Update

Gas-to-Liquids Technology *Gains Momentum*

Gerald Parkinson

With oil prices at record highs in recent months, the market prospects have never seemed better for liquid fuels produced from natural gas. As it happens, the high oil prices have coincided with some significant milestones in the progress of multi-billion-dollar gas-to-liquids projects (GTL) that are being developed by major oil companies (Box below).

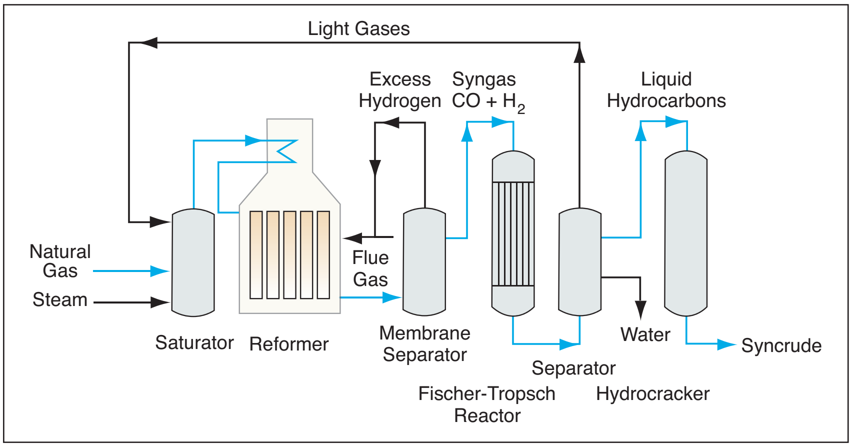
The projects herald a new era for the Fischer-Tropsch process, invented by two German scientists in 1923. Originally designed to produce liquid fuels from coal-derived synthesis gas, the process was used for that purpose in Germany during World War II and has been further developed and used commercially by coal-rich South Africa's Sasol Ltd. (Johannesburg) since the 1950s.

However, the future for the technology now lies mainly with natural gas — in particular, low-cost remote natural gas or gas associated with oil production that is now flared, but does not justify the cost and scale of liquefied natural gas (LNG) facilities. In these cases, GTL offers an economical way to convert the gas to liquid fuels or refinery feedstock that can be readily transported. Several major projects are in the works, mostly in the State of Qatar, which has large reserves of natural gas and has expressed its intention to be the world leader in the use of GTL technology.

Companies involved in GTL projects are hesitant about revealing the cost of gas in relation to oil prices. Industry spokespersons point out that while oil prices are high at the moment, the plants are designed to be competitive over the long term.

However, the high price of oil "supercharges the economics of GTL processes," says Kenneth Agee, chairman of Syntroleum Corp. (Tulsa, OK; www.syntroleum.com), noting that "these projects would have been profitable with oil at $25-30/bbl. It's a great time to be sitting here," says Agee, who founded Syntroleum some 20 years ago to develop a GTL process. "We paid our dues and now we are in the right place at the right time."

GTL technology is a three-step



■ **Figure 1. A generic flowsheet of a gas-to-liquids process. Courtesy of Davy Process Technology Ltd.**

Investing in Gas-to-Liquids

Projects that are currently underway, include:

• A 34,000-bbl/d GTL plant, the largest built to date, is scheduled to be commissioned in Qatar at the end of this year in a joint venture between Sasol and Qatar Petroleum. The plant, called Oryx GTL, will produce about 22,000 bbl/d of diesel fuel and 10,000 bbl/d of naphtha, plus liquid petroleum gas (LPG).

• In April, ChevronTexaco Corp. (San Ramon, CA; www.chevrontexaco.com) awarded a $1.7 billion engineering, procurement and construction contract for its 34,000-bbl/d Escravos gas-to-liquids (EGTL) project in Nigeria. The contract went to a consortium composed of JGC Corp. (Yokohama, Japan), KBR (Houston) and Snamprogetti SpA (Milan).

• Shell GTL Ltd., a subsidiary of Royal Dutch Shell Group (London), is working under a development and production sharing agreement with Qatar Petroleum on a project to convert more than 1.6 billion ft^3/d of natural gas into 140,000 bbl/d of liquid fuels and 60,000 bbl/d (oil equivalent) of natural gas liquids. The Pearl GTL project is expected to start production in 2009.

• ExxonMobil Corp. (Irving, TX; www.exxonmobil.com) has a heads of agreement with the State of Qatar for a 154,000-bbl/d plant, with startup scheduled for 2011. About half the product will be diesel fuel, 20% lubrication base stocks, and the rest naphtha and associated products.

These projects represent a significant investment — approximately $7 billion on the part of ExxonMobil and $6 billion for Shell. In Sasol's case, Sasol Chevron (London), the company's GTL joint venture with ChevronTexaco, has signed two memorandums of understanding with Qatar Petroleum. One is for a second GTL complex, Oryx II, to produce about 66,000 bbl/d of liquid fuels; the other to expand Oryx I to produce 8,500 bbl/d of high-quality base oils for lubricants. Sasol Chevron is also planning a 130,000-bbl/d plant in Qatar that will include gas production. The total value of these projects is about $6 billion.

process (Figure 1) that starts with the reforming of natural gas to produce a synthesis gas (syngas) that has a hydrogen:carbon monoxide ratio of approximately 2:1. The syngas is fed to the Fischer-Tropsch (FT) reactor and converted to mostly straight-chain, waxy paraffins. This product can then be readily upgraded by hydroprocessing to yield a clean, essentially sulfur-free diesel fuel, and naphtha (Box, right).

Each company in the GTL business has proprietary FT technology, but a common theme is that most use a slurry-phase reactor with a cobalt-based catalyst. Exceptions are Shell and BP, whose processes use a fixed-bed reactor, and Rentech, Inc. (Denver, CO; www.rentechinc.com), which uses an iron-based catalyst.

Most companies use autothermal reforming (ATR) rather than steam reforming because it is less expensive, especially when scaled up. "When you double the capacity of a steam reformer, you need double the number of tubes, so you pay about twice the price," says Niels Udengaard, principal technology specialist with Haldor Topsoe Inc. (Houston, TX; www.topsoe.com) Another reason is that steam reforming produces more hydrogen than is needed for the FT reaction.

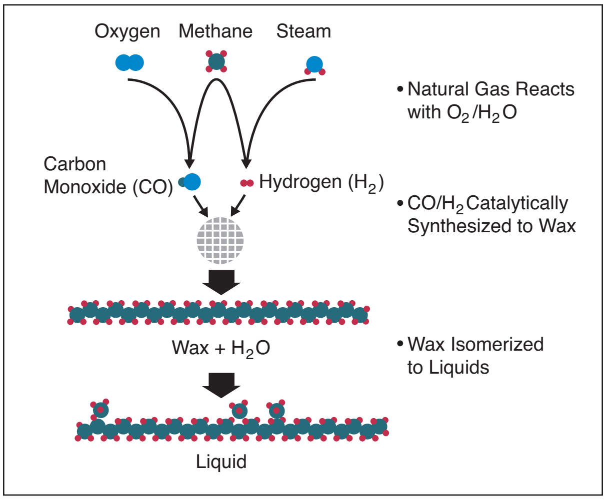
In ATR, gas and an appropriate volume of steam are fed to the reformer, along with enough oxygen to burn part of the fuel to preheat the gases before they pass over the catalyst. "ATR is actually a combination of partial oxidation with steam reforming," says Rocco Fiato, a coordinator for GTL with ExxonMobil Research & Engineering (Annandale, NJ), which has a proprietary ATR system. "You have endothermic and exothermic chemistries going on simultaneously in a single reactor, which allows the heat exchange to be more direct."

Haldor Topsoe, which is supplying ATRs to the Sasol Chevron and ChevronTexaco projects, has reduced the steam:carbon ratio of its reformers to 0.6:1, down from about 1.4:1 a few years ago. "The lower ratio enables the production of an appropriate syngas for the FT reaction," says Udengaard.

The biggest cost factor in ATR is the air-separation unit (ASU) to produce O_2, says Udengaard, but in contrast with a steam reformer, it gets relatively cheaper when scaled up. Even so, he notes that the reforming equipment typically accounts for more than half the cost of a GTL plant.

Syntroleum cuts this cost to about 44% by using air instead of oxygen in its ATR, thereby avoiding the cost of an ASU. The downside is that the resulting syngas contains nitrogen, which dilutes the syngas and precludes recycling of unreacted gases through the FT reactor. To compensate, Syntroleum's reactor is about 30% bigger than it might otherwise be, and the one-pass conversion is above 90%. "The bottom line," says Agee, "is that the elimination of the ASU simplifies the process design and the resultant smaller footprint allows the plant to be set on a barge or ship."

ConocoPhillips (www.conocophillips.com) has been testing a catalytic partial oxidation system called CoPOX in a 400-bbl/d pilot plant in Ponca City, OK, for about two years. Compared with conventional reformers, CoPOX has higher selectivity for CO over CO_2 and thus, reduces oxygen consumption, the company says.



■ **Figure 2. Shown above are the chemical reactions by which natural gas is converted to liquids in ExxonMobil's AGC-21 Advanced Gas Conversion Process. Courtesy of ExxonMobil Research and Engineering Co.**

BP's process is unusual in that it uses both steam reforming and a fixed-bed FT reactor. The reformer is a compact unit developed in cooperation with Davy Process Technology Ltd. (London). It has a thermal efficiency of 90%, vs. 60–65% for a conventional steam reformer, with about 30% of the weight. BP has tested the process in a 300-bbl/d pilot plant in Nikiski, Alaska, over the past three years. The company "has confirmed that the technology works" and is checking out the possibilities for using it around the world, says Kenneth Konrad, senior vice-president, Alaska Gas.

Scaling up

Sasol Chevron expects to increase production efficiency by about 30%

GTL Diesel Fuel Burns Cleanly

Diesel fuel produced by GTL processes has proved cleaner than that from petroleum refining in tests done by auto companies. DaimlerChrysler AG (Stuttgart) tested GTL fuel from Sasol Chevron in a diesel-powered Mercedes Benz and compared the results with the performance of European "sulfur-free" diesel fuel.

The GTL fuel showed significant reductions of hydrocarbons, CO and particulate matter (PM) without compromising oxides-of-nitrogen (NO_x) emissions, says Sasol Chevron, The company also points out that GTL diesel fuel has a cetane rating of more than 70, vs. an average of 52 for European diesel, and this is beneficial during cold starts and low-temperature operation.

Shell has also reported reduced exhaust emissions in a yearlong test of GTL diesel fuel in six trucks operated by a California water distributor. In tests without a particulate filter, emissions of NO_x and PM were reduced by 16% and 23%, respectively. When a catalyzed diesel particulate filter was used ,the reductions were 20% for NO_x and 97% for PM.

in its Oryx II plant, over that of Oryx I, mostly by scaling up the size of the equipment. "The 66,000-bbl/d plant will have only three trains, each of 22,000 bbl/d, vs. two trains for the 34,000-bbl/d Oryx I plant," says Charlene Pretorius, technical manager. The reactors in Oryx II will be identical to those of Oryx I, she says, but the throughput will be boosted by an improved catalyst developed by Sasol, that is being produced in DeMeern, Netherlands, by Engelhard Corp. (Iselin, NJ; www.engelhard. com). Oryx II will have an ASU and an ATR for each train, but a single isocracker will split the waxy FT product into LPG, naphtha and diesel fuel.

Smaller GTL technology companies that cannot tackle such large projects are pursuing niche markets. Syntroleum, which says it can build a compressed-footprint plant of around 20,000 bbl/d on a barge or ship, is pursuing undeveloped gas fields of 1–3 trillion ft^3. These are too small for LNG or competing GTL technologies, says Agee. Syntroleum has formed a consortium with five other companies to exploit both oil and gas in an oilfield off the coast of Nigeria.

Rentech is awaiting approval on various small overseas projects, but is especially excited over a patent it received 18 months ago on a way to ship excess hydrogen from a coal-based FT plant to an adjacent ammonia plant. "This can increase ammonia production without having to add equipment and there are a myriad opportunities for this application," says Mark Koenig, director of investor relations. The company recently entered into an agreement with Royster-Clark Nitrogen, Inc., which owns an 830-ton/d natural-gas-fed nitrogen fertilizer plant in Dubuque, IL. Rentech plans to build a coal-gasification plant and use the gas as feed for both the fertilizer plant and an FT plant, plus electricity production. CEP

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PROCESS TECHNOLOGY

Rapid Pyrolysis Process Now Works with Crudes

Last month, Ivanhoe Energy, Inc. (Vancouver, B.C.; www.ivanhoe-energy.com) completed the first commercial-scale test of Ensyn Petroleum International Ltd.'s (Boston, MA; www.ensyn.com) Rapid Thermal Processing (RTP) technology, originally developed to produce chemicals and fuels from biomass, for the conversion of heavy oil to light oil at a capacity of 1,000 bbl/d. This marks the satisfaction of requirements stipulated by Ivanhoe for the completion of its Ensyn acquisition. Ensyn's commercial demonstration facility (CDF; Bakersfield, CA) is a step up from its 20-bbl/d pilot facility in Canada. Now, Ivanhoe Energy and Ensyn Petroleum have awarded a contract to Colt Engineering Corp. of Calgary, Canada, to develop designs for fully commercial modules of 10,000–15,000 bbl/d of raw, heavy crude feed. Preliminary engineering for the first full-scale commercial facility is slated for completion by the end of 2005.

The Ensyn RTP process is a fast pyrolysis technology. A carbon-based feedstock is fed into a vessel heated to approximately 510°C where it is contacted with a stream of hot silica sand (the heat-transfer agent) and vaporized. Since airflow to the vessel is minimized, there is essentially no combustion. After the vapors are separated from the sand, they are sent to a distillation column and quenched, effecting upgraded heavy oil yields of 82–95 vol.%. The silica sand is sent to a reheater before being recycled to burn off excess coke laid down by the heavy crude. Energy produced from the combustion of coke and product gases is made available for on-site production of steam/power.

According to Ian Barnett, director of Ensyn Petroleum, RTP has lower residence times ($<$ 2 s for both pyrolysis and quenching) and pressures than seen with regular delayed coking, so the facilities are smaller and less costly. He adds that the process does not require hydrotreating and makes full use of the coke byproducts.

The CDF will serve as a test site for other local heavy oils, as well as a range of crude oils from potential projects around the world. ConocoPhillips' subsidiary, Canada Resources Corp. has a non-exclusive license to use the RTP technology in Canada. In addition, Ensyn and Ivanhoe have formed agreements with, Aera (a Shell-ExxonMobil joint venture), Ecopetrol (Colombia) and others to study the application of RTP systems at these potential customers' sites. "The modular design of the RTP process allows for economic small-field development, as well as efficient, large-scale field development, as production capacity builds up," says Barnett.

Dow and Snamprogetti Nurture an Economic Route to Styrene

Dow Chemical Co. (Midland, MI; ww.dow.com) and Snamprogetti S.p.A. (Milan, Italy; www.snamprogetti.eni.it) are jointly developing a new process for the production of styrene monomer from ethane and benzene that would represent a step change in the costs of styrene production, compared with conventional processes. Currently, ethylene and benzene are reacted to form ethylbenzene, which is then dehydrogenated to styrene in the presence of an iron catalyst. By using ethane, a low-cost feedstock, the need to purchase ethylene or invest in upstream ethylene production equipment is eliminated, explains Carol Dudley, vice president of R&D for Dow Hydrocarbons & Chemicals.

Dow and Snamprogetti combined their catalyst and engineering expertise to improve styrene monomer development in the 1990s, when Snamprogetti was issued a patent for a benzene-ethane based styrene production process. As described in the patent, benzene and the recycled product stream consisting of 2–50 wt.% ethylene and 50–98 wt.% ethane, are fed to the alkylation unit to effect a benzene:ethylene ratio ranging from 3:1 to 10:1. The alkylated product stream, composed mainly of ethylben-