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Research Opportunities for Fischer-Tropsch Technology

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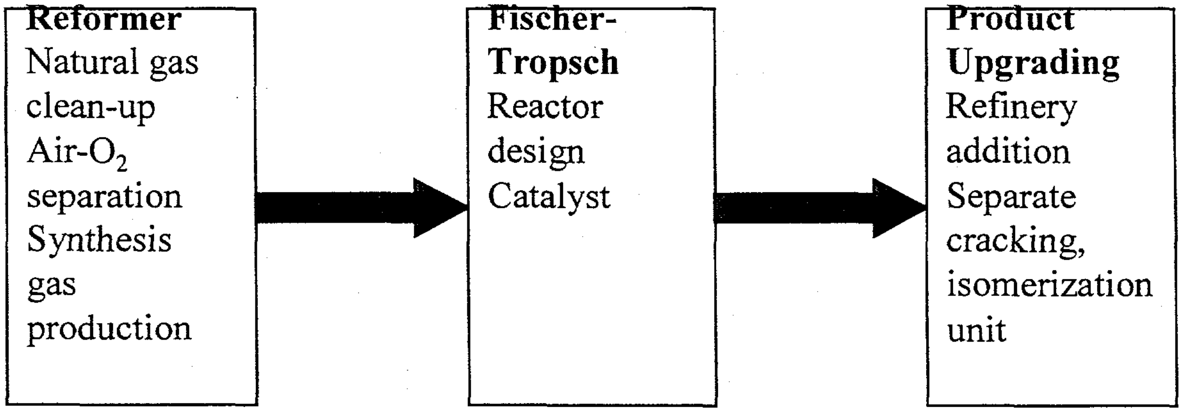
Fischer-Tropsch synthesis was discovered in Germany in the 1920's and has been studied by every generation since that time. As technology and chemistry, in general, improved through the decades, new insights, catalysts, and technologies were added to the Fischer-Tropsch process, improving it and making it more economical with each advancement. Opportunities for improving the Fischer-Tropsch process and making it more economical still exist. This paper gives an overview of the present Fischer-Tropsch processes and offers suggestions for areas where a research investment could improve those processes.

Gas-to-liquid technology, which utilizes the Fischer Tropsch process, consists of three principal steps: Production of synthesis gas (hydrogen and carbon monoxide) from natural gas, the production of liquid fuels from syngas using a Fischer-Tropsch process, and upgrading of Fischer-Tropsch fuels. Each step will be studied for opportunities for improvement and areas that are not likely to reap significant benefits without significant investment.



Reformer

There are three potential unit operations within this synthesis step. They include gas clean-up, separation of oxygen from air, and reforming of natural gas to synthesis gas.

Natural Gas Clean Up

Clean-up of the natural gas requires removal of sulfur, chlorine, particulates, and carbon dioxide, if a large amount is present. Sulfur needs to be removed from the feed stream, preferably to below the ppm level. The catalysts for reforming and Fischer-Tropsch are particularly sensitive to sulfur. Deactivation of a Fischer-Tropsch catalyst by sulfur results in a catalyst that can not be regenerated economically.

Separating oxygen from air

Preparing pure oxygen from air is a particularly difficult problem for the small and/or remote wellhead sights for gas-to-liquids technology. The most established and efficient technologies for this separation are the most economical in large-scale plants. Although air separation plants may contribute significantly towards capital expense, they are not a technically risky part of a large gas-to-liquids plant. Large oxygen plants are considered established technology that can be easily purchased or licensed from an experienced vendor.

The challenge regarding oxygen-nitrogen separation is for the smaller or remote site plant. For a small plant the cost of air-oxygen separation can be prohibitive. Many technologies are being investigated in order to find a small-scale low-cost air-oxygen separation system. Advancement in air separation would have a profound effect on the economics of the gas-to-liquids process and is an area that would benefit greatly from research. The most common technology being pursued in this application is a membrane or ion-conducting ceramic separation. Unfortunately, the problems preventing commercialization are not trivial. These challenges include 1) Synthesizing a membrane capable of separating oxygen from nitrogen in a defect-free manner so that there are no "holes" for the unwanted molecules to travel through; 2) Synthesizing a membrane that does not require a large pressure drop; 3) Synthesizing a ceramic that has enough mechanical integrity that it can have a long life time without breaking or cracking; 4) Bonding the ceramic membrane or ion-conductor to other parts of the equipment made out of steel or other metal in such a way that they can remain gas tight at high pressures and during large temperature swings. (Ceramic and metals have significantly different coefficients of expansion, i.e., they expand and contract at different rates during temperature changes.)

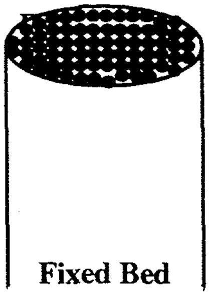
Synthesis Gas Production

The partial oxidation of methane to synthesis gas follows the chemical path shown below.

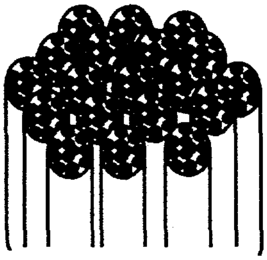
$$2CH_4 + O_2 \longrightarrow 2CO + 4H_2$$

If nitrogen is present, it acts primarily as an inert gas, not significantly effecting the outcome of the reforming process. There are concerns about NOx formation during the partial oxidation of methane since nitrogen, in the presence of an oxidant at high temperatures is likely to produce NOx. Besides NOx formation that can be addressed with several technologies, nitrogen presents a problem related to the excess volume it creates. In simplistic terms, a process designed for 100 ft^3 of methane would require a reforming reactor of 150 ft^3 if oxygen was used and 350 ft^3 if air was used. This would have an impact on capital expenses. Also, since Fischer-Tropsch reactors operate at elevated pressures, inclusion of nitrogen would significantly increase the amount of gas to be pressurized, an expensive, energy-consuming process. For the reactants (natural gas and oxygen) to be at the required partial pressure, the entire system would have to be at a higher pressure. In simplistic terms, a catalytic process requiring 100 psi when only methane and oxygen are present would require, with nitrogen present, a reactor pressure of 233 psi. Also, the option of recycle is no longer available when large amounts of nitrogen are present. Recycling the gaseous portion of the product back to the reformer would only introduce additional diluent to the process since separation of nitrogen from the stream would be prohibitively expensive. To successfully use the Fischer-Tropsch process without nitrogen-oxygen separation, one would need a particularly active catalyst, one that is active and shows a high molecular weight yield at lower pressures without significant methane production.

Fischer-Tropsch process



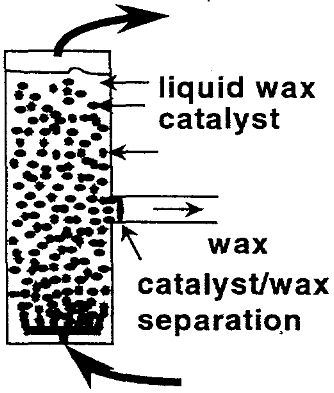
Fixed Bed Reactor



Multi-tubular Reactor

Reactor Design

There are two major issues in this step of the gas-to-liquids process. The first is the choice of reactor; the second is the choice of catalyst. There are a number of factors to consider about each when choosing a process. The Fischer-Tropsch process is an exothermic process, which means the reaction generates heat. It is critical that the temperature of the reaction be controlled and maintained at the appropriate temperature. A change in temperature will have a profound effect on the product slate of the Fischer-Tropsch catalyst. At high temperatures, methane and low weight hydrocarbons are the preferred product. Since heat is generated at the site of reaction, it is necessary to design for swift and continuous removal of that reaction heat in order to maintain product quality. The most commonly used design of chemical reactors and the type originally used by Sasol in the 1950's and 1960's is the fixed bed reactor. The fixed bed reactor is a tube packed with catalyst. As the diameter of the tube gets bigger and bigger, it gets more and more difficult to remove the heat of reaction and maintain temperature. Shell designed for its Fischer-Tropsch plant in Malaysia a multi-tubular reactor that allows a cooling media to flow between the tubes and maintain temperature control.



Slurry Phase Bubble Column Reactor

The slurry phase bubble column reactor is an ideal reactor for removing heat and maintaining a constant temperature at the surface of a catalyst, which is why it is either used or on the drawing board of many companies in the gas-to-liquid business. Shown to the left, the catalyst is suspended in wax and the synthesis gas is bubbled in from the bottom. The slurry provides continuous removal of heat from the small catalyst particles (60-120 microns). The technical difficulties associated with this reactor include the design of an efficient and thorough wax/catalyst separation step. Also, the high flow rates needed for an economically high throughput create a three-phase flow regime that is much more challenging to model and design than a simple reactor such as the fixed bed reactor.

Catalyst

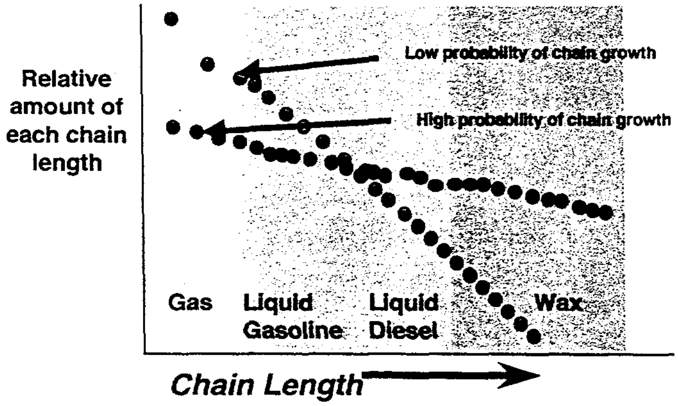
The catalysts used for Fischer-Tropsch synthesis are either iron or cobalt based. Iron catalysts were used by Sasol for many years and were particularly useful for their coal-derived rather than natural-gas-derived synthesis gas. Coal-derived synthesis gas has a lower hydrogen to carbon monoxide ratio (about 0.7) than natural gas derived synthesis gas (>2). The water-gas-shift properties of the iron catalyst make it an ideal catalyst for a low-hydrogen synthesis gas process.

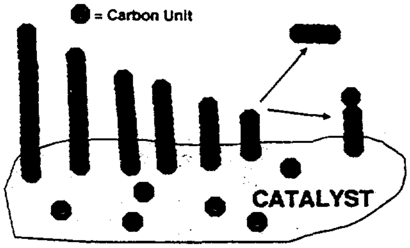
The major problem with an iron Fischer-Tropsch catalyst is that it tends to attrit (fall apart) during reaction. This attrition is not entirely due to the catalyst mechanical strength, but also to the chemical and morphological changes the catalyst experiences during reaction. It is the "chemical" portion of the attrition that is the greatest challenge, since many of the chemical changes that cause attrition -- including its conversion from iron to iron carbide -- are also what cause the catalyst to be active. Wax/catalyst separation is virtually impossible if the catalyst attrits to a submicron diameter size. Preventing attrition or designing an exceptional separation system is a hurdle that must be overcome if an iron Fischer-Tropsch catalyst is to be used in a slurry phase reactor.

Many active cobalt catalysts have been developed for Fischer-Tropsch synthesis. Since cobalt does not form cobalt carbide during reaction it does not undergo the same attrition problems that an iron catalyst does. Attrition can be a problem for a cobalt catalyst, but it can be addressed from a viewpoint of enhancing its mechanical strength rather than trying to change its chemistry. The negative sides to cobalt as a catalyst are that cobalt is more expensive than iron and there are presently more Fischer-Tropsch cobalt catalyst patents than iron catalyst patents. Since cobalt is a better hydrogenating catalyst than iron, cobalt catalyst formulations must compensate for cobalt's tendency to form unacceptable amounts of methane.

Chain limiting catalyst

In the almost 80 years in which Fischer-Tropsch catalysis has been studied around the world, there have been many who have thought that limiting the chain length of the hydrocarbons of the Fischer-Tropsch catalyst would produce an extraordinary catalyst which would bring gas-to-diesel in just two steps. However, an understanding of the mechanism of the Fischer-Tropsch catalyst (either iron, cobalt or ruthenium) explains why a chain limiting catalyst would be very difficult to achieve. The mechanism of Fischer Tropsch catalysis is a step-wise addition reaction. The chains formed in Fischer-Tropsch synthesis grow one carbon at a time. The one-carbon unit may be either CHx or CO, a discussion of which is beyond the scope of this paper, but the form it takes is not pertinent to the understanding of a chain growth reaction. Each chain on the surface of the catalyst can do one of two things: the chain can either grow one more one-carbon unit or it can quit growing and desorb as a completed chain. If it stopped growing when it was a four-carbon chain, it would be butane, a six-carbon chain, hexane, a ten-carbon chain, decane, and so on. The greater the probability that the chain will grow versus terminate, the more long-chain hydrocarbons that will be produced. On the graph showing chain length versus relative amount, the catalyst system with the high probability of chain growth shows far greater wax production than the low probability of chain growth system. Probability of chain growth is a factor of the catalyst composition and the local temperature and pressure of the reaction. This Fischer-Tropsch growth and termination process happens very rapidly and at any given moment the





chains growing on the surface of a catalyst are at a wide, random assortment of lengths. At present, there is no known way of making sure that new carbon units only add to short chains or no molecular-sized tweezers for plucking off the chains once they have reached sufficient length.

There are possible ways that a Fischer-Tropsch catalyst might be used to produce a product with limited chain length. A cracking catalyst could be added to the Fischer-Tropsch reactor to crack the long chains as they are formed. The Fischer-Tropsch catalyst could be placed inside a porous material that only allows shorter chains to escape from the surface. But these potential methods are fraught with problems. Research into a chain limiting catalyst would be a high risk venture which would need to be weighed against the relative ease with which Fischer-Tropsch liquids can presently be integrated into refinery streams.

Product Upgrading

Cracking and isomerization technology for Fischer-Tropsch wax upgrading is established technology that can be found in most refineries today. Fischer-Tropsch product may be either upgraded on sight or added to a refinery's feed stream. The lack of sulfur or other impurities in the Fischer-Tropsch product make it easy to process. It may be used to dilute the percentage of sulfur in the refinery's products.

Conclusions

In summary, there are still many opportunities for improving the economics of the Fischer-Tropsch gas-to-liquid process with the right investments in research, particularly for the remote gas-to-liquid technology. These include

- new technologies for providing pure oxygen to the natural gas reforming process,
- development of Fischer-Tropsch catalysts active enough to produce financially attractive products at low pressures or at low partial pressures of synthesis gas (nitrogen diluent present),
- development of iron catalysts that are attrition resistant,
- better understanding of the hydrodynamics of slurry phase bubble column reactors, and
- better liquid-solid separation systems for catalyst-wax separation.

Acknowledgments

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