Background

High crude oil prices beginning in the mid-2000s spurred worldwide interest in finding and developing additional sources of transportation fuels. One such consideration is the conversion of carbon-containing solids (coal, petroleum coke, and biomass) and natural gas into high-quality, clean-burning transportation fuel.

The most common methods for production of liquids from carbonaceous solids and natural gas start by first converting the feedstock to a mixture of carbon monoxide and hydrogen called synthesis gas (or syngas). This is accomplished by partial oxidation and/or reforming reactions in gasification and reforming units. Syngas can then be converted into hydrocarbons and oxygenates.

The most common technologies for converting syngas into liquids incorporate Fischer-Tropsch synthesis or Methanol synthesis. The Fischer-Tropsch process was discovered in the 1920s. It has been commercially practiced in several different forms to produce hydrocarbon liquids from coal and natural gas. These liquids can be converted like crude petroleum into refined fuels and petrochemical feedstocks.

Syngas can also be converted to methanol, which is the primary method of methanol production, and has been practiced converting both natural gas and coal into chemical-grade methanol. Methanol is typically produced as a building block to manufacture other chemicals and within limits has been blended with conventional gasoline.

An alternative commercially proven route for converting syngas to liquid fuels is through conversion of methanol to conventional gasoline. MTG gasoline meets the requirements for conventional gasoline, is fully compatible with refinery gasoline and meets the ASTM D4814 Specification for Automotive Spark-Ignition Engine Fuel. Mobil developed a fixed bed methanol-to-gasoline process (MTG) in the 1970s using a proprietary ZSM-5 zeolite catalyst. Mobil commercialized the first gas-to-gasoline plant in New Zealand in 1985. The New Zealand plant produced 14,500 kB/D of gasoline and was operated by the New Zealand Synthetic Fuels Corporation, a joint venture between the government of New Zealand and Mobil, until 1995. Operation of the first coal-to-gasoline plant via MTG technology began in 2009 in China by Jincheng Anthracite Mining Group (JAMG). This 2,500 B/D gasoline plant began operations in June 2009 and successfully demonstrated the coal-to-gasoline concept.
By 1979, a fixed bed design was completed and had been thoroughly demonstrated at 4 bbl/d capacity. In this design, methanol is first dehydrated over an amorphous alumina catalyst to an equilibrium mixture of di-methyl ether (DME), methanol, and water releasing about 1/6th of the methanol dehydration and hydrocarbon synthesis heat of reaction. The DME reactor effluent is mixed with inert recycle gas and introduced into the MTG reactors. In the MTG reactors, methanol and DME are completely dehydrated by a ZSM-5 zeolite catalyst forming light olefins and water. At the MTG reactor conditions, light olefins oligomerize into higher olefins, which combine through various reaction paths into paraffins, naphthenes, and methylated aromatics. The shape-selective MTG catalyst limits the hydrocarbon synthesis reactions to about C11.

In the MTG process, the conversion of methanol to hydrocarbons and water is virtually complete with the product being a mixture of synthesis hydrocarbons and water with a limited amount of C2 - gases. The dehydration and synthesis reactions release about 1.74 MJ of heat per kg of methanol.

Both the Fischer-Tropsch and MTG routes can convert synthesis gas to liquid transportation fuels. However, their respective product slates are very different. The Fischer-Tropsch process typically produces a broad spectrum of straight-chain paraffinic hydrocarbons that can be further refined to produce commercial-quality gasoline, jet fuel, and diesel. In contrast, MTG selectively converts methanol to one liquid product: ultra-low-sulfur, low-benzene regular octane gasoline.

**Figure 1:** Carbon conversion paths to liquid fuel through Syngas

![Figure 1: Carbon conversion paths to liquid fuel through Syngas](image)

**The ExxonMobil MTG Process**

Methanol-to-gasoline chemistry was discovered by Mobil scientists in the 1970s. Over years of extensive studies and pilot plant operations, ExxonMobil developed an understanding of the MTG reactions and process conditions necessary to consistently produce motor gasoline. A range of process schemes were considered, including a variety of fixed and fluid catalyst bed designs.

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**Figure 2:** MTG reaction paths

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This heat release would result in a temperature rise of about 600ºC in an adiabatic reactor system. In the MTG design, the temperature rise from methanol feed to MTG reactant is limited to about 100ºC by controlling the volume of recycle gas. The conversion reactor inlet temperature is controlled by adjusting the temperature of the recycle gas by heat exchange with the reactor effluent. Reactor effluent is also used to preheat, vaporize, and superheat the methanol feed to the DME reactor.

Reactor effluent is then further cooled to 25–35ºC and passed to a product separator, where light gases are disengaged and liquid hydrocarbon and water are separated. The gas phase (mostly light hydrocarbons) is returned to the recycle gas compressor. The water phase can be sent to effluent treatment or recycled within the overall complex. The liquid hydrocarbon product (raw gasoline) contains mainly gasoline boiling range material as well as dissolved hydrogen, carbon dioxide, and light hydrocarbons.

After separation of raw gasoline from light gases and water, the raw gasoline is processed through a de-ethanizer to remove remaining C₂ - gases, followed by a stabilizer column that removes C₃ ’s and C₄ ’s as LPG fractions to control the vapor pressure of the gasoline.

Figure 3: MTG reactor section process flow.

At this point, the MTG gasoline is consistent with conventional gasoline with the exception of a concentration of 1,2,4,5-tetramethylbenzene, or durene, that is higher than typical gasoline. Durene is a compound that crystallizes at moderate temperatures and affects gasoline performance and appearance. A maximum durene content of 2% has been set to ensure drivability and performance consistent with petroleum-based fuel. To achieve this level of durene content, MTG gasoline is split into a light fraction and heavy fraction, which concentrates the durene with the other higher aromatics. This heavy fraction is processed in a mild hydrotreater that reduces the durene content primarily through isomerization and de-methylation reactions with minimal effect on gasoline yield and octane.

New Zealand synfuels commercial MTG plant

Figure 4: New-Zealand Synfuels commercial MTG plant
In the late 1970s the government of New Zealand was evaluating ways to utilize available natural gas resources to address its growing demand for liquid transportation fuels in an environment of limited oil supplies. After examining its alternatives, New Zealand determined that the gas-to-methanol-to-gasoline route utilizing ExxonMobil’s MTG technology was the most attractive alternative and began developing a full-scale commercial project. The New Zealand Synfuels company was established as a joint venture between the government of New Zealand and Mobil Oil Corporation (one of the predecessors of the Exxon Mobil Corporation). This new company was charged with constructing and operating the first commercial gas-to-liquid fuel plant in the world utilizing established gas-to-methanol technology and the Mobil fixed bed MTG technology. On October 12, 1985, New Zealand Synfuel started up the 14,500 B/D gas-to-gasoline plant near New Plymouth, New Zealand. By all accounts, the start-up of the operation was a complete success for a world-scale, first-of-its-kind plant and achieved design rate within two days. The first gasoline was produced on October 17, 1985. The second methanol unit was commissioned on December 12th of that year. Subsequently, additional MTG reactors were streamed and the complex was operated at 100% of design capacity by December 27, 1985. The MTG plant was an excellent example of the ability to successfully scale up a plant from a small pilot plant (4 bbl/d). Production yields (Table 1), product qualities, and catalyst performance were consistent with all estimates developed from the pilot plant data. A comparison of the average gasoline properties and the range during the first year of MTG operation is provided (Table 2). It is clear that the operation is very predictable and stable with little variation in the product. It is also interesting to compare the MTG gasoline properties with today’s refinery gasoline.

Table 3 compares the MTG gasoline properties with the average properties of conventional gasoline sold in the U.S. markets in 2005. The two are virtually identical with the only noticeable difference being MTG gasoline’s lower benzene content and essentially zero sulphur.

**Second-generation MTG technology**

The current MTG technology is based on the original MTG process developed for the New Zealand plant, with improvements made by Mobil in the late 1990s leading to a second-generation technology. The second-generation technology incorporates improvements derived from the operation of the New Zealand plant. These reduce the heat-input requirements and reduce compressor duty and heat exchange surface area. These modifications reduce capital by an estimated 10% to 15% versus the original design.

In addition to the design modifications, ExxonMobil has continued to develop zeolite catalyst technology for the MTG process, and MTG catalyst research continues at ExxonMobil’s Clinton Technical Center in New Jersey, with a dedicated MTG pilot plant facility.

The first second-generation MTG plant began operating in June 2009 in Shanxi Province, China, by the Jincheng Anthracite Mining Group (JAMG). The 2,500 B/D MTG unit is part of a demonstration complex that includes coal gasification, gas cleanup, and a methanol synthesis. After two years of operation, JAMG and ExxonMobil agreed to a License and Engineering agreement for two additional MTG units at 12,500 B/D each and initiated engineering in October 2011. In addition to the coal-to-liquids plants in China, ExxonMobil has entered into license agreements for MTG technology for coal, biomass, and natural gas projects.
Advantages of the ExxonMobil methanol-to-gasoline option

Project development for various carbon-conversion concepts is a highly complex process that requires companies to consider many diverse factors when making the technology decision. ExxonMobil MTG, as a commercially proven technology, offers an option that improves the attractiveness for many projects.

Product simplicity

Both the MTG and Fischer-Tropsch processes convert coal into synthesis gas as an intermediary before producing the final products. However, their respective product slates are very different. The Fischer-Tropsch process produces a range of hydrocarbon, which requires refining and conversion to produce finished transportation fuels and/or chemicals. A minimum of two liquid products are produced. Due to the complexity of the product distribution, the economic justification for upgrading/processing multiple fuels or chemical feedstocks or petroleum specialties improves for large-scale projects located near developed markets.

Table 4 is a comparison of MTG product yields versus reported product distribution from both the low-temperature and high-temperature Fischer-Tropsch process reported by Sasol. In both cases, the liquid products require hydrocracking/hydrotreating and other reforming processes before the liquid products can be used as transportation fuels.

Low technical and project risk

All of the processes required to produce methanol from coal, coke, or natural gas are well proven and have been installed worldwide and continually improved by some of the world’s leading process technology providers, and engineered and constructed by many competent and competitive EPC contractors. Combining the thoroughly demonstrated ExxonMobil MTG technology with a proven methanol-production scheme provides a route to synthetic fuel from a variety of feed sources with minimal technical and project execution risk.

Process simplicity and scalability

The MTG process uses a conventional gas phase fixed bed reactor that is simple to operate and can be readily scaled to the desired size from 2,500 B/D to more than 20,000 B/D. In the first commercial application in New Zealand, the process was successfully scaled up from 4 BBL/D to 14,500 BBL/D.

MTG, in contrast, selectively converts methanol to a single fungible liquid fuel and a small LPG stream. The liquid product is conventional gasoline with virtually no sulphur and low benzene, which can be sold as is or blended with ethanol or methanol or with petroleum refinery stocks. This minimizes offsites and logistics complexity and investment for synthetic fuel distribution. Table 5 provides the typical properties and key composition characteristics of typical ExxonMobil MTG gasoline.
Summary
Interests in alternative clean transportation fuel technology will continue as an alternative to petroleum refining. ExxonMobil's commercially proven Methanol-to-gasoline (MTG) technology coupled with established commercial methanol synthesis technologies provides a competitive, low-risk option for the production of synthetic transportation fuels from coal, biomass, or natural gas.