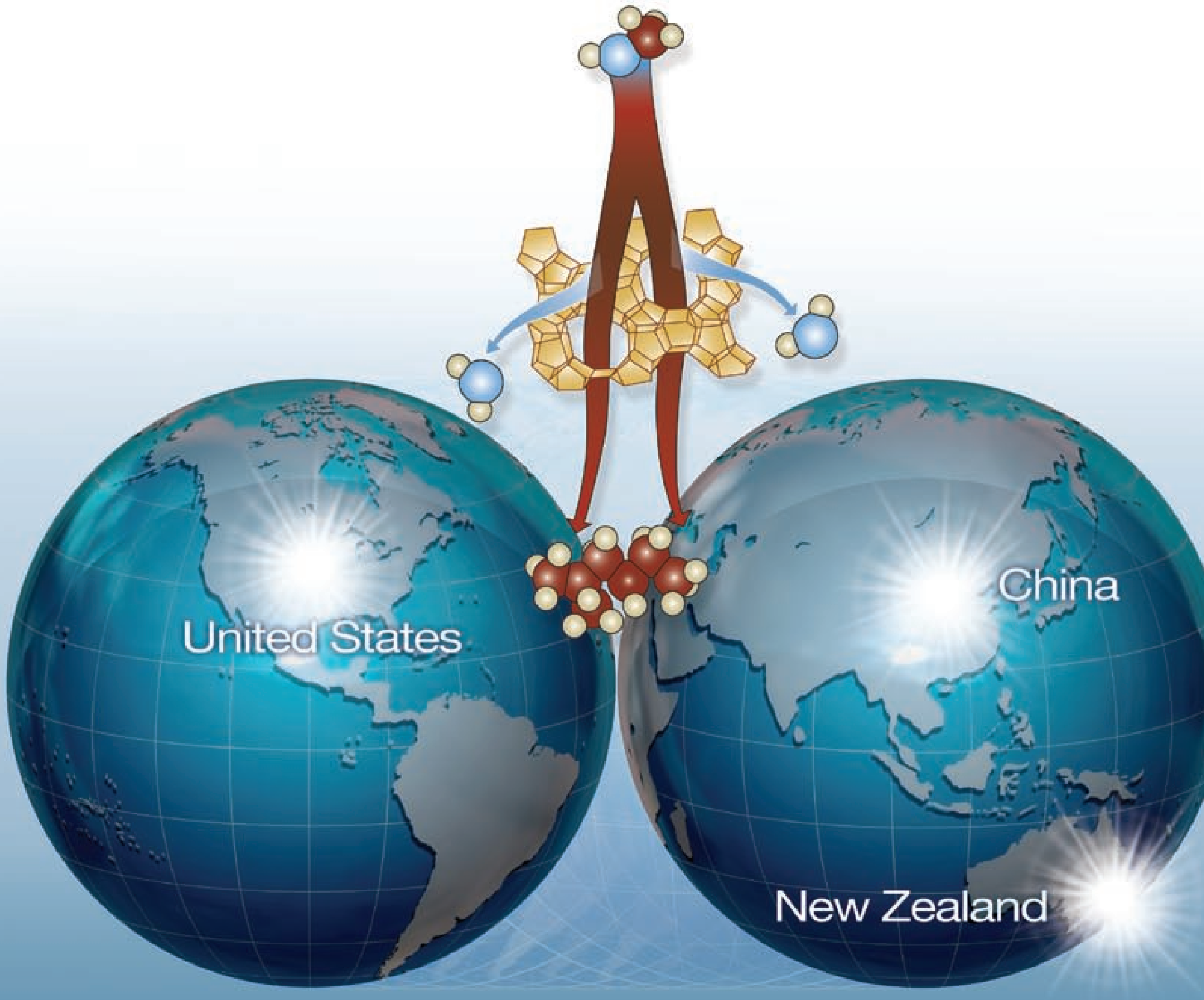
ExxonMobil
Research and Engineering

Methanol to Gasoline (MTG)
Production of Clean Gasoline from Coal



So Advanced, Yet So Simple.

Company Profile

ExxonMobil is the world's largest publicly traded integrated petroleum and natural gas company. Our company and its affiliates are present on a global scale.
We operate facilities and market products around the world, and explore for oil and natural gas on six continents. We lead the industry in almost every aspect of the energy and petrochemical business.

To help meet the world's growing energy needs, ExxonMobil is involved in the exploration and production of crude oil, natural gas; the manufacture of petroleum products; and the transportation and sale of crude oil, natural gas, and petroleum products. We are a major manufacturer and marketer of commodity and specialty petrochemicals and have interests in electric power generation facilities. Our extensive research programs support operations, enable continuous improvement in each of these businesses, and explore emerging energy sources and technologies.

Downstream

ExxonMobil's network of reliable and efficient manufacturing plants, trasnportation systems, and distribution centers provides clean fuels, lubricants, and other high-value products and feedstocks to customers around the world. ExxonMobil has interests in 38 refineries located in 21 countries and markets its products through more than 32,000 retail service stations. Our products and services are also provided to nearly 1 million customers worldwide through our three business-to-business segments: Industrial and Wholesale, Aviation, and Marine. In 2007, refinery throughput averaged 5.6 million barrels per day, and petroleum product sales were 7.1 million barrels per day. ExxonMobil is the world's No. 1 supplier of lube basestocks and a leader in marketing finished lubricants, asphalt, and specialty products. Worldwide, we market products under Exxon, Mobil and Esso brands.

Technology

Many natural resources are found in remote areas with difficult operating environments. The complexity of these environments places greater emphasis on technological innovation. Over the past five years, ExxonMobil has invested about $3.5 billion in research. As new technologies are developed, our global functional organization enables rapid deployment and value capture. We have remained an industry leader in technology by focusing on both breakthrough concepts and process modifications that enhance performance across our business lines.

High energy prices and volatility in 2008 have helped to spur worldwide interest in finding and developing additional sources of energy to meet increasing demand. Coal is expected to play a key role as an energy source in the rapidly growing economy in countries such as China, India and even the United States, in the coming decades, despite its higher CO_2 intensity.
To meet the need to increase supply while protecting the environment, continued technology advances will be needed. One such consideration is the conversion of coal into high quality, clean-burning transportation fuel.

There are two commercially demonstrated routes for converting coal to transportation fuels through gasification (Figure 1).
The first is the widely known Fischer-Tropsch process, discovered in the 1920's. It has been commercially practiced in several different forms to produce fuels from either coal or natural gas.

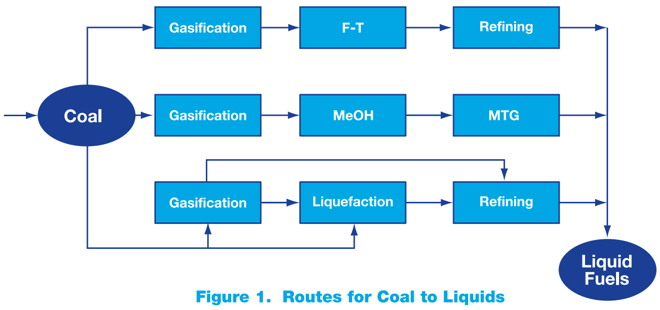
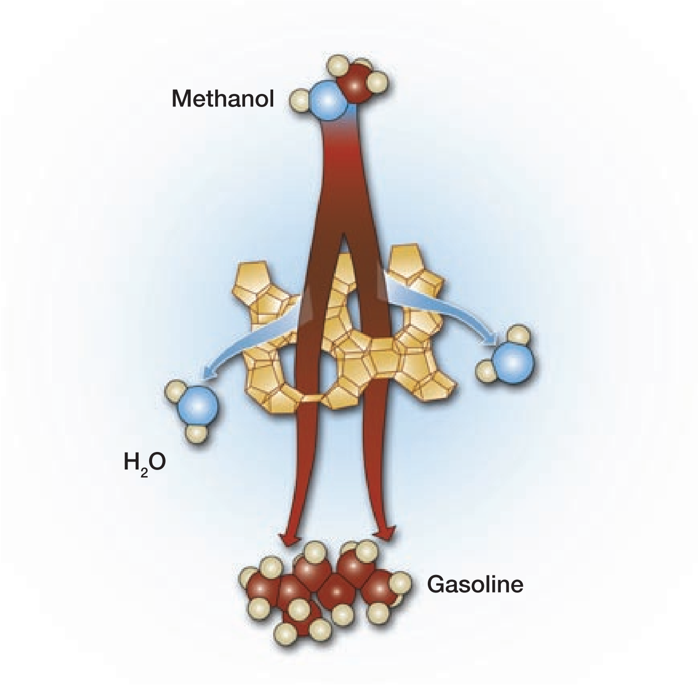


Figure 1. Routes for Coal to Liquids

Less known, is another commercially proven alternative for converting coal to gasoline through methanol.
ExxonMobil Research and Engineering Company's (EMRE) Methanol-to-Gasoline (MTG) process converts coal to high quality clean gasoline when coupled with commercially proven coal gasification and methanol synthesis technology. Exxon Mobil developed the methanol-to-gasoline process (MTG) in the 1970's and commercialized the technology in New Zealand in the mid-1980's. MTG gasoline is fully compatible with conventional refinery gasoline. MTG gasoline can be either blended with conventional refinery gasoline or sold separately with minimal further processing.

A third option for coal conversion, direct coal liquefaction, is also attracting renewed attention due to the 2008 start up of a commercial plant by Shenhua, a Chinese coal company, in Inner Mongolia. Although similar processes were demonstrated in the US at much smaller demonstration scales, no commercial plants were ever built or operated for direct coal liquefaction. Though the direct liquefaction route does not require synthesis gas feed, it does require the addition of hydrogen which would typically be produced from a separate coal gasification step. Also, the hydrocarbon fractions produced would require significant upgrading to commercial quality fuels products such as gasoline and diesel.



Both the Fisher-Tropsch and MTG processes convert coal into synthesis gas before converting it to the final liquid products. However, their respective product slates are very different. The Fisher-Tropsch process produces a broad spectrum of straight-chain paraffinic hydrocarbons that requires upgrading to produce commercial quality gasoline, jet fuel and diesel. In contrast, MTG selectively converts methanol to one liquid product: a very low sulfur, low benzene regular octane gasoline.

Due to the unique low sulfur and low benzene characteristics of the MTG gasoline product, it can be a valuable blending component for meeting environmental regulations specific to sulfur and benzene.

A recent surge in Coal to Liquid (CTL) activities has renewed market interest in MTG technology. The current MTG technology represents an advance beyond the technology commercialized in New Zealand in the mid-1980's The improvements result from programs undertaken by EMRE in the 1990's that reduce both capital investment and operating expenses. Construction of the first coal-to-gasoline process via MTG technology is underway in China by Jincheng Anthracite Mining Group (JAMG).

Both coal gasification and methanol synthesis are mature technologies with several commercially established routes for both steps. This brochure will provide an update of developments regarding the MTG process and the recent commercial activities for the production of gasoline from coal.

MTG chemistry

Methanol to Gasoline chemistry was discovered by ExxonMobil scientists in the 1970's. However, it took many years of extensive studies to fully understand the detailed chemistry behind the reaction. Methanol is first dehydrated to dimethylether (DME). Then an equilibrium mixture of methanol, DME and water is converted to light olefins (C2-C4). A final reaction step leads to the synthesis of higher olefins, n/iso-paraffins, aromatics and naphthenes. The shape selective MTG catalyst limits the hydrocarbon synthesis to C_{10} and lighter.

Methanol to Gasoline process

In the MTG process, the conversion of methanol to hydrocarbons and water is virtually complete and essentially stoichiometric. The reaction is exothermic with a heat of reaction of about 1.74 MJ/kg of methanol. In the fixed bed process commercialized in New Zealand plant, the reaction is managed by splitting the conversion into two parts. A schematic of the process is shown in Figure 2. In the first part, methanol is converted to an equilibrium mixture of methanol, dimethylether, and water. This step releases 15-20% of the overall heat of reaction and is controlled by chemical equilibrium. As such, it is inherently stable.

In the second step, the equilibrium mixture is mixed with recycle gas and passed over specially designed ZSM-5 catalyst to produce hydrocarbons and water. Most of the hydrocarbon products are in the gasoline range. Most of the gas is recycled to the ZSM-5 reactor. The water phase contains 0.1-0.2 wt% oxygenates which can be treated by conventional biological means.

The conversion reactor inlet temperatures are controlled individually by adjusting the flow of reactor effluent to the recycle gas / reactor effluent heat exchangers and by adjusting the temperature difference across exchangers. Reactor effluent is also used to preheat, vaporize and superheat the methanol feed to the DME reactor.

Methanol to Gasoline Plant in New Zealand

Reactor effluent is then further cooled to 25-35°C and passed to the product separator where gas, liquid hydrocarbon and water separate. 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 CTL complex. The liquid hydrocarbon product (raw gasoline) contains mainly gasoline boiling range material as well as dissolved hydrogen, carbon dioxide and light hydrocarbons (C1–C4). Essentially all of the non-hydrocarbons, C1, C2, C3 and part of the C4 hydrocarbons are removed by distillation to produce gasoline that meets the required volatility specifications. Methane, ethane and some propane are removed in a de-ethanizer. The liquid product from the de-ethanizer is then sent to a stabilizer where propane and part of the butane components are removed overhead (to fuel gas). Stabilized gasoline is then passed to a gasoline splitter where it is separated into light and heavy gasoline fractions.

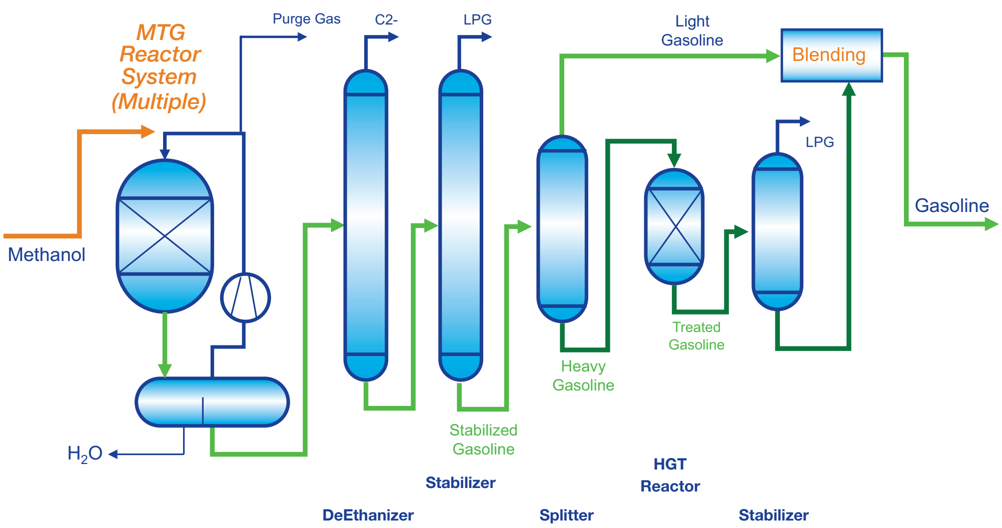


Figure 2. EMRE MTG Process Flow Diagram

MTG gasoline contains 1, 2, 4, 5-tetramethyl benzene (durene) at a higher level than conventional gasoline. A maximum durene limit for MTG gasoline is established to ensure drivability/performance. Durene is concentrated in the heavy gasoline fraction of a gasoline splitter and then subjected to a mild hydrofinishing process over a proprietary ExxonMobil catalyst in the heavy gasoline treater. The product is obtained in nearly quantitative yield with virtually unaltered octane but with greatly reduced durene content.

commercial success of the New Zealand MTG operation

By all accounts, the start-up of the New Zealand operation was a complete success for a world scale, first of its kind plant. The first methanol unit was brought on stream on October 12, 1985 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. 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 (500 kg/d to 1700 t/d). Production yields (Figure 3), product qualities and catalyst performance were consistent with all estimates developed from the pilot plant data.

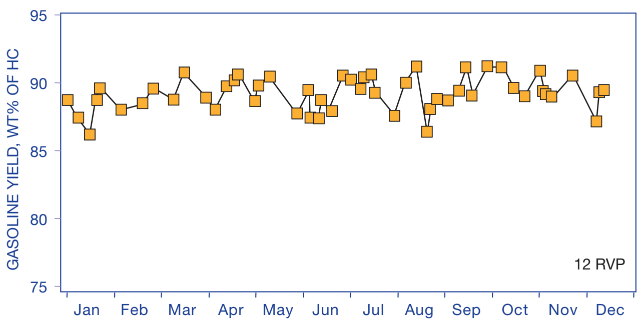


Figure 3 Commercial MTG Gasoline Yield in New Zealand Plant

A comparison of the average gasoline properties and the range during the first year of MTG operation is provided (Table 1.) 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 2 compares the MTG gasoline properties with the average properties of conventional gasoline sold in the US markets in 2005. The two are virtually identical with the only noticeable difference being MTG gasoline's lower benzene content and essentially zero sulfur.

second generation MTG technology

The current technology is based on the original MTG process developed by ExxonMobil in the 1980's, with improvements made by ExxonMobil in the late 1990's leading to a second generation technology.

The second generation technology incorporates significant improvements that are derived from the operation of the New Zealand plant. These significantly reduce the number of heaters, size of heat exchanges, and compressor requirements through better heat integration and process optimization. The combination of the improvements translates into a prospective capital reduction of 15-20% versus the original design.

Table 1.
MTG Product Properties

	Average	Range
Octane Number, RON	92.2	92.0-92.5
Octane Number, MON	82.6	82.2-83.0
Reid Vapor Pressure, kPa	85	82-90
Density, kg/m3	730	728-733
Induction Period, min.	325	260-370
Durene Content, wt%	2	1.74-2.29
Distillation		
% Evaporation at 70° C	31.5	29.5-34.5
% Evaporation at 100° C	53.2	51.5-55.5
% Evaoporation at 180° C	94.9	94-96.5
End Point, °C	204.5	196-209

Table 2.
MTG Gasoline vs. US Conventional Refinery Gasoline

	Summer 2005	Winter 2005	MTG Gasoline
Oxygen (Wl%)	0.95	1.08	
API Gravity	58.4	61.9	61.8
Aromatics (% Vol)	27.7	24.7	26.5
Olefins (% Vol)	12	11.6	12.6
RVP (psi)	8.3	12.12	9
T50 (F)	211.1	199.9	201
T90 (F)	330.7	324.1	320
Sulfur (ppm)	106	97	0
Benzene (% Vol)	1.21	1.15	0.3

*Oxygen is from oxygenate blending post refining.

Although it is well documented that the original MTG chemistry was developed based on ZSM-5 zeolite, it is worth mentioning that the MTG chemistry is also very specific to certain aspects of ZSM-5 properties. In fact, over one hundred different zeolites were tested during the original MTG technology development. Since the commercialization of the MTG process over twenty years ago, EMRE has continued R&D efforts and made significant improvements in zeolite applications and manufacturing capabilities. Many of the new learnings are readily applicable to the MTG process and will significantly improve MTG catalyst performance.

The first second generation MTG plant is now under construction in China by Jincheng Anthracite Mining Group (JAMG). The MTG plant is part of a demonstration scale complex which also includes a coal gasification plant and a methanol plant. The initial phase of the plant is designed for a gasoline capacity of 100,000 t/a, but it is expected to expand to 1,000,000 t/a for the second stage of the project. Start up of the first phase is expected early 2009.

EMRE and DKRW Advanced Fuels LLC (DKRW) announced in December 2007 the first U.S. CTL license based on MTG technology. DKRW, through its subsidiary Medicine Bow Fuel and Power LLC, plans to use EMRE's MTG technology for its 15,000 BPD CTL plant in Medicine Bow, Wyoming. In September, 2008, Synthesis Energy Systems, Inc. (SES), a global gasification company, and EMRE announced an agreement that provides SES the option to execute up to 15 MTG units at its coal gasification plants globally.

advantages of the methanol-to-gasoline option

Project development for CTL is a highly complex process that requires companies to consider many diverse factors when making the technology decision. MTG, as a commercially proven technology, offers a unique option which improves the attractiveness for many CTL projects.

product simplicity

As previously discussed, both the MTG and Fisher-Tropsch processes convert coal into synthesis gas as an intermediary before producing the final products. However, their respective product slates are very different.

The Fisher-Tropsch process produces a broad spectrum of straight-chain paraffinic hydrocarbon which requires upgrading to produce finished products such as gasoline, jet fuel, diesel fuel, and lube base stocks. Due to the complexity of the product distribution, the economic justification for further upgrading/processing of all the products improves for large scale projects (e.g. 50-80K BPD.)

MTG, in contrast, selectively converts methanol to high quality gasoline with virtually no sulfur and low benzene which can be sold as is or blended in the refinery gasoline pool. About 90% of the hydrocarbon in methanol is converted to gasoline as the single liquid product, with the remainder primarily LPG.
Table 3 is a comparison of MTG products vs. reported product distribution from both the low temperature and high temperature Fischer-Tropsch process reported by Sasol and coal liquefaction yields from H-Coal process reported by HRI. In both cases, the liquid products require hydrocracking/hydrotreating and other reforming processes before the liquid products can be used as transportation fuels.

Table 3. MTG Gasoline vs. Fischer-Tropsch Products

	Low Temp FT* *Co Catalyst @ 428F*	High Temp FT* *Fe Catalyst @ 644F*	H Coal TM** *Direct Liquefication*	MTG***
Methane	5	8	*No C1-C4 yields reported.*	0.7
Ethylene	0	4		-
Ethane	1	3		0.4
Propylene	2	11		0.2
Propane	1	2		4.3
Butylenes	2	9		1.1
Butane	1	1		10.9
C5 - 160C	19	36	36.5	82.3
Distillates	22	16	43.2	-
Heavy Oil/Wax	46	5	20	-
Water Sol. Oxygenates	1	5	0.3	0.1
Total	100	100	100	100

* Steyberg & Dry. "Fischer Tropsch Technology", Elsevier, 2004 (All FT yields are prior to refining for gasoline octane, and diesel pour point improvement)
** H-Coal data from HRI 1982 publication
*** Final plant product with gasoline Octane 92 R+O

technical risk

The MTG process converts methanol to high quality gasoline. When coupled with commercially proven coal gasification and methanol synthesis technology, MTG offers a commercially proven route for the production of clean gasoline from coal.

process simplicity

The MTG process uses a conventional gas phase fixed bed reactor which can be scaled up very readily. In the first commercial application in New Zealand, the process was successfully scaled up from 500 kg/d to 1,700,000 kg/d. On the other hand, most of the technology advancement for the new Fisher-Tropsch technology options relies on slurry phase reactors which are inherently more complex. Scale-up of slurry phase reactor requires significantly more sophisticated demonstration and modeling in the absence of direct commercial operational experience.

summary

Interests in coal to clean transportation fuel technology will continue as an alternative to petroleum refining. EMRE's commercially proven Methanol-to-Gasoline (MTG) technology, coupled with established commercial coal gasification and methanol technologies provides an economically competitive and low risk option for the production of clean gasoline from coal.

So Advanced, Yet So Simple.

Commercially Proven Route for The Production of Clean Gasoline from Coal through Coal Gasification, Methanol Synthesis, and Methanol Conversion

ExxonMobil Research and Engineering Company's Methanol-to-Gasoline (MTG) Technology, the key step for coal to gasoline conversion, was commercially operated in New Zealand for over ten years. Now we offer the second generation MTG technology which provides:

- Ultra clean, high octane gasoline
- A product fully compatible with refinery gasoline
- Simple, reliable fixed bed reactor design
- A more economically competitive offering

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