Promising Outlook for Products From Gas-to-Liquids Technology

Iraj Isaac Rahmim

Over the past two decades, several factors have increased interest in commercial gas-to-liquids (GTL) technologies and their variations. These include the following:

- Need to develop and exploit additional energy resources
- Existence of large reserves of stranded natural gas and the need to monetize them
- Desire for strategic diversification by both producers and consumers
- Environmental drivers ranging from a movement to reduce flaring to regulations about automobile emissions.

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Within the last few years, one new world-scale unit came on line, three others are in construction, and many more are planned, while other approaches and synergies, such as biomass-to-liquids (BTL) and coal-to-liquids (CTL), are also being explored.

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This article reviews recent GTL activities, key products, and likely implications on various markets.

PRODUCTS AND TECHNOLOGY

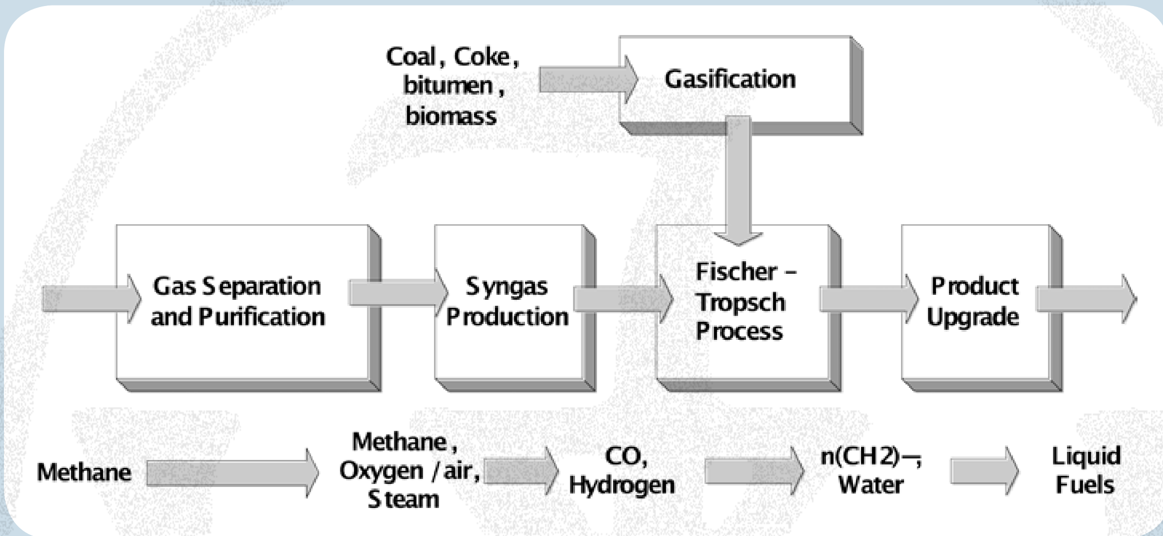
GTL products fall into the categories of fuels (primarily diesel and jet fuel but also liquid propane gas [LPG]), specialty streams (lube basestocks and waxes), and petrochemicals (naphtha for steam cracking).

GTL technology involves the multistep, indirect conversion of methane to higher-molecular-weight hydrocarbons ranging from LPG to paraffin waxes, often controlled to peak in the diesel range (**Exhibit 1**).

The first step after feed preparation and purification involves steam reforming and/or partial oxidation of methane to carbon monoxide and hydrogen. The key reactions include the following:

$$CH_4 + H_2O \Leftrightarrow CO + 3\ H_2$$

Exhibit 1. GTL and FT-Based Block Flow



$$CH_4 + \frac{1}{2} O_2 \Rightarrow CO + 2\, H_2$$

The synthesis gas is then converted to hydrocarbons in the Fischer-Tropsch (FT) section with cobalt (with natural gas as feed) or iron-based (with heavy feeds such as coal) catalysts:

$$CO + 2\, H_2 \Rightarrow \cdots\cdots(\text{—}CH_2\text{—}CH_2\text{—}CH_2\text{—}CH_2\text{—})\cdots\cdots + H_2O$$

The liquid products are separated in the final upgrading section, which often also involves mild hydrocracking to convert higher-molecular-weight waxes and lubes to LPG, naphtha, jet, and diesel.

In modern variations, GTL unit designs and operations are modulated to achieve desired product distribution and a range of product slates. Certain operations (low temperature and/or no hydrocracking) result in primarily wax, lubes, and diesel products, whereas other conditions (higher temperature and/or mild hydrocracking) increase diesel, straight-chain paraffinic naphtha, and LPG at the expense of lubes and waxes. Wax and lube production typically ranges from 0 to 30 percent, diesel from 50 percent to 80 percent, and the lighter products to as much as 25 percent of the final liquid products. The products are of generally high quality, with near-zero sulfur and high cetane for the diesel (**Exhibit 2**).

RECENT COMMERCIAL ACTIVITY

FT-based units have been in commercial operation since World War II, first in Germany during the war and later in South Africa to take advantage of existing coal deposits. Over the past two or three decades, interest in further commercialization of the technology has intensified. Currently, commercial-scale GTL and CTL units are in operation in South Africa, Malaysia, and Qatar. Additional units are under construction and are slated to come on stream in 2010 (Qatar, Trinidad & Tobago), 2011 (Qatar), and 2011–13 (Nigeria).

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A number of demonstration-scale facilities (tens to hundreds of barrels a day) are in existence and have been used for the development and optimization of GTL/CTL/BTL technologies by several U.S. and international companies. Additionally, a large number of facilities are at various stages of study, design, and financ-

 DOI 10.1002/gas

Exhibit 2. Sample Product Slate for 100 KBD Facility

	No HC	With HC	Comments	
LPG	2	4	Similar to other plant (LNG, refinery) LPG	Can be co-processed and marketed with them
Naphtha	18	26	Straight-chain paraffinic Near-zero sulfur	Preferred use: steam cracker feed
Jet-Kero/Diesel	50	70	High cetane Near-zero sulfur	Low density Low aromatics
Lubes	30	< 1	High grade Low volatility Low pour point	Low viscosity Low sulfur
Wax	10	< 1	High quality	
Specialty			α-olefins, solvents, detergents, . . . drilling fluids	

ing—of these, as is the norm, only a small subfraction are likely to be commercialized.

FT DIESEL SUPPLY, QUALITY, AND PRICING SCENARIOS

Current worldwide GTL/CTL diesel supply capacity stands at about 180,000 barrels a day (South Africa, Qatar, and Malaysia) with another 180,000 barrels a day under construction and slated to come on stream during the next two to three years. This is in addition to another 20,000 barrels a day of the similar direct coal-to-liquid (DCL) in Inner Mongolia (PRC) that began operation in late 2009. Today, none of the commercial activities are in the United States.

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These numbers, in general outlines, are in agreement with global GTL growth predictions by a variety of entities including the California Energy Commission and Sasol Chevron (400,000–800,000 barrels a day by 2016–19) and the U.S. Energy Information Administration (200,000–700,000 barrels a day by 2030; range due to investment scenarios).

Our analysis suggests that CTL growth (and resulting liquid products) is in the same, hundreds-of-thousands-of-barrels-a-day range. There are currently no commercial BTL units in existence, though several are under various stages of study and design.

Exhibit 3 shows the likely FT diesel production scenario in comparison with global middle distillates demand. Note that GTL/CTL are likely to supply only a small fraction of total supply (less than 4 percent of diesel by 2020) and, as such, are unlikely to have an adverse effect on the global market and its pricing. At the same time, local and regional markets can be impacted by FT diesel supply. As examples, Shell estimates that one large GTL plant would fully satisfy the city of London and, according to Baker and O'Brien, all U.S. PADD 4 and 20 percent of PADD 2 demand could be, potentially, supplied by U.S.-manufactured CTL diesel. In current commercial practice, FT diesel is sold in a number of markets worldwide in blended form (including in Greece, Germany, and South Africa). A 30 percent blend ("Pura"), for example, has been on sale in Thailand for some years.

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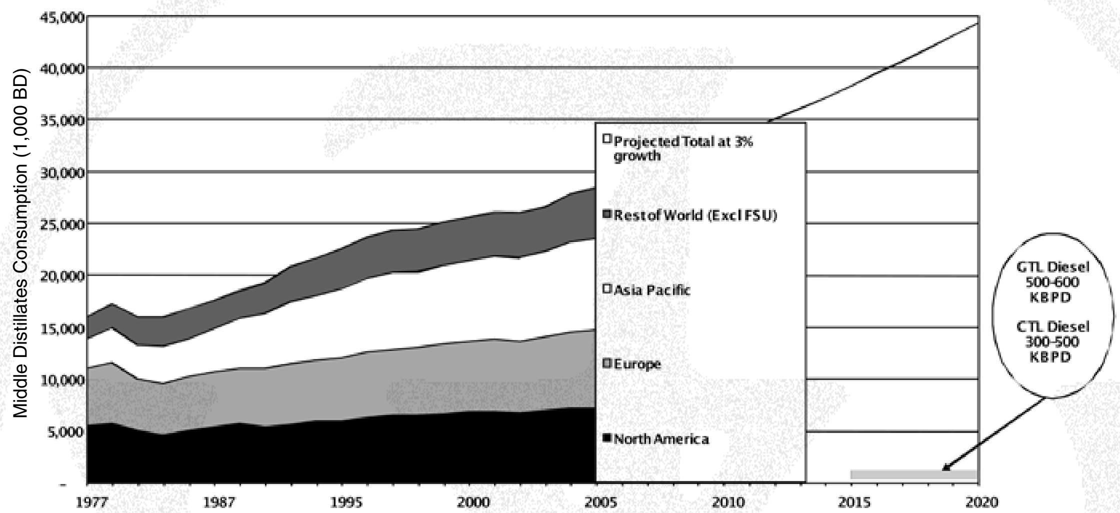
FT-based diesel differs from traditional refinery diesel in a number of ways. Produced from

Exhibit 3. FT Diesel vs. Global Middle Distillates Market



a blending of straight-run FT diesel and hydrocracked FT wax/lubes, the diesel is linear and paraffinic in nature. This results, primarily, in very high cetane numbers (70–80 compared to 40–50 for conventional diesel). Similarly, due to the nature of the feedstock (natural gas) and process (significant sulfur removal during the process), the FT diesel is essentially without sulfur, meeting key critical requirements in the United States, Europe, and other industrial jurisdictions. Additionally, FT diesel is low in aromatics (subject to tight specifications), colorless, and shown to result in reduced tailpipe emissions.

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At the same time, FT diesel is somewhat lower in density when compared with conventional diesel, has low lubricity, and shows poor cold start. However, these drawbacks have been resolved in commercial practice using blending and additives.

We believe that FT diesel will continue as a beneficial blendstock to traditional refinery diesel. In this manner, no separate infrastructure or auto modifications would be required and the key benefit of compatibility can be taken advantage of.

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Most analysts show a value premium for FT diesel when compared with ultra-low-sulfur diesel (ULSD)—in the 5–15 percent range. In the United States, the profitability of producing FT diesel is further helped by regulatory activity, including a $0.50-a-gallon incentive in the 2005 Transportation Bill (extended, with certain restrictions, in the 2007 Farm Bill).

JET FUEL

Jet fuel produced from FT exhibits a number of beneficial properties, including the following:

- Good cetane (55–60)
- No sulfur, no aromatics
- Excellent smoke and flash points and other combustion properties

 DOI 10.1002/gas /

- Acceptable freeze point

There is a large jet-fuel market (e.g., the U.S. 2008 jet market equaled 1.35 million barrels a day) with many interested parties, including government entities, airlines, and aircraft manufacturers. As such, jet fuel from FT (including GTL, CTL, and BTL) has been subject to significant activity during the recent past. These include the following:

- USAF Synthetic Fuel Initiative
  - Ground-tested several GE and P&W engines
  - Certified B-52 fleet for 50:50 GTL/JP-8 (August 2007)
  - C-17 transcontinental test flight using 50:50 GTL (October 2007)
  - Plan to certify all aircraft by 2011
  - Objective of 50 percent synfuel use by 2016
- Airbus A380 test flight between the United Kingdom and France using 50:50 Shell GTL jet (February 2008)
- Emissions-testing 100 percent GTL and 50:50 GTL/conventional jet in DC-8 by NASA-led group (February 2009)

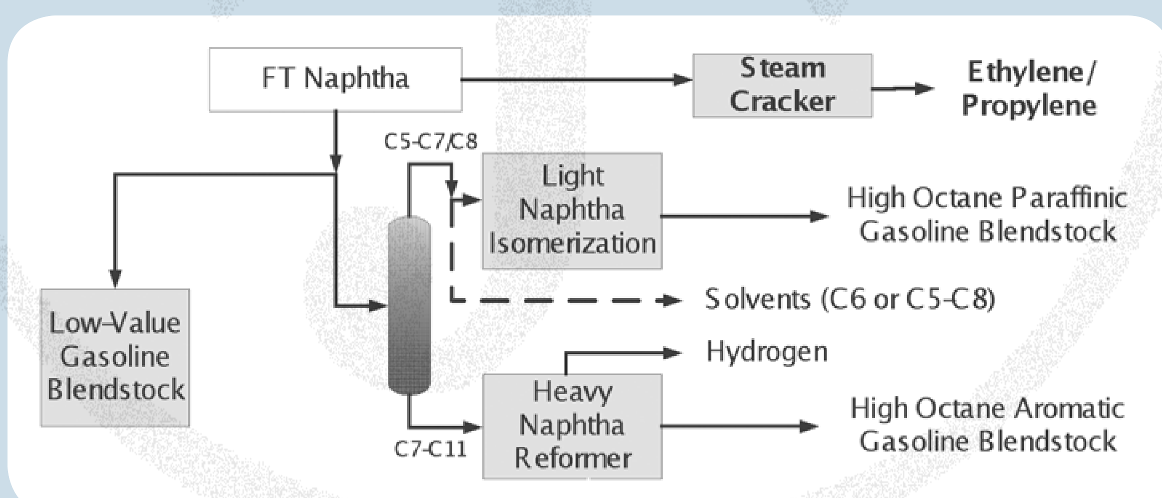
Subsequent to these activities, the 50:50 GTL jet was approved for use in civil aviation in September 2009 (ASTM D7566) with the first commercial flight (London-Doha, Qatar Airways) commenced around the same time.

FT NAPHTHA

A fairly large and robust worldwide market for refinery naphtha exists. The most common grade is "open spec" from the middle cut of paraffinic naphtha produced in simple or hydroskimming refineries. The largest use of this naphtha is in steam crackers to ethylene (and some propylene). The 2009 global ethylene capacity stood at 127 million tons a year, which (if used naphtha as cracker feed) would be equivalent to 3.7 million barrels a day of naphtha demand. A large portion of this trade occurs between Europe and East Asia (estimated at 1.5–2 million barrels a day), though the demand, tied to the consumer plastics market, fluctuates violently from year to year, resulting in significant shifts in pricing as well as outlets. As an example, due to such market variations, the price of naphtha to steam crackers ranged from near that of crude (2007) to a $100-a-metric-ton premium (summer of 2009).

Exhibit 4 shows the range of options and outlets for naphtha (refinery or FT) that exists in addition to use in steam crackers—including direct or indirect (through further processing) inclusion in the gasoline pool and use in the

Exhibit 4. Range of Options and Outlets for FT Naphtha



manufacture of hydrogen and certain solvents. FT naphtha, due to its structural properties (no aromatics, highly paraffinic), has been found to be an ideal feedstock for steam crackers, resulting in as much as a 10 percent increase in ethylene yield. Conversely, because of the same low aromaticity/high paraffinicity, it is not a particularly good direct gasoline blendstock due to its low blending octane.

FT LUBES

FT lubes are produced from the isomerization of FT waxes and have shown excellent properties, including the following:

- Virtually no sulfur, nitrogen, or aromatics
- Narrow hydrocarbon chain length distribution
- Excellent oxidation stability
- Excellent volatility and pour point
- Very high viscosity index (VI; 140-plus)

Studies suggest attractive economics for the production of FT lubes, with manufacturing costs similar to Group I/II and product quality similar to other 140+ VI basestocks.

Lubes market pricing is also very attractive (see **Exhibit 5**)—in the range of $1,000–$1,400 a metric ton in 2008–09 for FT-type base stocks. Indeed, FT lubricants (and waxes—see later in the article) are worth considerably more than many other FT products (including diesel). Regardless, in all commercial GTL/CTL facilities, a last step of the process includes hydrocracking the high-molecular-weight waxes and lubes to lower-molecular-weight (and lower-value) diesel, naphtha, and jet fuel.

In the main, this strategy is due to the relatively small market for lubes and waxes, when compared with the market for key transportation fuels. For example, the total worldwide lubes basestock market in the year 2008 stood at approximately 960,000 barrels a day with only 25 percent of this consisting of the higher-quality grades (Groups II/II+/III/IV) that are comparable to FT lubes. As such, GTL plants without hydrocracking could flood the lubes market, causing significant price deterioration. For example, one world-scale GTL could produce as much as 15,000–30,000 barrels a day of lube base stocks (equivalent to 6–11 percent of current worldwide demand for high-quality grades). Indeed, as a result of this, historical FT plants such as Sasolburg and Secunda in South Africa make few lubricants, and, in reality, all major GTL facilities will continue to include product cracking to control the manufacture of lubes and waxes.

FT WAXES

FT waxes primarily consist of liner hydrocarbons in the C20–C100 range. This range is in contrast to traditional, refinery-based waxes, which are a mix of iso- and n-paraffins. As such, FT wax has shown particular benefit in high melt applications.

Traditional waxes are considered a by-product of refinery lubes manufacture, with volumes even smaller (13 percent) than the global lubes' production and demand. In fact, total 2005 wax

Exhibit 5. Lube Markets and Price Fluctuation

Base Oil Prices ($/MT)	Europe			United States
	April-08	April-09	October-09	October-09
Grp I	900–1,220	365–805	790–835	710–1,013
Grp II/II+			875–990	802–1,016
Grp III			900–1,120	1,077
Grp III+				1,339
Comments	Europe inc. exports and FSU		Europe/ME/Africa	

For reference: 1,000 $/MT ~ 135 $/Barrel.

DOI 10.1002/gas / © 2010 Wiley Periodicals, Inc.

Exhibit 6. Wax Markets and Price Fluctuation

Wax Prices ($/MT)	Northwest Europe		U.S. Gulf
	April-08	April-09	April-09
Low Melt (52–54C)	1,438–1,484	1,037–1,104	
Mid Melt (56–58C)	1,516–1,609	1,104–1,157	1,098–1268
High Melt (60–62C)	1,547–1,719	1,224–1,277	
Comments			MP~52–60C

capacity of 10,900 million pounds is equivalent to just over 100,000 barrels a day. Of this wax, about half is fully refined, nearly 30 percent is traded in slack and semirefined state, and smaller amounts are as petrolatum and microcrystalline varieties. Also, today about 6 percent of the global wax is produced by FT plants in South Africa (Sasol) and Malaysia (Shell). Wax supply is relatively concentrated, with 75 percent of the production in 10 countries (largest: PRC) and by four companies (CNPC, XOM, Shell, and Sasol).

An opportunity exists for FT waxes to fill some of this high-value (see **Exhibit 6**) niche market.

Today, the traditional wax market is in significant flux, with rationalizations in North America, Europe, and Asia (especially PRC), along with relatively steady growth in demand. As such, an opportunity exists for FT waxes to fill some of this high-value (see **Exhibit 6**) niche market. However, it is critical that the wax market, being rather small, can be easily overwhelmed—a single GTL plant can, potentially, produce as much as 10–12 percent of the global wax demand. Therefore, it is likely that for the foreseeable future, similar to the case with lubes, the majority of FT waxes will be hydrocracked to lower-molecular-weight fuel products.

SPECIALTY PRODUCTS

A number of low-volume, high-value-added specialty products also can be produced in GTL/CTL plants. These can, depending on specifics, meet market demands and help improve facility economics. Examples of such products include the following:

- Linear α-olefins from raw FT diesel
  - Petrochemical building blocks for detergents, polymers, lubricants, and plastics
  - Processing required (including, in some cases, odd-even separation)
- Solvents from FT naphtha fraction
  - C5–C8, no aromatics or sulfur, low odor
  - Hexane, special boiling point solvents
  - Used in oil seed extraction, polymerization, dry cleaning, and rubber manufacture
- Hydrocracked wax fractions (high linear paraffin content, biodegradable, no sulfur)
  - C10–C13 for laundry detergent applications
  - C14–C17 used in making chloro-paraffins
- Drilling fluids from diesel fraction
  - Linear chains, biodegradable
  - C17–C22 fraction
  - Replacement for traditional “mud” in some applications

IN SUMMARY

GTL and sister processes can serve as important outlets for natural gas and other feedstocks while assisting in meeting the demands for growing fuels and specialty products markets. Several such units are in commercial operation, producing high-quality fuels such as jet and diesel as well as other, nonfuel products such as lubricants, waxes, and naphtha for steam crackers.

  / DOI 10.1002/gas