THE FINAL WORD
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AN ALTERNTIVE TO CRUDE OIL- GAS TO LIQUID TECHNOLOGY

The petroleum downstream industry, which converts petroleum to pure fuels and petrochemicals lives constantly with uncertainties related to guarantee of access and supply of crude oil in the quantity and quality required, problems related to the geopolitics or even about the exhaustion of existent recoverable reserves are driving forces to the development of alternatives technologies the crude oil.

One of the most promising and well-developed technologies currently is the conversion of syngas ($CO + H_2$) in longer-chain hydrocarbons such as gasoline, diesel, wax and other liquid fuel products, known as Gas to Liquids Technologies (GTL). The liquid hydrocarbons production can be carried out by direct syngas conversion to long chain hydrocarbon via well-known Fischer-Tropsch synthesis reactions.

Fischer-Tropsch (FT) is a chemical process through is possible the liquid hydrocarbon mixture production from synthesis gas (mixture of $CO+H_2$) according to the following chemical reactions:

Paraffin Production:

$$nCO + (2n+1)H_2 = CnH_{2n+2} + nH_2O$$

Olefin Production:

$$nCO + 2nH_2 = C_nH_{2n} + nH_2O$$

These reactions are strongly exothermic and the CO/H_2 ratio, reaction temperature and pressure is a key parameter to define the hydrocarbon chain extension and product distribution. Mixture of C_{10}-C_{60} hydrocarbon usually obtained by tuning of above parameters. It is also known as synthetic crude oil.

The reactions occur normally under temperatures that vary from 200 to 350 °C and operating pressures in the range of 15 to 30 bar.The catalyst commonly applied to these reactions is based on cobalt or iron as active metals deposited upon alumina as carrier.

Showed process in Figure 1 is based in the syngas gas generation from steam reforming of natural gas, this is the most common route, however, with slight variation, coal, petroleum coke, biomass or crude oil itself can be used as feed to produce syngas.

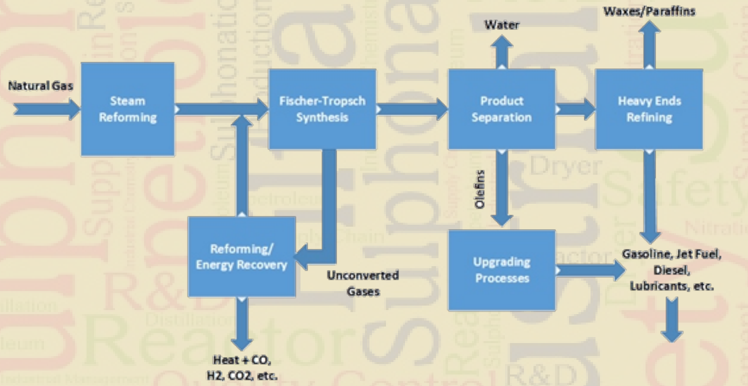

Figure 1 – Block Diagram to a Typical Fischer-Tropsch GTL Process Plant

In next step, syngas is used to produce hydrocarbon via controlled chain extension via Fischer-Tropsch (FT) synthesis step, Where CO and H2 fed to the FT reactors (elevated temperature and pressure), following the produced hydrocarbons are separated and sent to refining steps as isomerisation, hydro-treating, hydro cracking, catalytic reforming, etc. according to application of the produced derivative (gasoline, diesel, lubricant, etc.).

Some side reactions can occur during the hydrocarbons production process, leading to coke deposition on the catalyst, causing his deactivation according to following chemical reactions:

$$2CO = C + CO_2 \quad \text{(Boudouard Reaction)}$$

$$CO + H_2 = C + H_2O \quad \text{(CO Reduction)}$$

The type of reactor applied in the FT synthesis step have strong influence on the yield and quality of the obtained products, the campaign time of the process units also depends on the type of reactor. Fixed bed reactors are widely employed to FT synthesis mainly with longer life cobalt based catalyst, cobalt based catalyst are operated at lower temperature so known as low temperature FT reaction (LTFT). Advantage of cobalt catalyst is longer life, low reaction temperature, lower CO_2 formation via reduce side reaction and higher molecular weight products compare to iron catalysts. Iron catalyst based units apply fluidized bed or slurry phase reactors due to coke deposition on the catalyst and better heat distribution. Iron catalyst are typically operated at high temperature so it is known as high temperature FT reaction (HTFT).

The several geopolitics crises over the history motivated the development of new technologies and the improvement of the Fischer-Tropsch original process. There is a wide array of process technologies developed aiming to liquid hydrocarbons production from syngas, among the principal available technologies we can quote the processes SYNTHOL™ and SPD™ developed by Sasol company, the GASEL™ process by Axens company, the SCGP™ by Shell, the TIGAS™ developed by Haldor-Topsoe company etc.

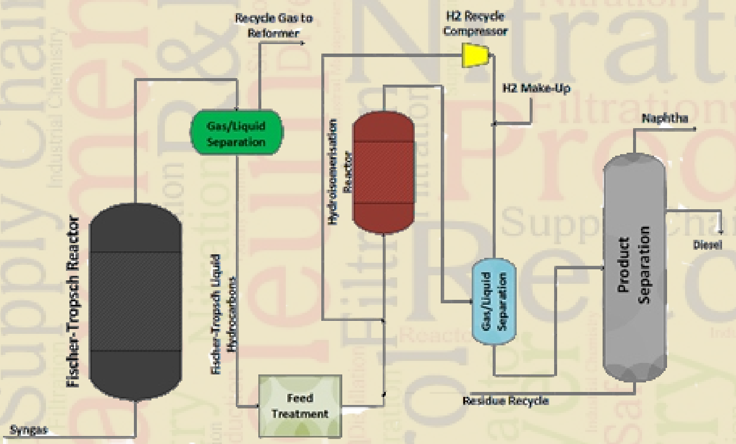

Figure 2 – Process Flow Diagram for GASEL™ Technology by Axens company

As cited earlier, one of the main advantages of GTL technologies is the possibility of application several raw materials to produce syngas, which ensures great flexibility. In regions like China and South Africa with large coal availability, same technology can be used to make syngas and known as coal gasification and this entire process to make petrochemicals and fuel is called Coal to Liquid (CTL) process. Another alternative is to apply renewable raw material (biomass) to produce syngas.

On the other hand, in regions with great availability and easy access to large natural gas reserves, the syngas production through natural gas reforming steam still is shown as the most economical route to produce this raw material in industrial scale. Qatar has limited crude oil, but have large amount of natural gas reserves, so they have large scale GTL plant to produce fuels and petrochemicals from natural gas via FT process.

An alternative route to produce liquid hydrocarbons from syngas is the conversion of the natural gas to syngas to methanol as per below reactions:

$$CH_4 + H_2O = CO + 3H_2 \quad \text{(Steam Reforming)}$$

$$2H_2 + CO = CH_3OH \quad \text{(Methanol Synthesis)}$$

In the sequence, the methanol is dehydrated to produce dimethyl ether (DME) which is dehydrated to produce ethylene, as shown in the sequence:

$$2CH_3OH = CH_3OCH_3 + H_2O \quad \text{(Methanol Dehydration)}$$

$$CH_3OCH_3 = C_2H_4 + H_2O \quad \text{(Dimethyl-Ether Dehydration)}$$

The methanol conversion to olefins into hydrocarbons is called Methanol to Olefins (MTO) or Methanol also can be converted to gasoline via some alternation of catalyst and process parameters and it is called Methanol to Gasoline (MTG) technologies. The most known processes dedicated to converting methanol in hydrocarbons are the processes MTG™ developed by ExxonMobil Company and the MTO-Hydro™ process, developed by UOP Company. Figure 3 presents the process flow diagram for the MTG™ process by ExxonMobil Company.

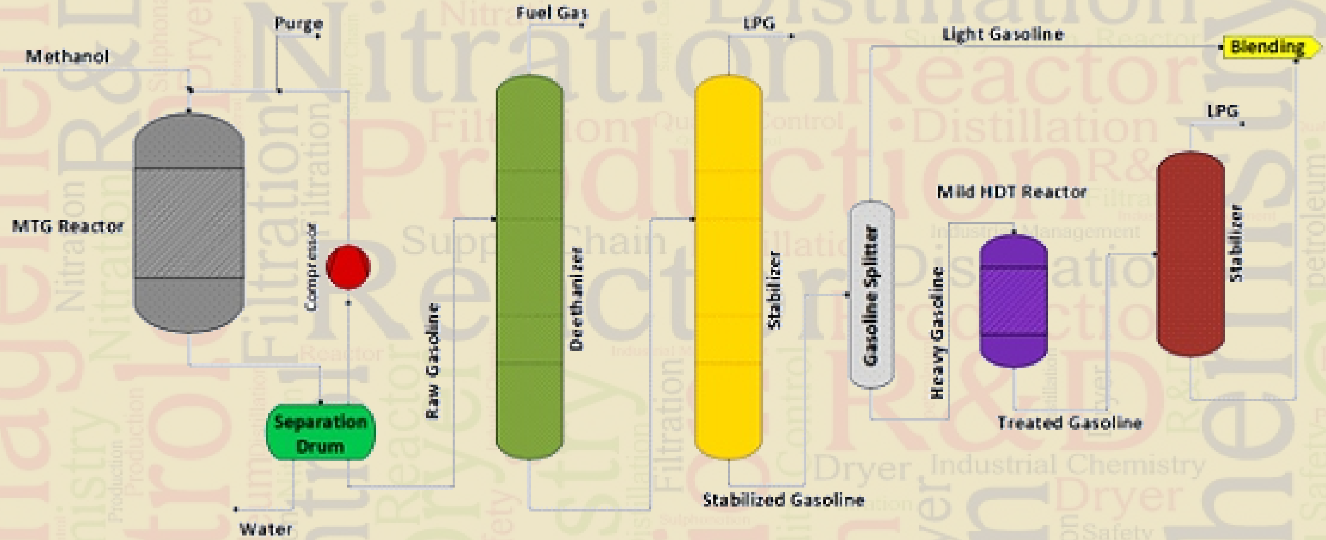

Figure 3 – Process Flow Diagram for MTG™ Technology by ExxonMobil

The MTO technologies presents some advantages in relation to Fischer-Tropsch processes, once show higher selectivity in the hydrocarbon production, furthermore, the obtained products require lower additional processing steps to achieve commercial specifications, another important point in that the installation cost is normally lower to MTO process plants when compared with FT units.

The streams produced by GTL technologies show reduced contaminants content (sulfur, nitrogen, etc.) which is a route to produce sulfur free diesel. High-quality that makes these products attractive from the point of view of environmental footprint and profitability. In scenarios with crude oil shortage or overprices, these technologies can be competitive and achieve strategically character to some nations.

Synthesis gas can be produced by various hydrocarbon feedstocks and it can be used to make large variety of petrochemicals products directly or indirectly. Also. Economy of GTL process is driven by price of feed stock viz. crude oil, natural gas and coal. It is very good option for countries have limited or no crude reserves, but have coal, natural gas or biomass reserves to produce fuels and chemicals. Also increased production of shale gas in USA, which can be ideal feedstock of GTL process.

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