBLI: Inside Battery Limit Costs

KJ: Kilojoules

LNG: Liquefied Natural gas

LPG: Liquefied Petroleum Gas

MATLAB: Matrix Laboratory software

MMbtu: Million British thermal unit

MMscfd: Million standard cubic feet per day

Mscf: Thousand standard Cubic Feet

MTG: Methanol-to-Gasoline

NGL: Natural Gas Liquids

NPV: Net Present Value

OPEX: Operating Expenditure

OSBL: Outside Battery Limit Costs

P/$: Profit-Per-Dollar Invested

PBLD: per Barrel-Liquid a Day

PFR: Plug Flow Reactor

POT: Pay-Out-Time

PPM: Parts per Million

Psig: Pounds per Square Inch Gauge

SPDC: Shell Petroleum Development Company

STG: Syngas-to-Gasoline Plus

US$: US dollars

APPENDIX

Appendix A: Calculation of GTL Plant Depreciation

Using the straight-line depreciation method, the deprecation for the GTL plant is given as

$$\text{Depreciation} = \frac{\text{US\$}347{,}618{,}177 - 0}{25} = \text{US\$}13{,}904{,}727/\text{year}$$

Appendix B: Calculation of the Cashflow/NCR for ATR Syngas GTL Plant

The cashflow is calculated with using equation 3.28. It is presented in the table below

Table A: cashflow calculation for ATR method

Annual revenue, (US$)	179462500
- Total annual operating cost (US$)	96263908.85
- depreciation (US$/year)	13904727
= taxable income (US$)	69293864.15
- income tax @35% (US$)	24252852.45
= Net income (US$)	45041011.7
+ depreciation (US$/year)	13904727
= Cash flow/NCR (US$)	58945738.7
POT (years)	**5.9**

Appendix C: Calculation of the Net Present Value for ATR Method

The net present value is the sum of the present worth of the project. It is calculated using the Excel spreadsheet as given in the table below

Table B: Net present value for ATR GTL method

YEAR	CAPEX	ANNUAL CASHFLOW (NCR)	UNDISCOUNTED CASHFLOW US$	CUMM. UNDISCOUNTED CASHFLOW US$	DISCOUNTED CASHFLOW (10%)	CUMM DISCO CASHF (10%)
0	347618177	-	-347618177	-347618177	-347618177	-34
1	-	58945738.7	58945738.7	-288,672,438.30	53587035.18	-2940
2	-	58945738.7	58945738.7	-229,726,699.60	48715486.53	-2453
3	-	58945738.7	58945738.7	-170,780,960.90	44286805.94	-2010
4	-	58945738.7	58945738.7	-111,835,222.20	40260732.67	-1607
5	-	58945738.7	58945738.7	-52,889,483.50	36600666.06	-1241
6	-	58945738.7	58945738.7	6,056,255.20	33273332.78	-9089
7	-	58945738.7	58945738.7	65,001,993.90	30248484.35	-6064
8	-	58945738.7	58945738.7	123,947,732.60	27498622.14	-3314
9	-	58945738.7	58945738.7	182,893,471.30	24998747.4	-8148
10	-	58945738.7	58945738.7	241,839,210.00	22726134	1457
11	-	58945738.7	58945738.7	300,784,948.70	20660121.81	3523
12	-	58945738.7	58945738.7	359,730,687.40	18781928.92	5401
13	-	58945738.7	58945738.7	418,676,426.10	17074480.84	7109
14	-	58945738.7	58945738.7	477,622,164.80	15522255.31	8661
15	-	58945738.7	58945738.7	536,567,903.50	14111141.19	1007
16	-	58945738.7	58945738.7	595,513,642.20	12828310.17	1135
17	-	58945738.7	58945738.7	654,459,380.90	11662100.16	1252
18	-	58945738.7	58945738.7	713,405,119.60	10601909.23	1358
19	-	58945738.7	58945738.7	772,350,858.30	9638099.303	14
20	-	58945738.7	58945738.7	831,296,597.00	8761908.457	1542
21	-	58945738.7	58945738.7	890,242,335.70	7965371.324	1621
22	-	58945738.7	58945738.7	949,188,074.40	7241246.659	1694
23	-	58945738.7	58945738.7	1,008,133,813.10	6582951.508	1760
24	-	58945738.7	58945738.7	1,067,079,551.80	5984501.371	1819
25	-	58945738.7	58945738.7	**1,126,025,290.50**	5440455.792	**1874**

Appendix D: Calculation of Cashflow/NCR for the Steam/CO_2 Reformer GTL Method

Table C: Cashflow/NCR for steam/CO_2 method

Annual revenue, (US$)	189630000
- Total annual operating cost (US$)	87480658.85
- Depreciation (US$/year)	13904727
= Taxable income (US$)	88244614.15
- Income tax @35% (US$)	30885614.95
= Net income (US$)	57358999.2
- Depreciation (US$/year)	13904727
- Cash flow/NCR (US$)	71263726.2
POT (years)	4.9

Appendix E: The Net Present Value for Steam/CO_2 Method

The table below gives the net present value for the steam/methane reformer GTL plant

Table D: Net Present Value for Steam/CO2 method

YEAR	CAPEX	ANNUAL CASHFLOW (NCR)	UNDISCOUNTED CASHFLOW US$	CUMM. UNDISCOUNTED CASHFLOW US$	DISCOUNTED CASHFLOW (10%)	CUMM. DISCOUNTED CASHFLOW (10%)
0	347618177		-347618177	-347618177	-347618177	-347618177
1		71263726.2	71263726.2	-276,354,450.80	64785205.64	-282832971.4
2		71263726.2	71263726.2	-205,090,724.60	58895641.49	-223937329.9
3		71263726.2	71263726.2	-133,826,998.40	53541492.26	-170395837.6
4		71263726.2	71263726.2	-62,563,272.20	48674083.87	-121721753.7
5		71263726.2	71263726.2	8,700,454.00	44249167.16	-77472586.58
6		71263726.2	71263726.2	79,964,180.20	40226515.6	-37246070.98
7		71263726.2	71263726.2	151,227,906.40	36569559.63	-676511.349
8		71263726.2	71263726.2	222,491,632.60	33245054.21	32568542.86
9		71263726.2	71263726.2	293,755,358.80	30222776.56	62791319.42
10		71263726.2	71263726.2	365,019,085.00	27475251.42	90266570.84
11		71263726.2	71263726.2	436,282,811.20	24977501.29	115244072.1
12		71263726.2	71263726.2	507,546,537.40	22706819.35	137950891.5
13		71263726.2	71263726.2	578,810,263.60	20642563.05	158593454.5
14		71263726.2	71263726.2	650,073,989.80	18765966.41	177359420.9
15		71263726.2	71263726.2	721,337,716.00	17059969.46	194419390.4
16		71263726.2	71263726.2	792,601,442.20	15509063.15	209928453.5
17		71263726.2	71263726.2	863,865,168.40	14099148.31	224027601.9
18		71263726.2	71263726.2	935,128,894.60	12817407.56	236845009.4
19		71263726.2	71263726.2	1,006,392,620.80	11652188.69	248497198.1
20		71263726.2	71263726.2	1,077,656,347.00	10592898.81	259090096.9
21		71263726.2	71263726.2	1,148,920,073.20	9629908.008	268720004.9
22		71263726.2	71263726.2	1,220,183,799.40	8754461.826	277474466.7
23		71263726.2	71263726.2	1,291,447,525.60	7958601.66	285433068.4
24		71263726.2	71263726.2	1,362,711,251.80	7235092.418	292668160.8
25		71263726.2	71263726.2	1,433,974,978.00	6577356.743	299245517.6