

Fischer Tropsch Gas To Liquid Technology (GTL)

A. Nafees and S. H. Al Hashimi

Chemical Engineering Program, The Petroleum Institute, Abu Dhabi, U.A.E.
salhashimi@pi.ac.ae

1. Introduction

Conversion of natural gas to hydrocarbons (gas-to-liquid Technology) is currently one of the most promising topics in the energy industry due to economic utilization of remote and stranded natural gas to environmentally clean fuels, specialty chemicals and waxes. More than one third of the global natural gas reserves are classified as stranded [Error! Reference source not found.]. Alternatively, coal or heavy residues can be used on sites where these are available at low costs. Fischer Tropsch gas to liquid technology has proven ability to convert low cost gases to high value hydrocarbon products. The process is carried out in two steps. Firstly, natural gas or coal is converted into synthesis gas, a mixture of predominantly CO and H₂, by either partial oxidation or steam reforming processes. The synthesis gas is then converted catalytically to hydrocarbons by Fischer Tropsch synthesis (FTS). The product stream of the FTS typically consists of a wide range of alkenes, alkanes, oxygenated compounds, viz. aldehydes, alcohols, ketones and acids (e.g., gasoline, diesel, oxygenates and wax). Despite advancement over the years in reactor and catalyst design, and process developments, the competitiveness of the Fischer Tropsch GTL technology is limited primarily due higher capital cost, and operational and maintenance costs than other commercial technologies. The objective of this poster is to highlight the features of the Fischer Tropsch GTL technology.

2. Key Features

The important features of this research are presented in three sections. The first section summarizes the features of FTS technology aspects. Major commercial GTL plants are briefly summarized in the second section. The aim of the third section is to elaborate the research issues of FTS technology.

3. Fischer Tropsch Synthesis Technology

There are two types of Fischer Tropsch synthesis, low temperature (LTFT, 220-250°C) and high temperature (HTFT, 330-350°C). The LTFT process mainly produces syncrude with a large fraction of heavy, waxy hydrocarbon, while HTFT produces light syncrude and olefins. Multitubular fixed bed, bubble column/slurry phase, circulating bed and fluidized bed reactors have been commercially used. Fixed bed reactors operate at temperatures between 180 and 250°C, and pressures between 10 and 15 bar in three phase gas-liquid-solid trickle bed mode and produce more paraffinic and waxy product spectrum [2]. These reactors are commercially used by Sasol in ARGE process and by Shell in Shell middle distillate synthesis (SMDS) process. Slurry phase or bubble column reactors consist of a vessel containing slurry consisting of process-derived wax with catalyst dispersed in it [3]. These types of reactors are used by Sasol in Sasol slurry phase distillate (SSPD) processes [3]. High temperature F-T synthesis is carried out in fluidized bed reactors. The reactor operates in two phase gas-solid mode and produce predominantly gasoline and lighter olefins. The advantage of the Sasol advanced synthol (SAS) reactor includes its simplicity, ease of operation, low operating cost, high thermal efficiency and capacity, and high conversion at high gas load. There is consensus that cobalt-based catalysts are the best compromise between the performance and cost of the synthesis. Cobalt catalysts were first discovered in the 1930's. In subsequent years, catalyst technology has advanced from a simple cobalt oxide on asbestos to sophisticated, high activity, highly optimized catalysts supported on modified alumina, silica or titania carriers and promoted with noble metals and basic oxides. The application of iron catalysts for F-T synthesis was demonstrated in the 1950's. From the 1950's to the 1970's, most F-T studies were focused on iron catalysts, resulting in significant advancement in catalyst design, support and promoters [4].

4. Commercial Fischer Tropsch GTL Processes

Sasol, Syntroleum, BP, Shell, Rentech, Exxon and Statoil are the major companies that have been actively pursuing the development of GTL technology. South Africa-based Sasol have been operating

commercial FTS plants since the 1950's. The first commercial plant in Sasolburg (Sasol 1) uses multitubular fixed bed and entrained bed Kellogg reactors. In the 1980's, Sasol 2 and Sasol 3 plants in Secunda went on stream. These plants use circulating fluidized bed reactors for the production of fuels and low molecular weight olefins. Currently, Sasol has two new processes for the Fischer-Tropsch synthesis, a HTFT for the production of gasoline and light olefins, and a LTFT for wax production. A SAS reactor with gas-solid fluidization was developed recently. Shell started a Fischer Tropsch synthesis plant in Bintulu, Malaysia in 1993. The SMDS process produces heavy paraffins on a cobalt catalyst in multitubular trickle bed reactors. Part of these products are sold as wax specialties; another part is hydro-cracked over a noble metal catalyst into clean transportation fuels. The plant converts 100 million cubic feet/day of natural gas from off-shore fields by non-catalytic partial oxidation into 12,500 bbl/day of hydrocarbons. Statoil formed an alliance with Sasol for the development of floating Fischer-Tropsch plants on ships or floating production systems. These floating off-shore plants can be used to utilize natural gas associated with oil production. Syntroleum claims that their process eliminates a costly air separation unit, since their Auto-thermal Reformer produces nitrogen-diluted synthesis gas from natural gas. Nitrogen can be used to remove some of the generated heat during the FT reaction. The Syntroleum process is the basis of an agreement between Texaco, Brown & Root and Syntroleum to develop a 2,500 bbl/day GTL plant. Energy International developed slurry bubble column reactors for the FT process. They claim the major advantage of their process to be low capital costs in comparison to other processes. Highly active cobalt catalyst on alumina carriers produces a high liquid fuel yield relative to other cobalt catalysts. Rentech licenses developed a slurry phase process for the production of ultrapure Fischer Tropsch diesel. Rentech built a Fischer Tropsch plant using slurry reactor in Colorado to produce 235 bbl/day in 1992. The Exxon's process is known as AGC 21 (Advanced Gas Conversion 21st Century).

5. Commercial Fischer Tropsch GTL Processes

The most important issue of the F-T synthesis is the absence of accurate models for product distribution and reaction kinetics, necessary for reliable design and scale up of industrial processes. An optimal design requires a deep understanding of hydrodynamics, reaction kinetics, catalytic system and Fischer Tropsch process chemistry. The major problem for the development of reliable kinetic expressions is the complexity of the Fischer Tropsch reaction mechanism, which involves a large number of intermediates and products. In the literature, most catalytic studies aim at catalyst improvement and postulate empirical power law kinetics for both the carbon monoxide conversions and the carbon dioxide formation rate. Fischer Tropsch synthesis products form a complex multi-component mixture with significant variation in carbon number and product type. As per Anderson, the product distribution of hydrocarbons can be described by the Anderson-Schulz-Flory (ASF) equation:

$$m_n = (1 - \alpha)\alpha^{n-1} \quad (1)$$

where m_n is the mole fraction of a hydrocarbon with chain length n , and the growth probability factor α independent of n . The total carbon number distribution of the FT products is governed by α , which depends on reaction conditions and catalyst type. Significant deviations from the ASF distribution (high methane yield, low ethane yield, change in change growth parameter, etc.) are reported in the literature. A comprehensive review of the mathematical modeling of the Fischer Tropsch process was done by Saxena [5], who found that none of the available models is accurate enough for a reliable reactor design. The bottleneck appears to be the lack of reliable kinetic equations for all products and reactants based on realistic reaction mechanisms. Until now, none of the available literature models obtain enough details to describe the complete product distribution of the Fischer-Tropsch synthesis at industrial conditions (high temperature and pressure) as a function of the overall consumption of synthesis gas components and operating conditions.

5. Conclusions

By converting the stranded natural gas reserve to high value hydrocarbon fuels and chemicals, Fischer Tropsch GTL technology can positively contribute to the world energy security and supplies. The application of the FTS technology has been limited due to number constraints such as high technology cost, limited plant capacity reactor design and catalyst deactivation. Significant breakthroughs have been achieved in every aspects of the F-T technology. With more and more companies investing F-T facilities and plants, the future of the F-T technology looks very pragmatic and positive.

6. References

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Author Biographies

Dr. Saleh H. Al Hashimi is Assistant Professor of Chemical Engineering at The Petroleum Institute, Abu Dhabi. His research interests include reactor design, process intensification, process development, optimization and control.

Mr. Ahmad Nafees is a Teaching Assistant in the Chemical Engineering Program at The Petroleum Institute. Ahmad's research interest includes catalyst development and modeling of Fischer Tropsch synthesis, gas to liquid technology (GTL), and low temperature fuel cells (PEMFCs).