GAS TO LIQUID

Iranian Oil,Gas and Petrochemical

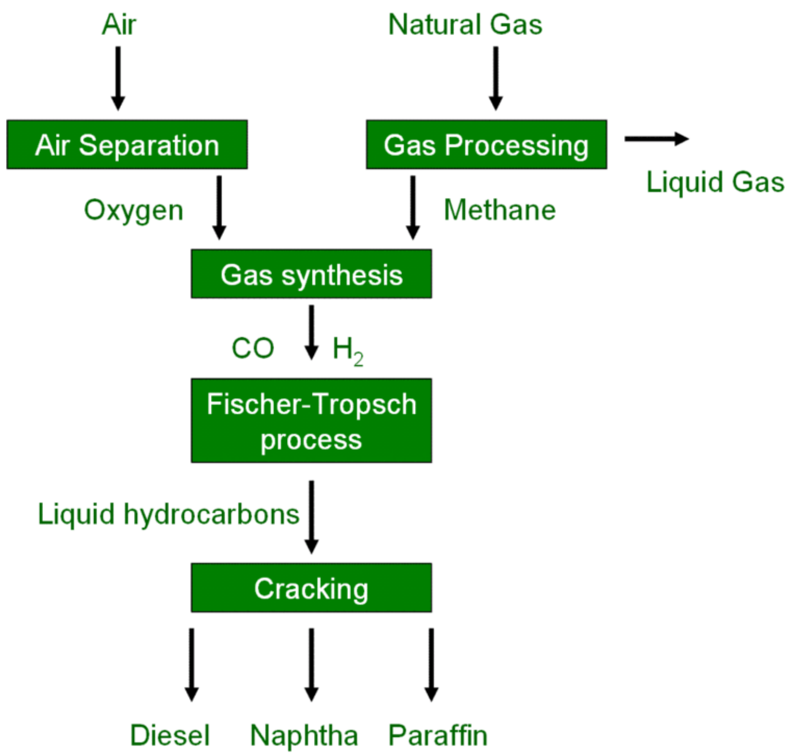
Products Exporters' Union

Article — Research ☑

Gas to liquids (GTL) is a refinery process to convert natural gas or other gaseous hydrocarbons into longer-chain hydrocarbons such as gasoline or diesel fuel. Methane-rich gases are converted into liquid synthetic fuels either via direct conversion—using non-catalytic processes that convert methane to methanol in one step—or via syngas as an intermediate, such as in the Fischer Tropsch, Mobil and syngas to gasoline plus processes.

Fischer Tropsch process

The Fischer Tropsch process starts with partial oxidation of methane (natural gas) to carbon dioxide, carbon monoxide, hydrogen gas and water. The ratio of carbon monoxide to hydrogen is adjusted using the water gas shift reaction, while the excess carbon dioxide is removed with aqueous solutions of alkanolamines (or physical solvent). Removing the water yields synthesis gas (syngas) which is chemically reacted over an iron or cobalt catalyst to produce liquid hydrocarbons and other byproducts. Oxygen is provided from a cryogenic air separation unit.



Syngas generation

The first step in a GTL process is to convert the natural gas feed into synthesis gas or syngas. Before being fed to the syngas generation unit, the natural gas is typically processed to remove impurities such as:

- Sulfides
- Mercaptans
- Mercury
- Any impurities that will poison the various catalysts that are used in the GTL conversion steps

The cleaned feed gas is then fed to a syngas generation unit. In this step, the bond between the carbon and hydrogen is broken, and two separate molecules (CO and H_2) are formed. The ratio of H_2 to CO in the syngas is a critical factor in the FT process.

There are several ways to produce synthesis gas from natural gas and air or oxygen. These include steam reforming of feedstock in the presence of a catalyst,

$$CH_4 + H_2O = CO + 3H_2$$

and the partial oxidation process in which air or oxygen is burned together with natural gas at high temperatures and pressure. No catalyst is used.

$$CH_4 + {}^{1}/_{2}O_2 = CO + 2H_2$$

For GTL plants that require large quantities of oxygen, a cryogenic air separation plant is currently the most economical option. Natural gas and oxygen are preheated and compressed (if necessary) to required conditions before being sent to the synthesis gas reactor.

Another method is autothermal reforming, which involves partial oxidation, coupled with steam reforming.

$$3CH_4 + H_2O + O_2 = 3CO + 7H_2$$

The syngas fed to the downstream FT synthesis unit must have a ratio of H_2 to CO of approximately 2. This ratio has favored the development of partial oxidation and autothermal reformer (ATR) processes (by themselves or in combination with other processes) over the steam-reforming process because the latter requires additional processing to achieve the desired H_2:CO product ratio. Even though the technology for syngas generation is considered proven, its application in GTL plants is complex and costly. Significant research is ongoing in this area to reduce cost.

Fischer-Tropsch synthesis

The FT synthesis section involves the conversion of synthesis gas to long-chain, heavy paraffinic liquid. Paraffin is a mixture of high-molecular-weight alkanes (i.e., saturated hydrocarbons with the general formula C_nH_{2n+2}, where n is an integer). Large quantities of water are produced as a byproduct, which is required to be treated before disposal or reuse. Small quantities of CO_2, olefins, oxygenates, and alcohols are also produced as byproducts. The reaction is highly exothermic, with heat of reaction of approximately −39.4 kcal/gmol of CO. Large quantities of heat are generated in the process that must be removed. This energy is partially recovered by the production of steam.

The product slate from a FT reactor is dependent on the type of catalyst and the operating conditions of the reactor. Generally, an iron-based or cobalt-based catalyst is used for FT synthesis. The choice of the catalyst is to some extent related to the type of feed to the GTL plant. For natural gas feed, a cobalt-based catalyst is more likely to be used.

There are several different reactor types to produce FT products:

- Fixed-bed
- Fluidized-bed
- Slurry-phase reactors

Several publications discuss the pros and cons of the various reactor designs. The operating conditions of the FT reactors typically range from 220 to 250°C and pressure of 20 to 60 bar. The operating conditions vary depending on:

- Desired product mix
- Type of catalyst
- Reactor type

The FT product is totally free of sulfur, nitrogen, metals, asphaltenes, and aromatics that are normally found in the petroleum products produced from crude oil. **Table 1** compares the quality of the products from the FT process with that of conventional refinery-based products.

Quality of FT GTL products

Stream	Physical Property	GTL Product	Product From Conventional Refinery
Naphtha (full range)	Density, g/cm³ 60°F	0.69	0.74
	Sulfur, wt%	0	0.07
	RON, clear	<40	67
	N+2A	5	51
Jet/Kerosene	Density, g/cm³ 60°F	0.77	0.80
	Sulfur, wt%	0	0.12
	Smoke point, mm	45	22
	Freeze point, °F	−53	−53
Diesel	Density, g/cm³ 60°F	0.78	0.84
	Sulfur, wt%	0	0.37
	Aromatics, lv %	<1	29
	Cetane number	>70	56
	Viscosity, cSt at 100°F	2.3	4.0

Methane to Methanol process

Methanol is made of methane (natural gas) in a series of three reactions:

Steam reforming

$$CH_4 + H_2O \rightarrow CO + 3\ H_2 \quad \Delta_r H = +206\ kJ\ mol^{-1}$$

Water shift reaction

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta_r H = -41\ kJ\ mol^{-1}$$

Synthesis

$$2\ H_2 + CO \rightarrow CH_3OH \quad \Delta_r H = -92\ kJ\ mol^{-1}$$

The methanol thus formed may be converted to gasoline by the Mobil process.

Methanol to Gasoline process

In the early 1970s, Mobil developed an alternative procedure in which natural gas is converted to syngas, and then methanol. The methanol polymerized over a zeolite catalyst to form alkanes.

First methanol is dehydrated to give dimethyl ether:

$$2\ CH_3OH \rightarrow CH_3OCH_3 + H_2O$$

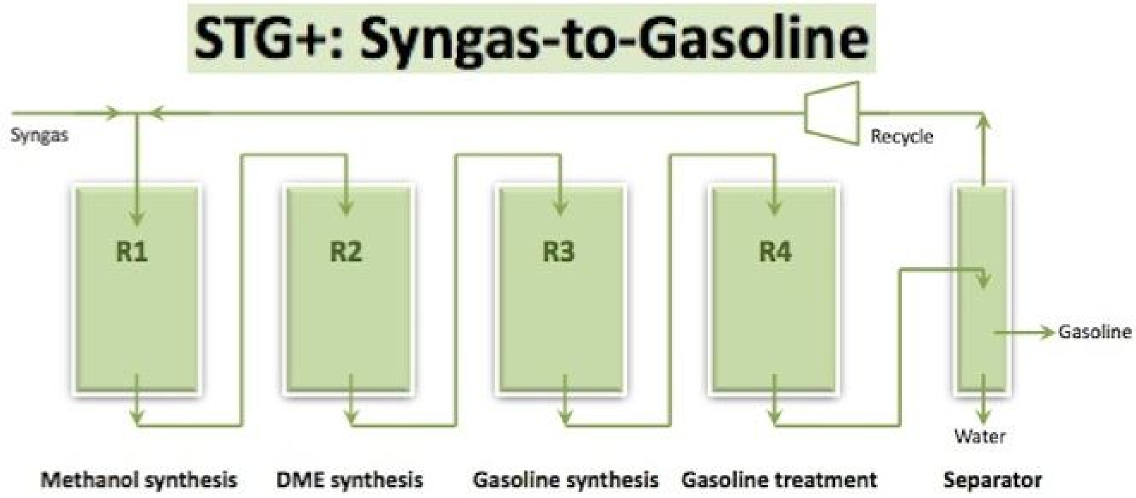
This is then further dehydrated over a zeolite catalyst such as ZSM-5, which would theoretically yield ethylene:

$$CH_3OCH_3 \rightarrow C_2H_4 + H_2O$$

but which in practice is polymerized and hydrogenated to give a gasoline with hydrocarbons of five or more carbon atoms making up 80% of the fuel by weight.

Syngas to Gasoline plus process

A third gas-to-liquids process builds on the MTG technology by converting natural gas-derived syngas directly into drop-in gasoline and jet fuel via a thermochemical single-loop process.

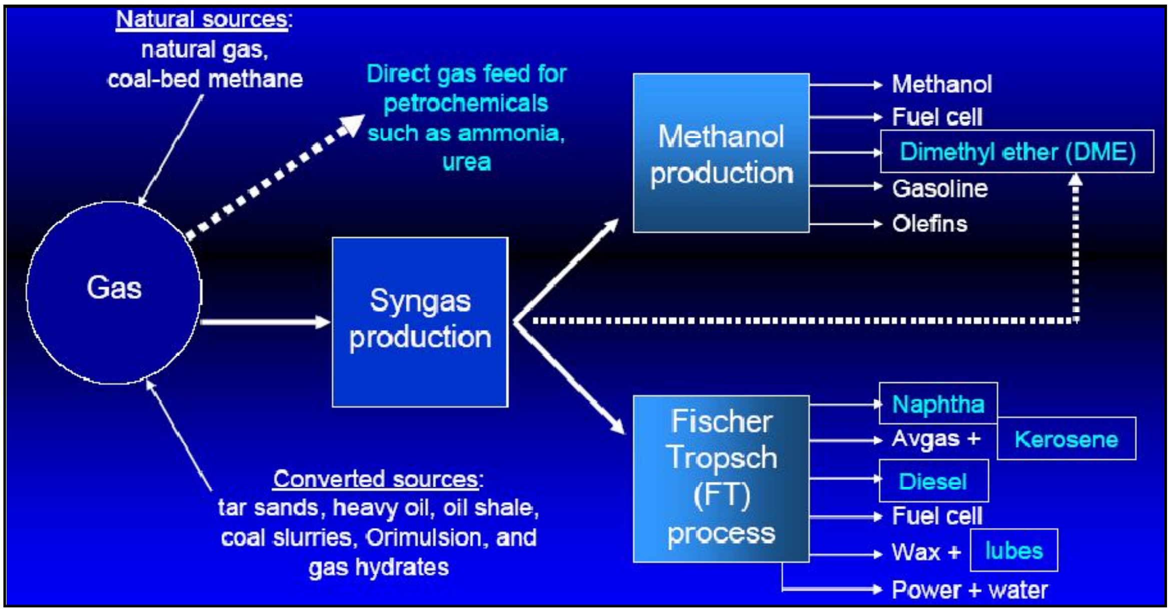


The STG+ process follows four principal steps in one continuous process loop. This process consists of four fixed bed reactors in series in which asyngas is converted to synthetic fuels. The steps for producing high-octane synthetic gasoline are as follows:

1. Methanol Synthesis: Syngas is fed to Reactor 1, the first of four reactors, which converts most of the syngas (CO and H_2) to methanol (CH_3OH) when passing through the catalyst bed.
2. Dimethyl Ether (DME) Synthesis: The methanol-rich gas from Reactor 1 is next fed to Reactor 2, the second STG+ reactor. The methanol is exposed to a catalyst and much of it is converted to DME, which involves a dehydration from methanol to form DME (CH3OCH3).

3. Gasoline synthesis: The Reactor 2 product gas is next fed to Reactor 3, the third reactor containing the catalyst for conversion of DME to hydrocarbons including paraffins (alkanes), aromatics, naphthenes (cycloalkanes) and small amounts of olefins (alkenes), mostly from C6 (number of carbon atoms in the hydrocarbon molecule) to C10.
4. Gasoline Treatment: The fourth reactor provides transalkylation and hydrogenation treatment to the products coming from Reactor 3. The treatment reduces durene (tetramethylbenzene)/isodurene and trimethylbenzene components that have high freezing points and must be minimized in gasoline. As a result, the synthetic gasoline product has high octane and desirable viscometric properties.
5. Separator: Finally, the mixture from Reactor 4 is condensed to obtain gasoline. The non-condensed gas and gasoline are separated in a conventional condenser/separator. Most of the non-condensed gas from the product separator becomes recycled gas and is sent back to the feed stream to Reactor 1, leaving the synthetic gasoline product composed of paraffins, aromatics and naphthenes.

The application of synthesis gas in various industries



Commercial uses

Using gas-to-liquids processes, refineries can convert some of their gaseous waste products (flare gas) into valuable fuel oils, which can be sold as is or blended only with diesel fuel. The World Bank estimates that over 150 billion cubic metres (5.3×10^{12} cu ft) of natural gas are flared or vented annually, an amount worth approximately $30.6 billion, equivalent to 25% of the United States' gas consumption or 30% of the European Union's annual gas consumption,a resource that could be useful using GTL. Gas-to-liquids processes may also be used for the economic extraction of gas deposits in locations where it is not economical to build a pipeline. This process will be increasingly significant as crude oil resources are depleted.

The use of microchannel reactors shows promise for the conversion of unconventional, remote and problem gas into valuable liquid fuels. GTL plants based on microchannel reactors are significantly smaller than those using conventional fixed bed or slurry bed reactors, enabling modular plants that can be deployed cost effectively in remote locations and on smaller fields than is possible with competing systems.

On August 1, 2014, Biofuels Power Corporation (BFLS)signed a letter of intent with ThyssenKrupp Industrial Solutions and Liberty GTL, Inc. to build a small scale gas-to-liquid demonstration facility in Houston,Texas. The parties have established a non-binding target date to complete installation and commissioning of the GTL Pilot Plant on or before December 31, 2014. The purpose of the GTL Pilot Plant is to commercially demonstrate converting stranded natural gas resources to synthetic crude oil. BFLS will operate the GTL Pilot Plant for the 2-year demonstration. ThyssenKrupp will provide technical services and contribute a previously operating auto-thermal reformer pilot plant of proven design ("ATR"), which will be used to generate synthesis gas feedstock for the production of synthetic crude oil. Liberty will provide intellectual property and operating know-how regarding crude oil synthesis along with the relevant catalyst supply. The Liberty technical team is also credited for designing the FT (Fischer Tropsch) Reactor which will convert the synthetic gas to synthetic crude oil. The GTL Pilot Plant will be assembled at the Houston Clean Energy Park, which is an industrial estate owned by BFLS. The Houston site is located between the Eagle Ford Natural Gas Field and numerous refineries.

One other proposed solution is to use a novel FPSO for offshore conversion of gas to liquids such as methanol, diesel, petrol, synthetic crude, and naphtha.

Two companies, SASOL and Royal Dutch Shell, have technology proven to work on a commercial scale. PetroSA completed semi-commercialdemonstrations of gas-to-liquids used by the company in 2011. Royal Dutch Shell produces a diesel from natural gas in a factory in Bintulu, Malaysia. Another Shell GTL facility is the Pearl GTL plant in Qatar, the world's largest GTL facility and there are reports that Shell is looking at the feasibility of a GTL facility in Louisiana, US. SASOL has recently built the Oryx GTL facility in Ras Laffan Industrial City, Qatar and together with Uzbekneftegaz and Petronas builds the Uzbekistan GTL plant. Chevron Corporation, in a joint venture with the Nigerian National Petroleum Corporation is commissioning the Escravos GTL in Nigeria, which uses Sasol technology.

On 1 February 2008, an Airbus A380 flew a three-hour test flight between Britain and France, with one of the A380's four Rolls-Royce Trent 900 engines using a mix of 60% standard jet kerosene and 40% gas to liquids fuel supplied by Shell. The aircraft engine needed no modification to use the GTL fuel, which was designed to be mixed with normal jet fuel. The fuel used was no cleaner in CO_2 terms than standard fuel but it had local air quality benefits because the GTL portion contains no sulphur. On 12 October 2009, a Qatar AirwaysAirbus A340-600 conducted the world's first commercial passenger flight using a mixture of kerosene and synthetic GTL fuel in its flight from London's Gatwick Airport to Doha.

Brazilian oil company Petrobras has ordered two small experimental GTL production facilities intended to be posted at offshore oil fields too distant or deep to justify gas pipelines to onshore GTL plant. In January 2012 Petrobras' Cenpes Research and Development Centre approved for commercial deployment the technology supplied by UK-based gas-to-liquids company CompactGTL. Petrobras is now assessing microchannel reactor technology supplied by Velocys.

The STG+ technology is currently operating at pre-commercial scale in Hillsborough, New Jersey at a plant owned by alternative fuels company Primus Green Energy. The plant produces approximately 100,000 gallons of high-quality, drop-in gasoline per year directly from natural gas. Further, the company announced the findings of an independent engineer’s report prepared by E3 Consulting, which found that STG+ system and catalyst performance exceeded expectations during plant operation.The pre-commercial demonstration plant has also achieved 720 hours of continuous operation.