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Monetizing the Flared Associated Natural Gas in Real-Time Via Synthetic Fuels Production

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Abstract:

The basic organic compound which serve as raw materials for the preparation of the many specific synthetic compounds are obtained from four sources: plant live, wastes, coal tar, petroleum (crude oil and natural gas). Wood was the first of man's fuel and is still the primary energy source in most parts of the world. At the onset of the industrial revolution, charcoal from wood was replaced by coke from coal. Subsequently, the development of the internal-combustion engine and the automobile created a vast new market for gasoline product made from crude oil; kerosene use for lighting and heating oil began to replace coal in many energy markets. Thus, the industrial revolution lead to the change from the use of hand tools, using human mechanical energy to machine and power tools, which allowed the conversion of energy in falling water to mechanical energy (water wheels) or conversion of chemical energy in wood or coal to mechanical energy (steam engine) for industrial processes. Synthetic fuels are liquid or gaseous fuels extracted or fabricated from solid earth materials that are rich in hydrocarbons, such asbiomass (plants and plant-derived substance e.g., waste), coal, oil shale, tar sands, natural gas instead of refining crude oil. This paper reviewed the development of the GTL process technology from its recognition in 1902, to the evolving micro-channel technology. By 1953, Sasol of South Africa, was using natural gas to produce 30,000 bbl/d (4800 m³/d) synthetic fuels; while in Nigeria, flaring of associated stranded natural gas commenced in 1956 with the first successful well drilled at Oloibiri: Until 1984, the country flared virtually 100% of all the produced associated stranded natural gas. It reduced to 70% in 1999, and to, between 43-52 % in 2004, about where it remains up to date. Meanwhile, Nigeria's only GTL Project, by Chevron Nigeria Limited (CNL), which started with pre-feasibility study in 1998, contracted in 2005 with 34,000 bpd capacity at Escravos is still under construction today. On the other hand, the premier oil refinery in Nigeria was built and commissioned in 1965 with maximum capacity of 60,000 bpd, while the other three refineries are built at: Warri in 1978 with capacity 125,000 bpd; Kaduna in 1980 with 110,000 bpd capacity; and Port Harcourt in 1985 with 150,000 bpd capacity. For well over 20 years now, Nigeria imports more than 75% petrol products for transportation, because all the refineries either operate below 5% capacity or are fully short down (non-operational). Since it is technically feasible to synthesize almost any hydrocarbon from any other, this work is aimed at establishing the daily quantity of synfuels obtainable from any gas flare line give the composition and flow rate. The study obtained 1,414.88 barrels (equivalent to 59,424.96 gallons or 226,240 litres) of synfuels plus 13MW electric power daily from 20 MM scfd flare line. This takes advantage of the fact that the size of GTL plants varies from small (5 to 15,000 bpd) to large (>50,000 bpd). Thus, no matter the quantity of gas being flared from a particular line, there is a plant size design that can produce synfuels, generate electricity from waste heat, plus water and other petrochemicals/ chemicals. End products are determined by the length of the hydrocarbon chain which, in turn, is determined by catalyst selectivity and reaction conditions (temperature, pressure and residence time). In general, the product range include the light hydrocarbon (C₁ and C₂), LPG (C₃ –C₄), naphtha (C₅ –C₁₂), kerosene-diesel fuel (C₁₃ – C₂₂), low-molecular weight wax (C₂₃ –C₃₂), linear alpha olefins et cetera. Synfuels are cleaner than those produced via petroleum distillation. With virtually zero aromatics, sulfur, and high Octane/cetane numbers they are used to upgrade conventional gasoil by blending it with GTL gasoil.

Keywords: Associated natural gas, diesel, distillation gasoline, monetizing, synthetic fuel

1. Introduction

Fuels are substances or material (such as wood, coal, crude oil, natural gas, uranium atoms, plutonium atoms, et cetera) consumed, oxidized or otherwise changed in the process of releasing heat energy or doing work (i.e. power, fire, charge). Thus, these substances contain energy components, which are released when they undergo certain form of chemical reaction, oxidation reaction, nuclear reaction (fission) (Wikipedia, fuel).

The heat energy released by reactions of fuels is converted into mechanical energy via heat engines or the heat itself is directly used for warmth, cooking, industrial processes, illumination et cetera.

Wood was the first of man's fuel and is still the primary energy source in much of the world.

Nuclear energy is created from the energetic splitting of large atoms of uranium or plutonium into smaller atoms in a process called fission. Fission releases energy that can be used to make steam, which is used to power a steam turbine to generate electricity.

Coal, petroleum (crude oil and natural gas) are referred to as fossil fuels, because they come from the remains of ancient life, buried beneath the earth surface (Kopp, 2017). These substances are extracted from the earth's crust and refined into suitable fuel products. Coal is a common fuel burned to generate electric power. Crude oil is refined into gasoline, diesel fuel, and jet fuel, which power the world's transportation system. Also, some are processed into plastics, chemicals, lubricants, and other nonfuel products. Natural gas is primarily composed of methane and is mostly used in commercial and industrial buildings for heating water/air, air conditioning, fuel for stoves and other heating appliances.

In contrast, synthetic liquid fuels or synfuels are liquid fuels which are produced from other source apart from crude oil product or sometimes gaseous fuels derived or obtained from either gasification of solid earth material feedstock that are rich in hydrocarbons (compounds containing hydrogen and carbon). In principal, substitute/synthetic natural gas (S.N.G.) otherwise known as syngas can be produced from any carbon source e.g. fossil fuels (such as coal, crude oil, shale oil/ oil shale, tar sands), biocrops/biomass (plants and plant-derived substances), or other recyclable material (garbage, human and animal waste) or virtually any hydrocarbon feedstock, by reaction with steam or oxygen or by reforming of natural gas (Cui, 2014; Wikipedia, Synthetic Fuel). Coal is converted into liquid fuel by, combined gasification and liquefaction processes. Liquid fuel (oil) is extracted from oil shale by a process called retorting. Biomass is converted to ethanol (bio fuel) by fermentation and to methane (biogas) by hydration.

Precisely, coal or biomass can be gasified to produce a synthesis gas (syngas or biosyngas) a mixture of hydrogen and carbon monoxide, which can be converted using Fischer-Tropsch catalyst/reactor (either fixed bed, fluidized bed, slurry bubble or micro-channel module) into straight chain paraffinic waxes that are hydro-cracked to make variety of products (ranging from diesel, naphtha, lube oil, base stocks down to gases), that is upgraded to yield clean sulphur free liquid stream with properties similar to the crude oil products (e.g. gasoline, diesel etc). All of these fuels can also be produced from natural gas using a similar process. 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-methylether 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 (figure 1), such as fischer-tropsch method, Mobil process, and the syngas to gasoline plus (STG+) process (Wikipedia, gas-to-liquid), as alternatives to the traditional refining of crude and other natural gas commercialization routes such as liquefied natural gas (LNG), liquefied petroleum gas (LPG).

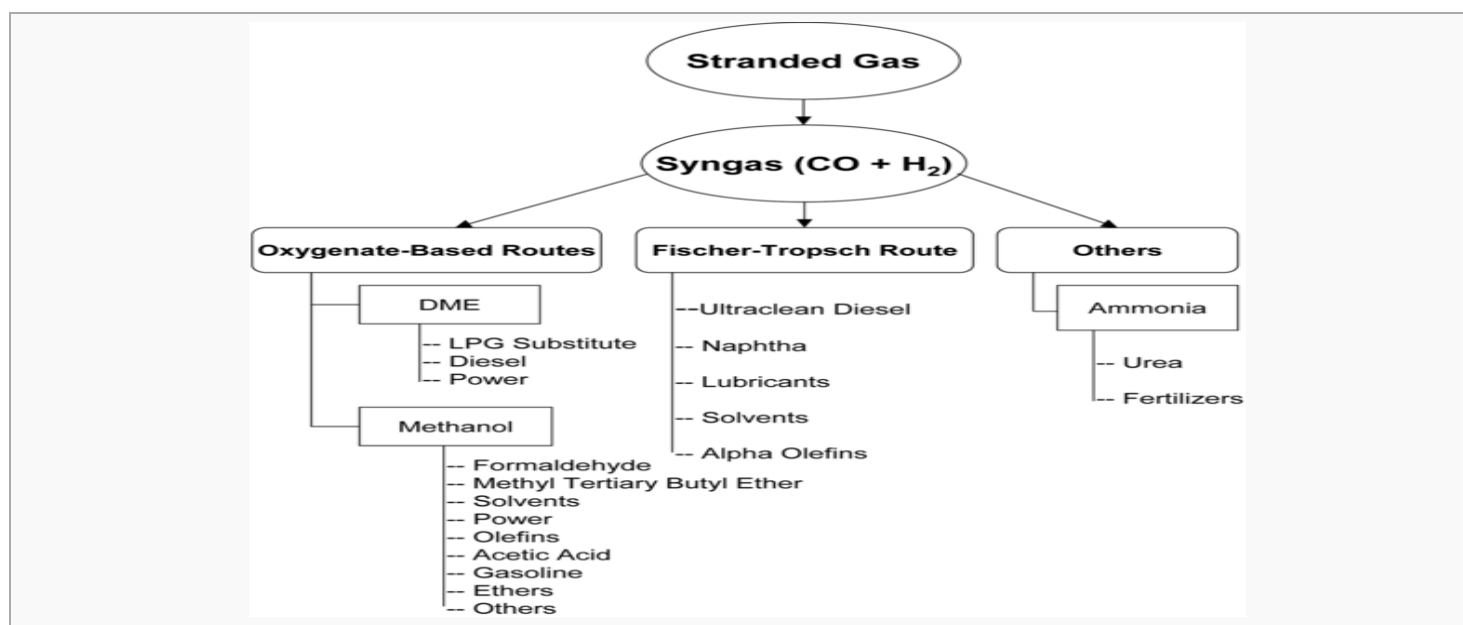


Figure 1: Indirect GTL routes to gas monetization
Source: Adapted from PetroWiki, Shah and Durr, KBR

Currently, the indirect conversion approach is mostly used in the industry. The gas to liquid process starts with synthetic gas production i.e. the source material is converted to carbon monoxide and hydrogen using a reformer or gasifier (figure 2). This technology is similar to that used in making methanol and ammonia.

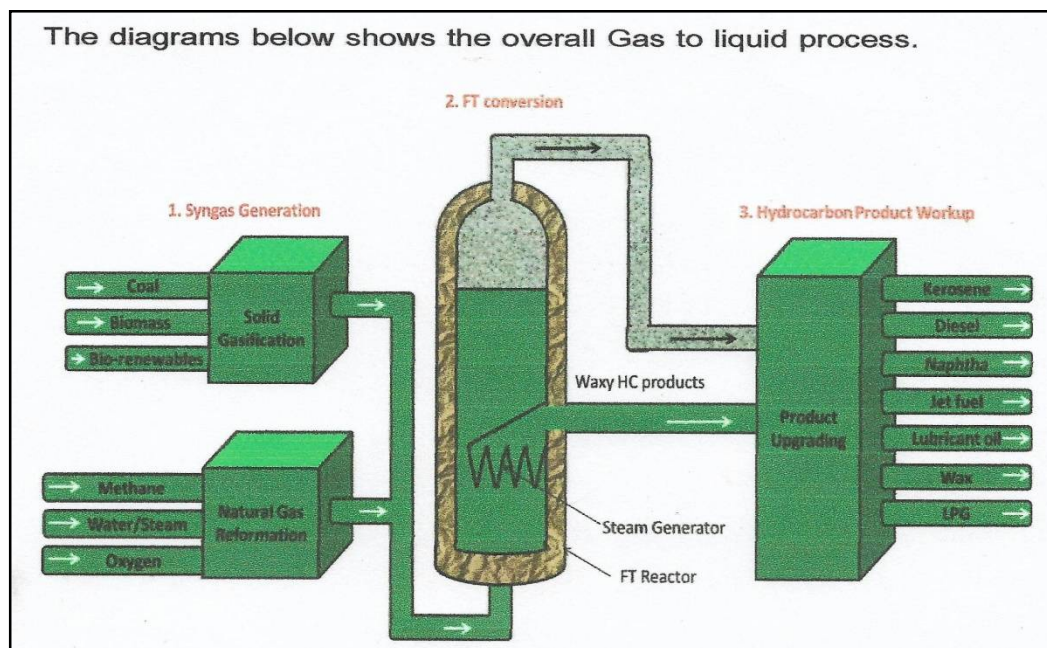


Figure 2: Schematic of the Gas-to-Liquid Process

Source: Adapted from Unpublished Final Year project in Federal University of Technology, 2014

1.1. Review of GTL Technology

The first recognition of the benefits that can be obtained from Gas-To-Liquid (GTL) technology was achieved from the creation of methane from hydrogen and carbon monoxide (synthesis gas) by the combined efforts of Paul Sabatier and Jean Senderens in 1902. (Fischer, 2001). Friedrich Bergius (1884-1949) in Rheinau-mannheim began the German drive for energy independence with his invention and development of high-pressure coal hydrogenation or liquefaction in the years 1910-1925 (Stranges, 2001). A decade after, (in 1923) two German Scientists, Franz Fischer (1877-1947) and Hans Tropsch (1889-1935) who explored ways to synthesize liquid petroleum from the country's abundant coal supplier, as a result of the economic sanctions following World War I (28 July 1914-11 November 1918) invented a second process by successfully converting methane obtained from heated solid fuel (coal) into synthesis gas (H_2 and CO), which was subsequently polymerized in high temperature into high-quality hydrocarbon chains of varying lengths such as diesel fuel, lubricating oil and waxes at the Kaiser-wilhelm Institute for coal research in Mulheim Germany (Ekekepe and Onyekonwu, 2007; Warner Jr., 2007). Hence the plants are usually referred to as Fischer-Tropsch (F-T) process or F-T synthesis. By 1944, German chemical companies had constructed nine coal-derived gas F.T plants for generating clean synthetic liquid fuels (Glebova, 2013). After World War 2 (1 Sept 1939- 2 Sept. 1945), USA and South Africa (largely driven by restrictions on oil imports) used different catalysts at different temperature and pressures on the Fischer-Tropsch process. And by 1953 South African developed a concept which put into operation (Oil Field Review Schlumber, 2003). Subsequently Petro SA used conventional natural gas piped in from Mozambique on an F-T plant, to produce 30,000 bbl/d ($4800 m^3/d$) synthetic fuels. It is this aspect of GTL technology, the production of easily transportable liquid fuels from conventional natural gas that intrigues the world's large oil and gas companies (oil field review Schlumber, 2003).

To date, hundreds of modifications and patents have been applied to the original complex F-T energy intensive process, and further developments continue to evolve, mostly on lowering capital expenditures, overall energy required for processing through the use of proprietary catalyst and on the manner in which oxygen is added to the system. For instance, Sasol, a South African petrochemical company developed Sasol Slurry Phase Distillate (SSPD) which converts natural gas into synthetic diesel, kerosene and naphtha. Sasol also assisted Mossgas, another South African firm, in developing a commercial scale international GTL Plant at Mossel Bay, using natural gas in 1993. In the same 1993 Shell (an international oil and gas company) after investigating on GTL technique for 20 yrs, commissioned a plant in Bintulu Malaysia using the patented Shell Middle Distillate Synthesis (SMDS), process, which produces 12,500 bbl/d ($1990 m^3/d$) of middle distillates of clean diesel, kerosene and naphtha. The present capacity of the plant is 14,700 bpd (Repair, 2010). Since 1997, Conoco Phillips has designed, manufactured and tested more than 5000 catalysts for gas-synthesis F-T processes. The 2003 demonstration plant at Oklahoma converts 4MMcf ($114,600 m^3$) per day of natural gas to 400 bpd ($64 m^3/d$) of sulfur-free diesel and naphtha. The first BP plant design in Alaska produce 250 bpd ($40 m^3/d$), with a compact gas-reformer, which is one-fortieth of the size used at other GTL plants. In 2002 the Japan National Oil Corporation (JNOC) manufactured the first GTL product with their pilot plant which has a maximum liquid-fuel production capacity of 6.9 bpd ($1.1 m^3/d$) designed for commercialization (Schlumberger Oilfield Review, 2003).

Most, newer designs of GTL, plants are specialty plant (specifically targeted at either chemical, blend stocks, super/ultra clean synthetic transportation fuels, waxes, maximizing yields of middle distillates notably kerosene, diesel and gas oil) and some lower distillates (i.e. motor gasoline) et cetera. Importantly also, some plants include a self-contained power generation capability, ensuring that the plant is a stand-alone facility, not requiring any outside utility or infrastructure support. Thus, each plant makes GTLs +

electricity + water, all directly from natural gas, in the fully integrated, skid-mounted, self-contained, portable and automated micro-GTL processing plant. Also, some are modularized into multi-unit applications so that it can be sized to fit the customer's needs, with facilities that can be easily expanded or downsized as gas supplies grow or decline.

On the other hand, synfuels international has developed a direct GTL (non-FT GTL) plant, while there are over five hundred methanol plants in operation around the world. Figure 3, shows the overall process scheme of gas to liquid process.

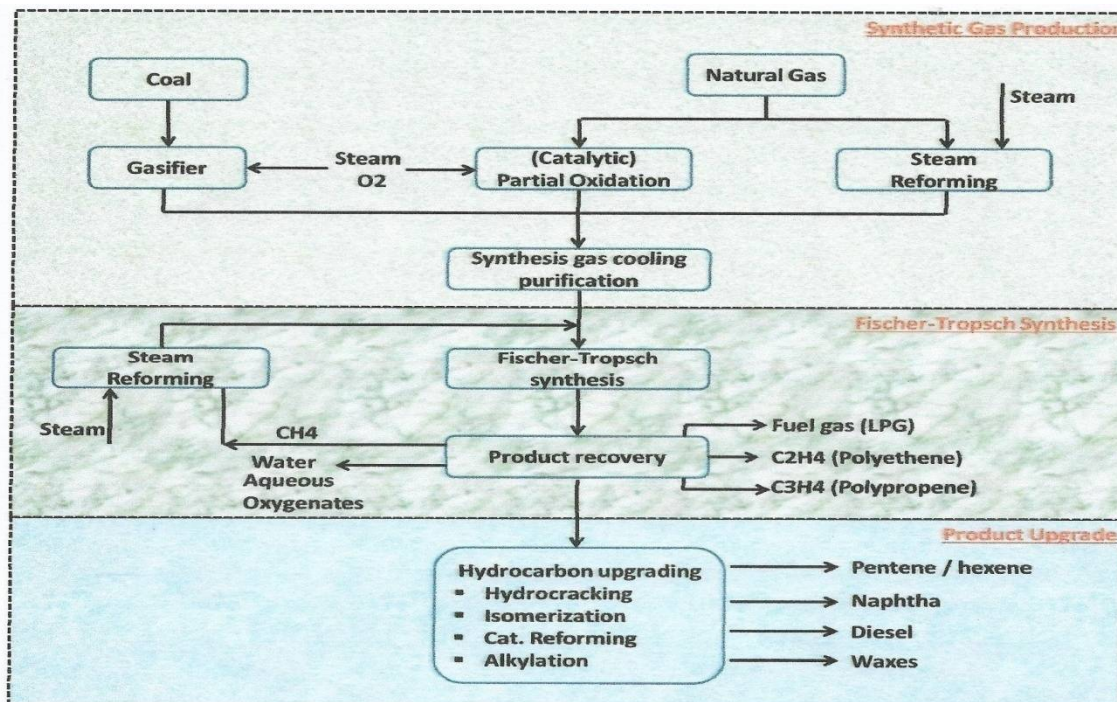


Figure 3: Overall scheme for the gas-to-liquid process.

Source: Adapted from Unpublished Final Year project in Federal University of Technology, 2014

1.2. GTL in Nigeria

Nigeria's only GTL project is the Chevron Nigeria Limited (CNL), Escravos Gas –to-Liquid Project (EGTL), located in Niger Delta, approximately 62 miles (100 kilometers) South East of Lagos. The pre- feasibility study started in April 1998, while the front-End Engineering and Design (FEED) which commenced in July 2001, was completed in 2002 (Escravos GTL, Wikipedia). In April 2005, the plant Engineering, Procurement and Construction (EPC) contract cost of \$1.7 billion (N226.1 billion) was awarded to Team JKS, a consortium composed of JGC Corporation of Japan, Kellogg- Brown-Root (KBR) of the U.S and Snamprogetti of Italy (Escravos Gas-to-Liquid Project, Wikipedia). The project was expected to be commissioned around the end of 2009, converting about 340 million standard cubic feet per day (MMscfd) of dry natural gas from the Escravos Gas project phase – 3 (EGP-3), to 34,000 barrels per day (5,400 m³/d) liquid petroleum products (synfuels), diesel, naphtha and LPG. The contract cost soared from the initial \$1.7 billion in 2005, to \$2.5 billion in 2007, rising to \$5.9 billion in 2009, escalated to \$8.4 billion in 2011 and to around \$10.3 billion as at June 7, 2016 (Onuwuemenyi, 2016). The project was 76% complete by June 2011, test ran in September 2014 (PetroleumAfrica; Gas-to-Liquid technology-Chevron) and is expected to be expanded to 120,000 bpd capacity within ten years of its completion. Currently, the plant is still under construction.

1.3. Crude Oil Refining in Nigeria

The premier oil refinery in Nigeria was built and commissioned in 1965 at Port Harcourt with maximum capacity of 60,000 bpd of refined products. The second refinery, NNPC Warri refinery was awarded in October 1976 and Commission in 1978 with initial full production capacity of 100,000 bpd, but was later debottlenecked to 125,000 bpd (19,900m³/d) (Refinery, DPR; List of oil Refineries in Nigeria). The third refinery, NNPC Kaduna refinery was awarded in April 15, 1977 and Commission 1980 with initial full production capacity of 100,000 bpd, but later debottlenecked to 110,000 bpd (17,000m³/d). Contract for the fourth refinery in Port Harcourt was awarded on 11th February 1985, with full production capacity of 150,000 bpd (24,000m³/d) (Petroleum Industry in Nigeria, Wikipedia). But early in 1988, when NNPC commercialized its activities, the fourth refinery, then still under construction was merged with the existing Nigerian Petroleum Refining Company (NPRC) to form the now Port Harcourt Refining Company (PHRC) Limited; with capacity of 210,000 bpd (33,000 m³/d). The refineries have a combined installed capacity of 445,000bpd (70700m³/d) (Refineries and Petrochemicals). Presently as a result of various problems with the different refineries, they are all under refurbishment and the country have relied on importation of more than 75 percent of petrol products (Okafor, 2015) for well over 15 years now. On the 23rd Jan. 2017, the Federal Government told International oil companies (IOC's) operating in the country to invest on building refineries on direct sales model to recoup the investment within a short period (Obosi, Eboh, 2017).

Meanwhile, at the Lekki free Trade Zone in Lagos the Dangote group is building a 650,000 bpd (103,000 m³/d) Dangote Refinery Complex, including fertilizer plant (2.8 million metric tonnes per annum of Urea and Ammonia) and Petrochemical Units (750,000 metric tonnes per year of polypropylene) while Oron mega refinery & petrochemical complex under the African Eagle Development Group have proposed to build 450,000 bpd (72,000 m³/d) capacity refinery.

1.4. Study Significance

Presently, Nigeria still flares around 50 per cent of its associated stranded natural gas, whereas over 75 per cent of liquid fuels used in Nigeria are imported. The National Bureau of Statistics' Petroleum Products Imports Statistics indicate that in 2015 Nigeria imported refined Petroleum Products comprising approximately (Udoma and Osagie, 2017):

*19 billion litres of Premium motor spirit;

*3.9 billion litres of diesel; and

*1.7 billion litres of household kerosene.

While according to the NNPC's July 2016 financial and operations report, the Country traded 252,390 bpd of crude oil for refined petroleum products in June 2016 under the NNPC's direct sales-direct purchase scheme.

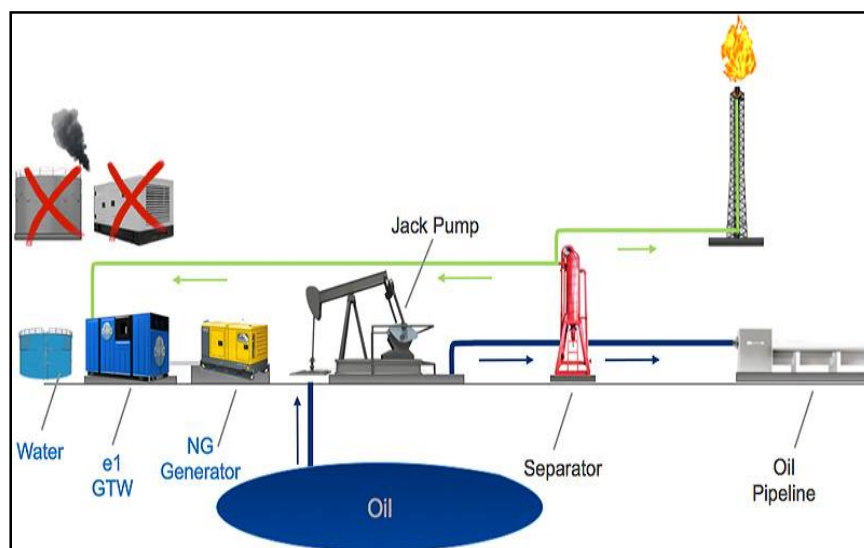


Figure 4: A typical associated gas flare from an Oil Well without GTL Facility

Source: Adapted from Images of the complete flare line from the wellhead to the flare stack

This paper is aimed at evaluating the real-time synthetic fuels recoverable from specific flare lines (figures 4 and 5) based on their parameters, such as flow rate, gas composition et cetera. Processing the flared associated stranded natural gas for synthetic fuel will not only alleviate the liquid fuel scarcity, but also produced various petrochemicals, chemicals as well as generate power electricity, thereby creating numerous job opportunities in Nigeria.

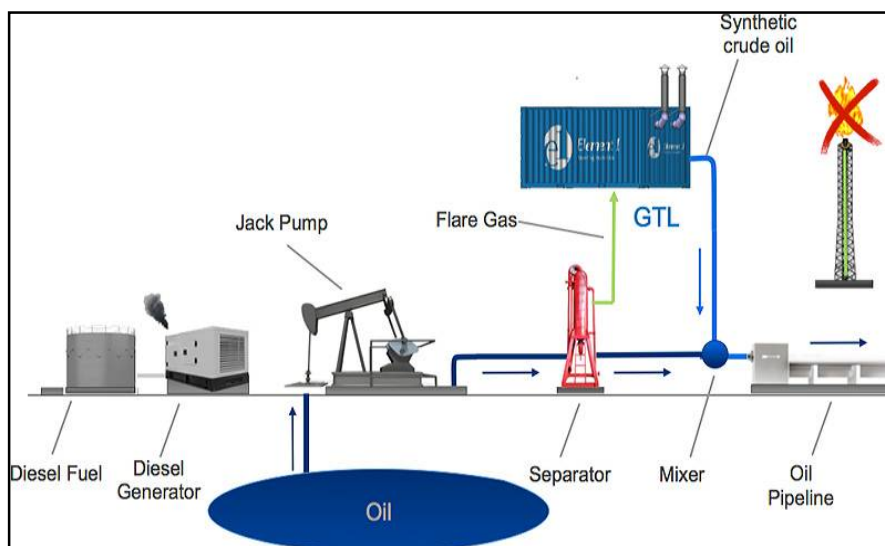


Figure 5: A typical associated gas flare from an Oil Well with GTL Facility

Source: Adapted from Images of the complete flare line from the wellhead to the flare stack

2. Back Ground

It is technically feasible to synthesize almost any hydrocarbon from any other and since 1902 several processes have been developed to synthesize liquid hydrocarbon from different sources.

The overall GTL facility more closely resembles an oil refinery in its process and operations, so much that it could be referred to as "Natural Gas Refining" (NGR). The GTL process starts with pretreatment or fuel preparation which, for coal and biomass includes size reduction, preheating to distill off the volatile matter, and conversion to gas (i.e. gasification), mixture of CO and H₂, while for natural gas, it starts with a gas treatment plant for removal of sulfur, carbon dioxide, water, heavier hydrocarbon components, and other contaminants, and gas reformation to CO and H₂ mixture.

Over the years, the gaseous mixture of H₂ and CO has had many names depending on how it was formed; producer gas, town gas, blue water gas and synthesis gas or syngas based on the reformation of purified natural methane that is breaking its molecules into a mixture of two diatomic molecules, hydrogen and carbon monoxide (H₂ and CO), with a ratio of 2: 1, that provide the building blocks upon which an entire field of fuel science and technology is based.

Unlike methane, syngas is very reactive and can be converted by a wide range of processes (reforming process) into a variety of useful chemicals and materials. It is a crucial intermediate resource for the production of hydrogen, ammonia, methanol and synthetic hydrocarbon fuel. Gas-to-liquids (GTL), coal-to-liquids (CTL) Biomass-to-liquids (BTL) all rely on the catalytic conversion of syngas (figures 6, 7 and 8).

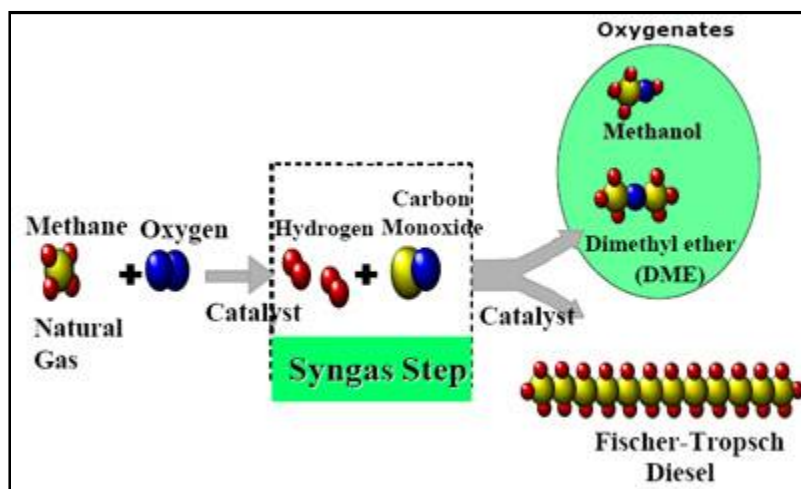


Figure 6: Schematic of gas to liquid chemistry

Source: Adapted from Images of the overall gas to liquid process

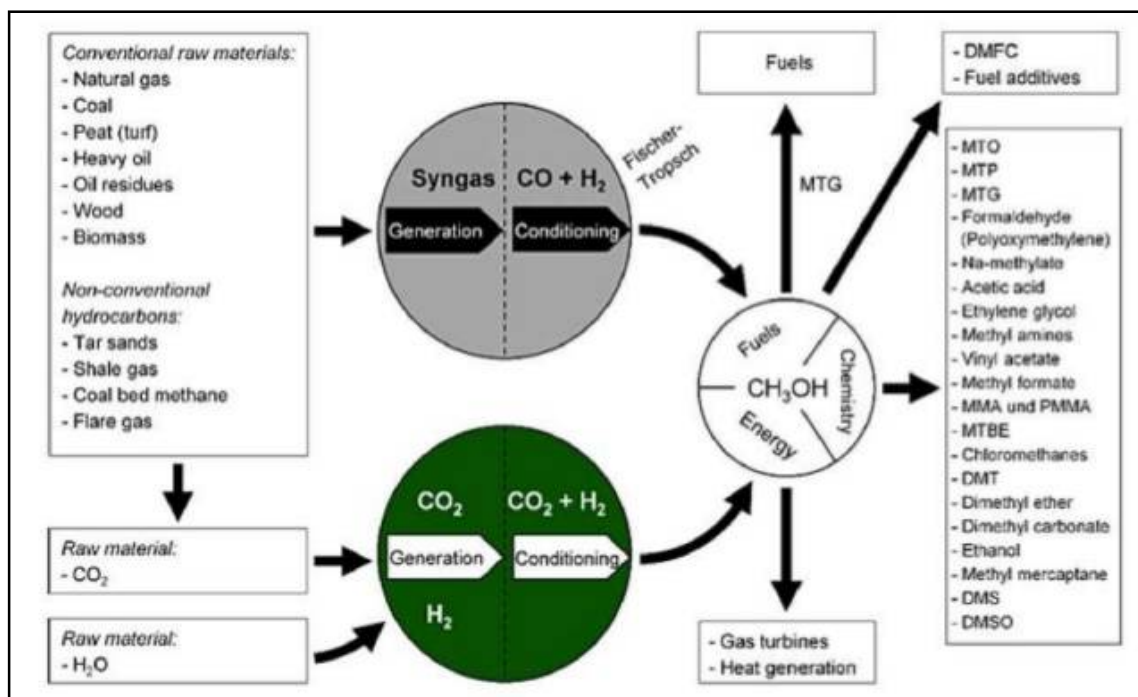


Figure 7: Schematic of Major Sources of Syngas Production and the End Products

Source: Adapted from Images of the overall gas to liquid process

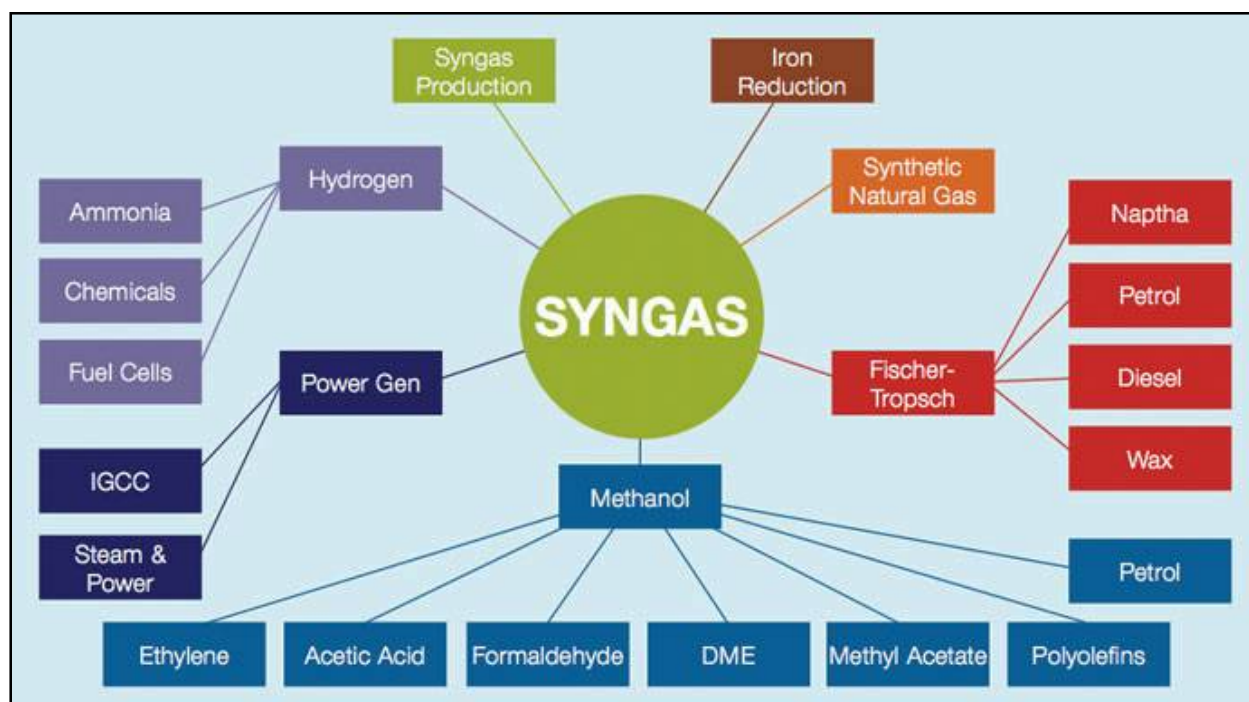


Figure 8: Schematic of Major products from Syngas
Source: Adapted from Images of the overall gas to liquid process

The formation of syngas can either be, strongly endothermic (steam reforming) or exothermic (partial oxidation reforming) and requires high temperatures.

Basically, GTL plants that use natural gas (flared associated stranded) are especially ideal as the “back end” of LPG operation: valuable LPG’s are stripped from the feedstock gas stream, and then, each plant can be configured to use the remaining C₁ and C₂ gas stream to make synfuels + electricity + water-all directly from flared associated stranded natural gas. Thus, every bit of value is being realized from previously flared natural resources.

Conventionally, for GTL, the Gas treating Unit (GTU), process gas stream C₁ to C₈ to remove C₃⁺ components, and other contaminants such as sulfurated, hydrogenated, and silicone compounds, as well as carbon dioxide, Nitrogen and oxygen.

Six principal technologies for syngas production from natural gas have been commercialized or are at an advanced stage of development: They include: -

- (1) Steam-Methane- Reforming (SMR)
- (2) Partial Oxidation (POX) or non- catalytic reforming
- (3) Autothermal reforming (ATR)
- (4) Catalytic reforming (CPOX)
- (5) Heat exchanger reforming (HER)
- (6) Compact reforming (CPR).

The first three listed reformers are the basic types, and all industrial plants use either variants or combinations of these.

In steam –methane reforming (SMR), natural gas and steam are converted to syngas via endothermic and over a nickel catalyst contained in tubes within a fire box. The heat of reaction is supplied by burning some of the feedstock.



Partial oxidation (POX) of methane, combines natural gas and oxygen to produce syngas via exothermic and non-catalytic reaction at high temperatures.



Autothermal reforming (ATR) is a hybrid which combines steam reforming and partial oxidation in one reaction to produce syngas. Mixtures of natural gas, steam, and oxygen or air are reacted adiabatically over a fixed bed of nickel catalyst (figure 9).

Its operating temperature is higher than that of steam methane reforming and lower than that of partial oxidation. It has a higher thermal efficiency and desired H₂: CO ratio. While Figure 10 represents the Conventional Natural Gas -to-Liquid Process Flow Diagram.

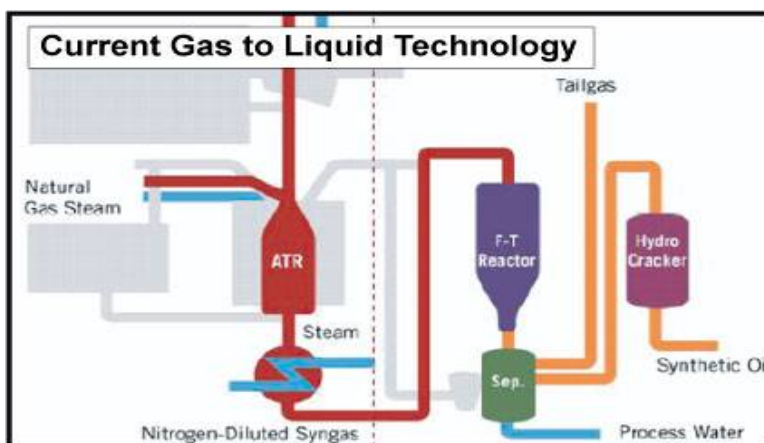


Figure 9: Current operational Gas-to-Liquid Conversion Process
 Source: Adapted from Images of Gas-to-Liquid Processes

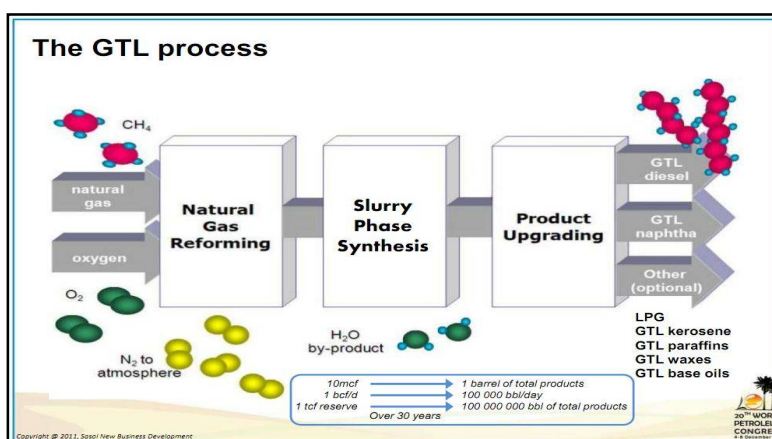


Figure 10: Conventional Natural Gas -to-Liquid Process Flow Diagram
 Source: Adapted from Images of Gas-to-Liquid Processes

Alternative routes to syngas, such as reduction of CO₂ from flue gas with H₂ from electrolytic splitting of water may become interesting from the view point of storage of wind or solar energy.

The direct approach to convert natural gas (methane) into synfuels (liquid hydrocarbons) eliminates the cost of producing synthesis gas (H₂ and CO) as intermediate step (since syngas unit is typically 60% of a plant cost) but it involves high activation energy and is difficult to control. This is due to the fact that methane has one of the strongest bonds among hydrocarbons, while its reaction products usually have weaker bond. As such, any catalyst for use in the conversion process needs to break the tight carbon- hydrogen bonds in the methane. A single- step process could solve many of the problems that currently keep GTL from being economically viable. Figure 11 Shows the first generation Low Temperature Direct Hydrocarbon Conversion (LTDHC) Technology for Fuels and Chemicals Developed by the PEERI (Power Environmental Energy Research Institute) Covina, CA in U.S.A.

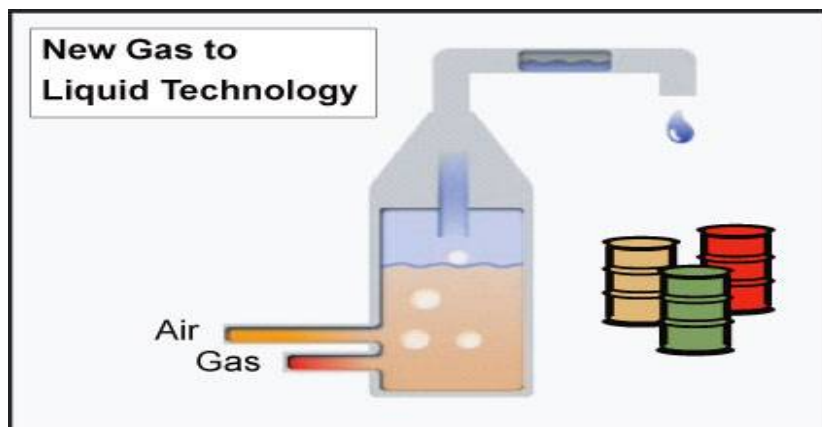


Figure 11: Low Temperature Direct Gas-to-Liquid Conversion Process
 Source: Adapted from Images of Gas-to-Liquid Processes

3. Material

Table 1 shows the typical representative composition of the flared associated stranded natural gas stream in Nigeria, obtained from statistical analysis of 36 flare streams, selected from 150 flare line data samples. And table 2 contains the average operational parameters of the Nigeria flare gas stream.

Component	Mole %
Methane	78.5375
Ethane	78.5375
Propane	5.9625
i-butane	1.4842
n-butane	1.8882
i-pentane	0.6964
n-pentane	0.4982
Hexane plus	0.7550
Nitrogen	0.1729
Carbon dioxide	2.0105
Other undesirables	0.2066
	100.0000

Table 1: A Typical Representative Composition of Flare Associated Stranded Natural Gas in Nigeria
Source: Adapted from Ekejiuba, 2017

Parameter	Range	Value for the Study
Gas Gravity (air)	0.607 to 0.996	0.755
Flow rate MMscfd	5 to 63	20
Pressure Psig	7 to 75	10
Pressure	21.7 to 89.7	25
Temperature °F	60 to 115	80
Base Temperature During Analysis	-	60°F
Base Pressure During Analysis	-	14.7psia

Table 2: Flare Conditions of the Associated Stranded Natural Gas in Nigeria
Source: Adapted from Ekejiuba, 2017

Sweetening the typical representative flared associated stranded natural gas table (1) for GTLs synthetic fuels entails removing the undesirable components, which in this case, constitutes 2.39% of the flare gas stream.

Assuming that each molecular component release exactly, equal amount (moles) of the undesirable in sweetening the stream, that is $(2.39/97.61 = 0.0244)$ per mole. It implies that the sweetened compositional (mole %) for methane becomes $78.5375 + (78.5375 \times 0.0244) = 80.4538$.

And the overall compositional (mole %) for the entire flare stream on component by component basis is as shown in table (3).

Component	Mole %
Methane	80.4538
Ethane	7.9780
Propane	6.1079
i-butane	1.5204
n-butane	1.9343
i-pentane	0.7134
n-pentane	0.5104
Hexane plus	0.7734
Permissible undesirable	0.0084
	100.0000

Table 3: Sweetened Composition of the Typical Flared Associated Stranded Natural Gas
Source: Adapted from Ekejiuba, 2017

Table 4: shows the estimated real-time component by component quantity of natural gas liquids (barrels) production based on the sweetened typical, natural gas composition table 3 and 20MM scfd flow rate.

On the average, GTL converts every 10,000 cu ft to 1 barrel (42 US gallons) or (160 liters).

Thus, for instance Ethane's 1.596 MMscfd will yield 159.6 barrels.

Component	Fractional Composition	Daily MMscf	Daily Liquid Equivalent: Barrels	Daily Liquid Equivalent: US Gallons	Daily Liquid Equivalent: Liters
Methane	0.8045	16.090	1,609.0	67,578	257,440
Ethane	0.0798	1.596	159.6	6,703.2	25,536
Propane	0.0611	1.222	1.222	5,132.4	19,552
i-butane	0.0150	0.300	30.0	1,260	4,800
n-butane	0.0193	0.386	38.6	1,621.2	6,176 NGLs
i-pentane	0.0071	0.142	14.2	596.4	2,272
n-pentane	0.0051	0.102	10.2	428.4	1,632
Hexane plus	0.0077	0.154	15.4	646.8	2,464

Table 4: Real-Time Daily Flare Stream Component by Component NGLs Quantities for 20 MM scfd. Flow Rate
Source: Adapted from Ekejiuba, 2017

4. Theoretical Model

The GTL technologies available from different licensors differ in process configuration, thermal efficiencies and capital costs. But, overall the size of GTL plants varies from small (5 to 15, 000 bpd) to large (> 50,000 bpd).

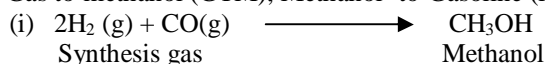
These plants consist of the synthesis gas generation (manufacture), the methanol or FT synthesis facilities and the upgrading process. No matter the source material, once a mixture of CO and H₂ is manufactured, with help from a catalyst, the syngas is transformed into waxy hydrocarbons, which in turn can be cracked into smaller, diesel- like fuel molecules.

4.1. Syngas Conversion

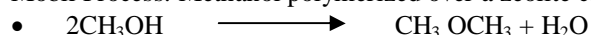
There are two routes for the production of synfuels via syngas. Basically, the syngas is converted to hydrocarbon building blocks (-CH₂-) or hydrocarbon chain extension in the presence of a catalyst which produces different compound of hydrocarbon (liquid) via polymerization of the hydrocarbon building block.

The current three major processes that can convert synthesized natural gas to synthetic liquid fuels are:

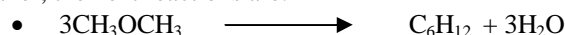
- (a) GTM- MTG Process: Gas to methanol (liquid) and further to Gasoline via di-methyl ether (DME)-figures 12, 13, 14 and 15.
 - (b) STG + Process: Syngas to gasoline plus which builds on MTG via thermo chemical single loop- process.
 - (c) FT- GTL Process: Gas to synthetic fuel (liquid) diesel, gasoline, naphtha via fischer-tropsch synthesis.
- (A) Gas to-methanol (GTM); Methanol- to-Gasoline (MTG) Process.



(ii) Mobil Process: Methanol polymerized over a zeolite catalyst to form alkanes via dimethyl ether (DME).



And further, the next reactions are:



In this process, hydrocarbon of five or more carbon atoms (gasoline) makes up over 80% of the fuel yield.

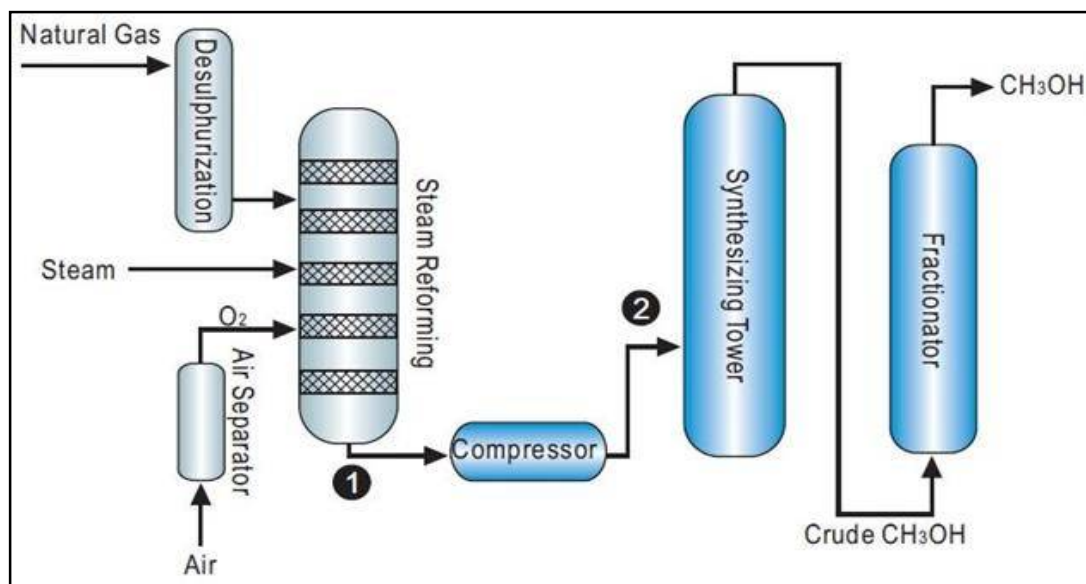


Figure 12: Raw Natural Gas to Methanol (GTM) process Layout
Source: Adapted from Images of Gas-to-Liquid Processes

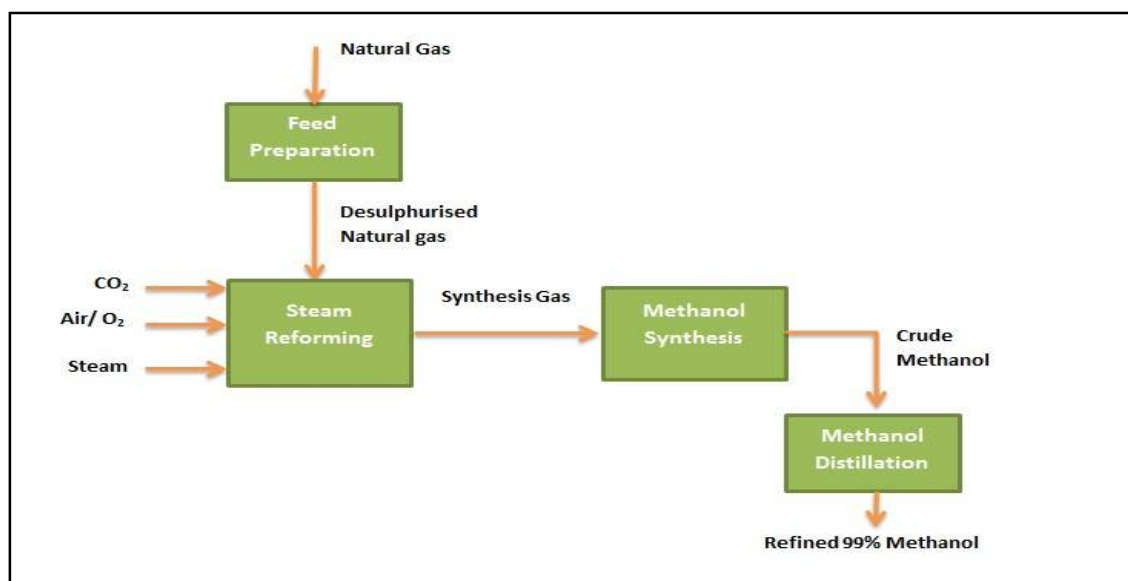


Figure 13: Gas to Methanol Flow Diagram
 Source: Adapted from Images of Gas-to-Liquid Processes

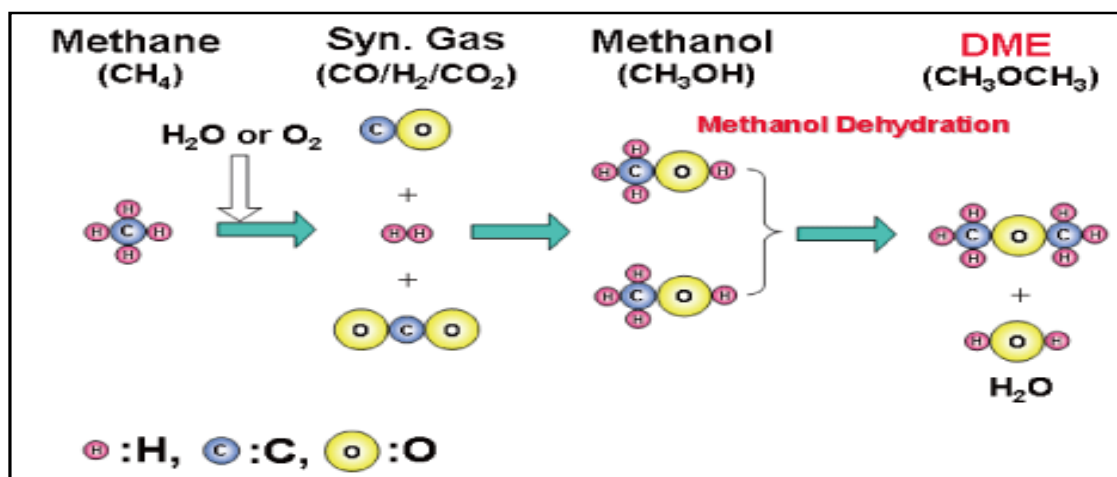


Figure 14: Natural Gas (methane) to methanol/ dimethyl ether (DME) reaction formula
 Source: Adapted from Images of Gas-to-Liquid Processes

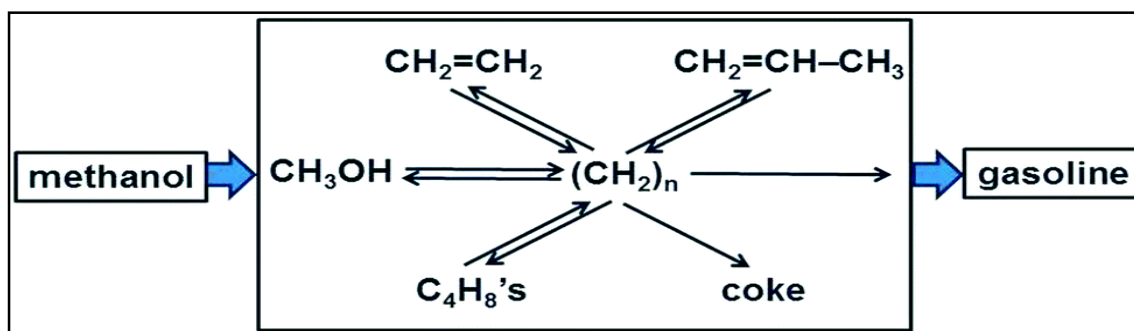
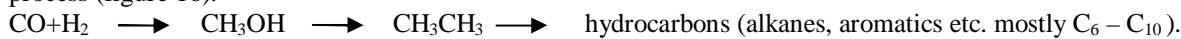


Figure 15: Methanol to Gasoline reactions
 Source: Adapted from Images of Gas-to-Liquid Processes

(B) Syngas to Gasoline Plus (STG +) Process:

The process is similar to the MTG technology, but converts syngas directly into gasoline and jet fuel via a thermochemical single –loop process (figure 16).



Gasoline yield is 85 to 90% in this process.

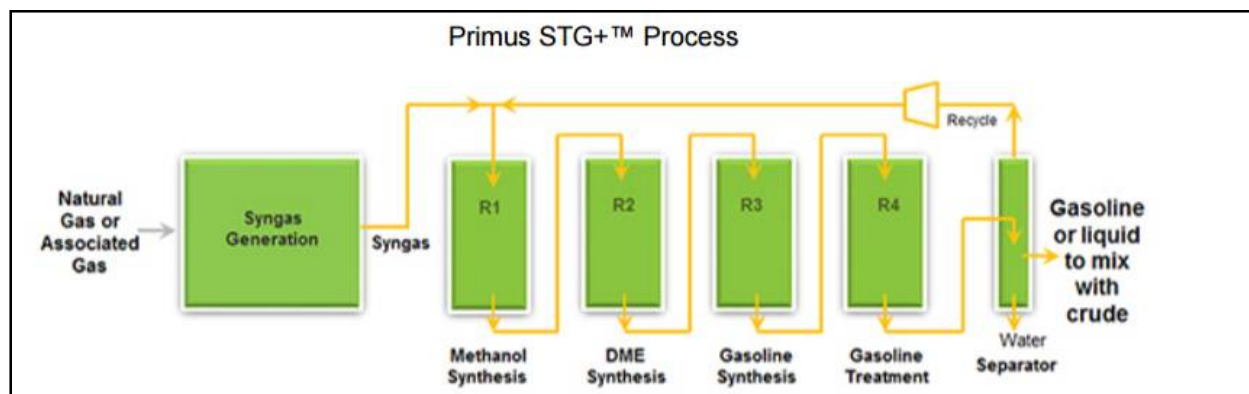


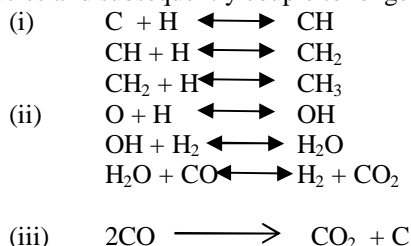
Figure 16: Syngas to gasoline plus (thermo-chemical single loop- process).

Source: Adapted from Images of Gas-to-Liquid Processes

(C) Fischer- Tropsch Synthesis

Essentially the FT Synthesis is a bond forming exothermic reaction that actually converts syngas (CO and H₂) into hydrocarbon distribution such as liquids, methane, alkanes (C₁ - C₁₀₀), alkenes (n ≥ 2), alcohols (oxygenated products) oxygen containing compounds, chemicals, waxes et cetera, with the help of selectivity catalysts, targeted at market demand (figures 17, 18 and 19). Generally, the temperature, pressure and catalyst determine the direction of the three chain growth reactions occurring at the same time with syngas.

The first product direction involves dissociation (splitting) carbon monoxide CO into C and O, after which C- atoms hydrogenate to CH_x species and subsequently couple to longer hydrocarbon as follows:



Which is responsible for the deposition of carbon in the reactor tubes.

The overall reactions which hides the mechanistic complexity can be described by chemical equations of the form.

- (1) Formation of alkanes (paraffins)
 $n\text{CO} + (2n + 1) \text{H}_2 \longrightarrow \text{C}_n \text{H}_{2n+2} + n\text{H}_2\text{O} + \text{heat}$
- (2) Formation of alkenes (Olefins)
 $n\text{CO} + 2n\text{H}_2 \longrightarrow \text{C}_n \text{H}_{2n} + n\text{H}_2\text{O} + \text{heat}$
- (3) Formation of oxygenates: alcohols or other oxygen containing compounds
 $n\text{CO} + 2n\text{H}_2 \longrightarrow \text{C}_n \text{H}_{2n+1} \text{OH} + (n-1) (\text{H}_2\text{O}) + \text{heat}$

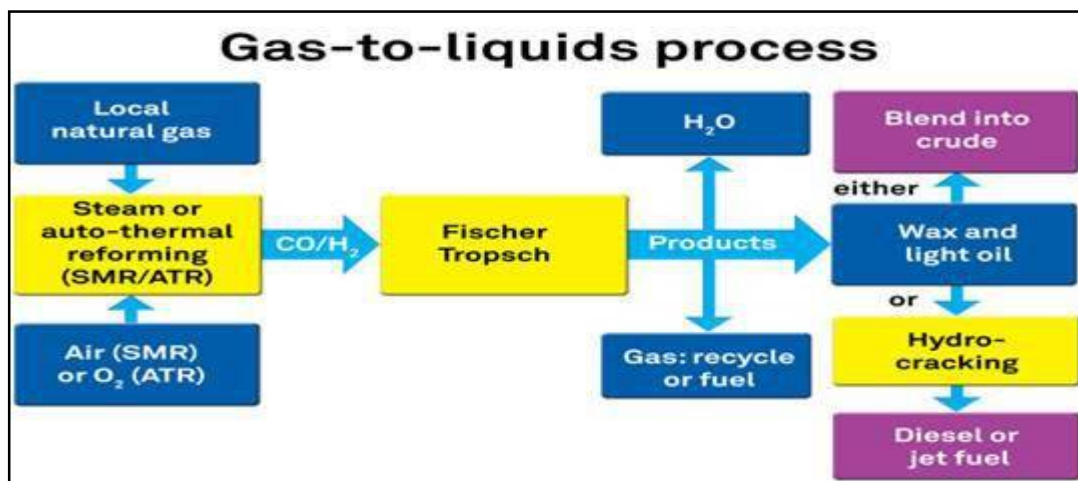


Figure 17: Fischer-Tropsch Gas -to -Liquids Process

Source: Adapted from Images of Gas-to-Liquid Processes

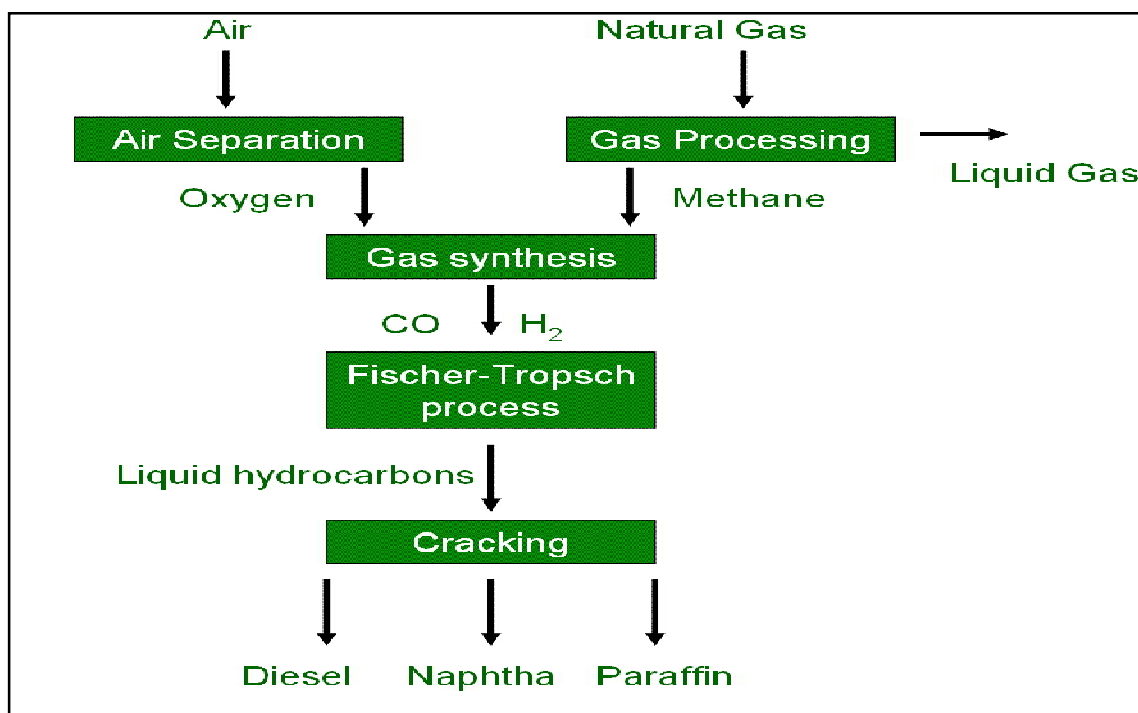


Figure 18: Natural Gas to Liquid (GTL) Flow Diagram for the Fischer-Tropsch Process
Source: Adapted from Images of Gas-to-Liquid Processes

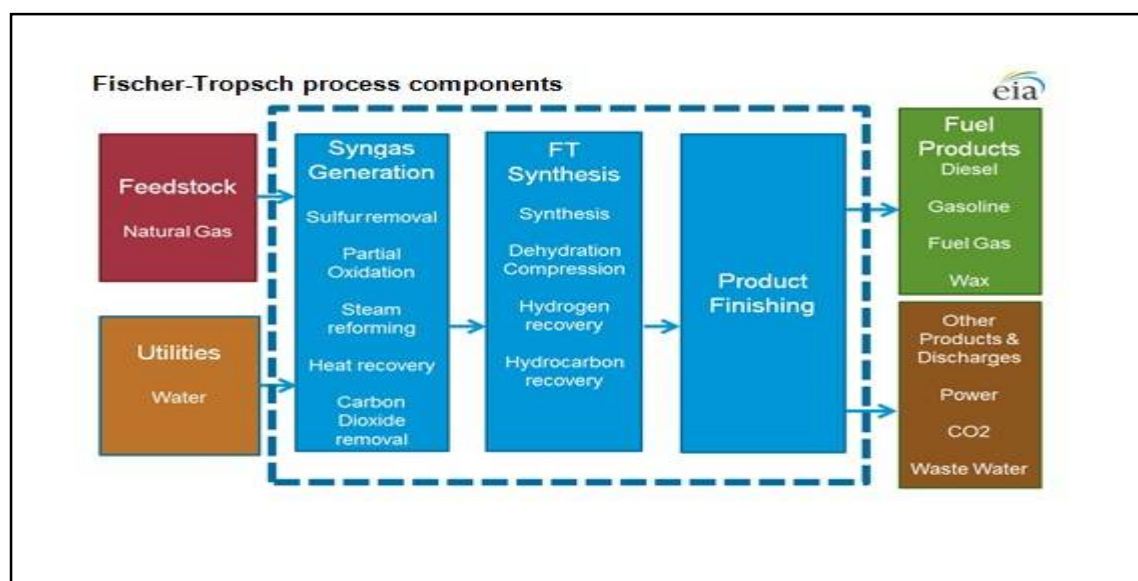
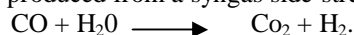


Figure 19: Fischer-Tropsch (GTL) Process Components with other possible end products
Source: Adapted from Images of Gas-to-Liquid Processes

5. Upgrading Process

This process is used to improve liquid fuel selectivity and quality by converting the heavier FT syncrude products (paraffins, olefins and oxygenates), to a range of final products comprising light hydrocarbons (C₁ and C₂) LPG (C₃ and C₄), ultra-clean naphtha (C₅ – C₁₁), ultra-clean diesel (C₁₂ – C₂₀) and wax (>C₂₀) fractions, high quality lubes and white oils, using conventional refinery processes such as wax hydrocracking, distillate hydrocracking, catalytic reforming, Oligomerization of the C₃ to C₆ olefins hydrogenation, isomerization and fractionation with 98% efficiency.

For instance, a much higher yield of diesel can be achieved when wax is hydrocracked. Hydrocracking requires additional hydrogen, which can be produced from a syngas side-stream that is completely shifted to hydrogen via the water-gas-shift (WGS) reaction:



And naphtha fraction may be further upgraded to gasoline with catalytic reforming or alternatively, the naphtha could be used as steam cracker for olefins production.

Typical output yield for a GTL process consists of about 70% ultra-clean diesel fuel, 25% naphtha and a few percent LPG's, Lubes and waxes.

6. Model Application

Conventionally, processing the flared associated stranded natural gas to remove undesirable components such as, carbon dioxide, hydrogen sulfide and other sulfur components, and nitrogen is termed sweetening (Campbell, 1976). Figure 20, is the proposed design process layout for the overall sweetening of the associated flared natural gas and the detailed possible Gas-to-Liquids alternative route and their end products.

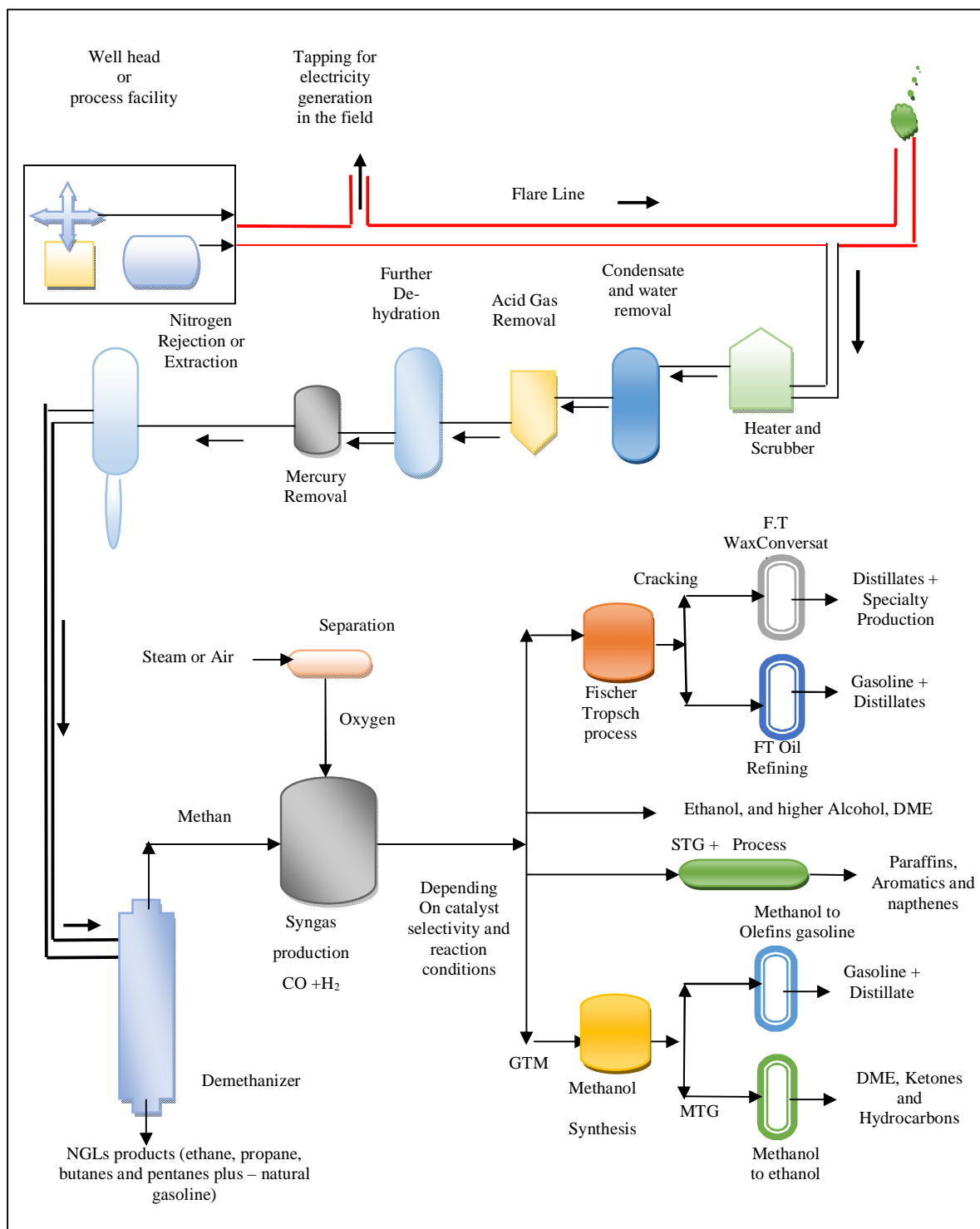


Figure 20: Process Layout for the Overall Real-Time Monetization of Flare Stream via Synthetic Liquid Fuels

The GTL processes in operation converts 10,000 cubic feet (286 m³) of gas into slightly more than 1 barrel (0.16m³) of liquid synthetic fuels. Although this can vary, depending on the scale of the GTL plant, the range for gas consumption is between 8,500 to 12,000 cubic feet/ barrel. On the other hand, some GTL designs converts every 15MM Btu (15 million Btu) – 20MM Btu into one barrel of clean- burning, synthetic fuel.

The flow rate for associated stranded natural gas flare lines in flow stations, refineries, offshores and terminal operations facilities in Nigeria ranges from 5 to 63MM scfd (0.1415MM to 1.7829MM m³/d).

For this analysis, 20MM scfd (0.566MM m³/d) was used on the typical sweetened composition of the Nigerian flare stream, table 3, to yield table 4.

The available feedstock for this analysis, is the sum of the daily components of methane and ethane flared on the stream, i.e. 16.090MM scf plus 1.596MM scf (17.686MMscf). And the calorific value is 17.686 MMscf x 1000 Btu/scf.

$$= 17.686\text{MMM Btu}$$

And since 1 Btu = 1.055 KJoules, the kilo joules equivalent becomes:

$$17.686\text{ MMM Btu's} \times 1.055\text{ KJ/ Btu}$$

$$= 18.65873\text{ MMM KJ}$$

$$= 18.65873\text{ billion KJ.}$$

Conventionally, the selectivity of GTL processes, especially the FT process to C₅₊ products (i.e. liquid and wax) is 95% (nC₅₊), while the other 5% are gaseous C₁ – C₄ products. Also, only 80% of the energy in the 95% syngas for conversion into C₅₊, is retained in the FT products, while the remaining 15% is released as reaction heat.

This implies that about 20% of the syngas energy might be available for electricity generation (i.e. the 5% contained in the FT off gas-unconverted syngas and other by products plus the 15% released as reaction heat). Other by products are water or carbon dioxide.

Thus, the GTL process can be configured to produce electricity, steam, or desalinated water if they are desired locally.

(A) Therefore, the actual daily synthetic fuel obtainable from table 4 is estimated as follows:

Methane	-	16.090 MMscfd
Ethane	-	<u>1.596 MMscfs</u>
		17.686 MMscfd

With 80% selectivity for nC₅₊ it becomes

$$0.8 \times 17.686\text{ MMscfd} = 14,148,800\text{ scfd}$$

Applying the 10,000 scf conversion to approximately 1 barrel general rule, yields:

$$14,148,800\text{ scf}/10,000\text{ scf} = 1,414.88\text{ barrels.}$$

OR

$$1,414.88\text{ barrels} \times 42\text{ gallons/barrel} = 59,424.96\text{ gallons}$$

OR

$$1,414.88\text{ barrels} \times 160\text{ liters/barrel} = 226,240\text{ liters.}$$

The possible products range from light hydrocarbons C₁ and C₂ to C₁₀₀ components.

(B) The possible electricity generation from the 20% released reaction heat and unconverted syngas/ C₁ – C₄ products is estimated as follows:

$$17,686,000\text{ scf/d} \times 0.2 = 3,537,200\text{ scf/d}$$

$$\text{Dividing by 24 implies } 3,537,200/24 = 147,383.33\text{ scf/h}$$

For a Gas turbine generator with 30% efficiency, and applying the gas conversion assumed calorific value of 1000 Btu/scf. The heat rate becomes 3412/0.3 = 11,373.33 Btu/kWh.

Using the relation

Power Output (kW)

$$= \{\text{Fuel Burned (scf/hr)} \times \text{Heating Value Btu/scf}\} / \text{Heat rate Btu/kWh}$$

$$= \{147,383.33 \times 1000\text{ Btu/scf}\} / \{11,373.33\text{ Btu/kWh}\}$$

$$= 12,958\text{ kW}$$

Approximately 13MW.

7. Upgraded Products

The final upgraded end products are determined by the length of the hydrocarbon chain which, in turn, is determined by catalyst selectivity and reaction conditions i.e. temperature, pressure and residence time. The overall products range can be group as follows:

(1) Methane and Alkanes C_n H_{2n+2} (With n from 1 to 100)

(a) Methane –rich C₁ is either sold as pipeline fuel gas or sent to a gas reforming unit to be reformed back to synthesis fuel or feed gas by utilizing preheated oxygen and super-heated steam.

(b) Ethane- rich C₂, stream could be split into ethylene and ethane. And the ethane fraction could also be cracked to yield ethylene.

(c) Also, LPG, propane, butane, fuel oil, illuminated paraffin, petrol (gasoline), diesel and bitumen are produced.

Usually, hydrocarbons that fall within the C₅ – C₁₀ range are referred to as either “heavy cut” or “oil stream”.

(2) Alkenes or Olefins C_nH_{2n}, n ≥, Linear Alpha Olefins

Similarly, the propylene or C₃H₆, got from the light hydrocarbon gases could be used to produce polypropylene. And together with ammonia, propylene is also used to produce acrylonitrile, which in turn is converted to produce acrylic fibers.

- (3) Liquid Hydrocarbons: LPG, Gasoline, naphtha, kerosene/jet fuels, diesel, weight waxes, high quality lubes, white oils which are utilized in the food and pharmaceutical industry and to a lesser extent oxygenated product such as alcohols. As an alternative to fuels, the waxy portion could be converted to lubricant, drilling fluids waxes and other specialty product. The naphtha however, would be low in octane and requires isomerising or reforming if used as a fuel but represents a good petrochemical feedstock. The fuel produced via this process has higher cetane index 70 + (measure of the ignition quantities of diesel) and actane number (a measure that quantifies combustion of gasoline), emits less toxic substances to the environment when combusted, it is also a clear fuel than those produced via petroleum distillation. With virtually zero aromatics and sulfur, and high cetane, it can possibly be used to upgrade conventional gas oil by blending it with GTL gasoil. For reason of their purity, these synthetic fuels could also be used for fuel cells instead of methanol. Oxygenates are purified to produce higher alcohols, acetic acid and ketones including acetone, methyl ethyl ketone and methyl iso butyl ketone.
- (4) The GTL technology also embraces the production of alternative fuels from Natural gas. The term fuel includes methanol, ethanol and other alcohols, mixture containing methanol and other alcohols with gasoline or other fuel which are not derived from petroleum products. Conventional petroleum refineries products include: propane, butane, petrochemical feedstock, gasoline (naphtha specialties, aviation gasoline, and motor gasoline), distillates (jet fuels, diesel, stove, oil, kerosene, and furnace oil), heavy fuel oil, lubricating oils, waxes, asphalts and still gas (refinery gas).
- (5) Ammonia which can also be produced, could be sold or utilized to produce explosives and fertilizers.

8. Conclusion

Both conventional fuels and synthetic fuels release substances with certain energy components which undergo some form of chemical reactions, oxidation reaction or nuclear reaction. There has been steady and progressive development of the techniques of obtaining synthetic liquids from natural gas, since the first recognition of the technology in 1902 by Paul Sabatier and Senderens, and its commercialization by two German scientists, Fischer and Tropsch in 1923, following economic sanctions after world war I (23 July 1914 -11 November 1918). Currently there are hundreds of modification and patents to the original complex, energy intensive process. Most newer designs are specialty plant.

Basically, it is technically feasible to synthesize almost any hydrocarbon from any other, so far, conversion of the source material to synthesis gas (syngas) is the major backbone of the entire synfuels production technology.

Upgrading the syncrude using virtually all the conventional refining processes yields all the different crude oil refinery products, such as gasoline, kerosene, diesel, naphtha, LPG waxes et cetera as well as alternative fuels including methanol, ethanol and other alcohols, which are not derived from petroleum products. Other potentially valuable by-products include heat for electricity generation and agricultural grade water.

Overall, the size of GTL plants varies from small (5 to 15,000 bpd) to large (> 50,000 bpd), converting between 8,500 -12,000 scf of natural gas to about one barrel of synfuel depending on scale of the plant, or between 15MM Btu to 20MM Btu, to about one barrel. The study estimates that 1,414.88 barrels (equivalent to 59,424.96 gallons or 226,240 litres), Synfuel products plus 13 MW electricity could be obtainable daily from a 20 MMscfd flare line.

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