Advances in the Conversion of Methanol to Gasoline

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ExxonMobil Research & Engineering Company (EMRE)

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Routes for Synthetic Transportation Fuel

- Both are 3 Step Process
- Thermal Efficiencies are Essentially Governed by initial C/H Ratios...
  - Fuels are $\sim C/H_2$
  - Coal is CH to Fuels plus CO$_2$
  - Natural gas is CH$_4$ to Fuels plus H$_2$O
Methanol to Gasoline

Commercial technology with multiple technology suppliers

Natural Gas
Coal
BioMass

SynGas Generation

Steam

Methanol Generation

Methanol to Gasoline

Gasoline
MTG Technology Is Easily Integrated Into Existing Methanol Plant Infrastructure

Facility essentially un-coupled with intermediate storage tank

- Natural Gas
- Coal
- BioMass
- Steam

Flowchart:
- SynGas Generation
- Methanol Generation
- Methanol to Gasoline
MTG Process
Methanol to Gasoline Chemistry

2 CH$_3$OH $\rightleftharpoons$ CH$_3$OCH$_3$ + H$_2$O
Methanol $\rightleftharpoons$ Di-Methyl Ether

CH$_3$OH, CH$_3$OCH$_3$ $\rightarrow$ Light Olefins + H$_2$O
Methanol, Di-Methyl Ether $\rightarrow$ Light Olefins

Light Olefins $\rightarrow$ C$_5^+$ Olefins

C$_5^+$ Olefins $\rightarrow$ Paraffins, Naphthenes, Aromatics $\rightarrow$ Gasoline
EMRE MTG Process: MTG Reactor Section

- Methanol is vaporized by heat from the MTG reaction and fed into a DME reactor.
- DME reactor effluent is mixed with recycle gas & fed to the MTG reactors.
- Recycle gas controls reactor temperatures.
- MTG reactor effluent is cooled by the methanol feed, recycle gas & air or water.
- Condensed effluent is separated into gasoline, water and gas.
- Raw gasoline is pumped to a recovery section.
Raw Gasoline Recovery Section

- Raw MTG gasoline is fed to de-ethanizer and stabilizer columns to remove fuel gas and LPG fractions from the gasoline
- Stabilized gasoline is split into light and heavy gasoline fractions
- Heavy gasoline is mildly hydro-treated to reduce Durene (1,2,4,5 tetra-methyl benzene) content
- Treated heavy gasoline and light gasoline or blended into finished product
## MTG Yields and Properties/Composition

<table>
<thead>
<tr>
<th>MTG GASOLINE YIELDS</th>
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<tbody>
<tr>
<td></td>
<td>Percent of Feed</td>
<td>Percent of Hydrocarbon Product</td>
</tr>
<tr>
<td><strong>Gas</strong></td>
<td>1%</td>
<td>2%</td>
</tr>
<tr>
<td><strong>LPG</strong></td>
<td>5%</td>
<td>11%</td>
</tr>
<tr>
<td><strong>Gasoline</strong></td>
<td>38%</td>
<td>87%</td>
</tr>
<tr>
<td><strong>H₂O</strong></td>
<td>56%</td>
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<table>
<thead>
<tr>
<th>MTG GASOLINE PROPERTIES/COMPOSITION</th>
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<tbody>
<tr>
<td>Octane, RON</td>
<td>92</td>
</tr>
<tr>
<td>Octane, MON</td>
<td>82</td>
</tr>
<tr>
<td>(R+M)/2</td>
<td>87</td>
</tr>
<tr>
<td>Paraffins, vol%</td>
<td>53</td>
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<tr>
<td>Olefins, vol%</td>
<td>12</td>
</tr>
<tr>
<td>Naphthenes, vol%</td>
<td>9</td>
</tr>
<tr>
<td>Aromatics, vol%</td>
<td>26</td>
</tr>
<tr>
<td>Benzene, vol%</td>
<td>0.3</td>
</tr>
<tr>
<td>Sulfur</td>
<td>nil</td>
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MTG
Commercial Experience
The New Zealand Synfuels plant started up in 1985. The plant was operated until 1997.
New Zealand Synfuel Plant Built with Modular Construction

- A Methanol Plant Compressor in Route

- Modular Construction History
  - Maximum Module
    - 33 by 15 Meters
    - 600 tonnes
  - Total Lift
    - 66 Modules
    - 15,000 tonnes
New Zealand MTG Fixed Bed Reactor

Loading the Fixed Bed
MTG Reactor
New Zealand MTG Plant Reliability

- On-stream factor greater than 96% over 7 year period
In 2009, Jincheng Anthracite Mining Group (JAMG) plant in Shanxi Province China became the first 2nd generation MTG Plant; 2,500 Barrels per day of Gasoline.

In 2011, JAMG licensed a 25,000 Barrels per day MTG Complex (JAMG II).
JAMG 2,500 B/D MTG Unit, Shanxi Province
Second JAMG Grassroots MTG Plant (2 x 12.5 kbd) Construction, 1Q2014
MTG Licenses
Current MTG Licenses

- JAMG, Shanxi Province China, 2,500 B/D, CTL, S/U in 2009
- JAMG, Shanxi Province China, 25 KBD (2 x 12.5 KBD), S/U 2016
- G2X Energy: Multi-License Gas to Gasoline Agreement
  - Lake Charles, LA, USA, 12.5 KBD
- Sundrop Fuel, Louisiana, USA, 3.5 KBD GTL/BTL
- DKRW, Wyoming, USA, 15 KBD, Coal to Liquids
- Synthesis Energy Systems, West Virginia, USA, Coal to Liquids
- ZeoGas LLC, Gulf Coast, USA, Gas to Gasoline, 16 KBD
G2X is in advanced stages of development for its first Gasoline Plant

**Key Highlights**

- 200 acre site owned by the Port of Lake Charles
- Located five miles south of Lake Charles, LA, on the deep water Industrial Canal
  - Access to Gulf Intracoastal Waterway
  - Access to Gulf of Mexico
- Close proximity to multiple interstate natural gas pipelines
- Water (for process and cooling) and power connection easily accessible

**Site Location & Plant Rendering**
Big Lake Fuels project in Lake Charles
G2X has assembled the critical components for success

G2X Energy has assembled proven processes, proven expertise, and proven partners, to develop mid-stream infrastructure projects in order to create high-value fuels from abundant supplies of low-cost natural gas located in North America.

**PROVEN**

**TEAM**

▲ With a 30-year record of success in starting, capitalizing and building businesses, G2X Energy’s leadership team is equipped to develop, finance, build, and operate large-scale natural gas to gasoline projects in North America.

**PROCESS**

▲ Proman Group, the world leader in building and operating methanol plants, is an investor in G2X Energy as well as a strategic partner that will contribute important development, construction and operational capabilities.

**TECHNOLOGY**

▲ ExxonMobil Research and Engineering, who has developed a clean and proven methanol to gasoline technology, has granted G2X certain license rights to its technology.
ZeoGas LLC Awarded Methanol-to-Gasoline Technology License by ExxonMobil

Proven ExxonMobil technology to support new ZeoGas gas-to-liquids project on U.S. Gulf Coast

July 21, 2014 09:52 AM Eastern Daylight Time

HOUSTON--(BUSINESS WIRE)--ZeoGas LLC (ZeoGas), a developer of natural gas-to-gasoline projects, has entered into a license agreement to use ExxonMobil Research and Engineering Company’s (ExxonMobil) methanol-to-gasoline technology in the development of a natural gas-to-gasoline plant on the U.S. Gulf Coast.

ZeoGas is developing a portfolio of projects to convert natural gas to gasoline to take advantage of the abundant and relatively low cost of natural gas in North America. Coupled with the 5,000 tons-per-day of planned methanol production, ZeoGas will produce more than **16,000 barrels per day of ASTM-spec, 87 Octane gasoline** with zero sulfur and about 50 percent less benzene than allowable standards.
MTG
Economic Considerations
U.S. Gasoline Market Considerations

- In 2011 gasoline was 60% of the U.S. transportation fuel market.

- Improved fuel economy projected to reduce gasoline demand over time.

- The U.S. EIA projects by 2040 gasoline to be under 50% of the U.S. transportation fuel market but double diesel demand.

- On a BTU basis, Diesel & Gasoline typically trade within about $1/MBTU.
  - Shift to a slight premium for diesel since 2011.

- The primary driver is the large gas to liquid spread since 2009.

Source: U.S. EIA; Refiner Petroleum Product Prices by Sales Type, Sales for Resale: Motor Gasoline, No. 1 Distillate Fuel, HH Natural Gas.
Gas to Methanol

Based on the New Zealand case, Gas-to-Gasoline capital was split roughly 2/3 to methanol & 1/3 to MTG
- Methanol produced from 2 x 2.2 KTD methanol units

- World scale gas based methanol technology has advanced significantly since New Zealand

- Six 5 KT/D Gas to Methanol trains built since 2004
  - 5 KT/D of MeOH yields 16 KBD of MTG Gasoline
  - Nominally 160 MM scf/D of Gas

- Multiple technologies available at world scale for Reforming and Methanol Synthesis
The MTG Advantage
Advantages of Carbon Conversion via EMRE MTG

• **Low Technical Risk** – All technology components are proven at a scale up to 15KBD

• **Low Project Risk**
  ▪ Multiple proven technologies and experienced contractors for methanol front end

• **Project Simplicity**: Single liquid product suitable for transportation fuel

• **Proven Scalability** (2.5 kBD – 14.5 kBD) provides for range of applications
EMRE Licensing, Catalyst and Technical Services

- EMRE Licenses Methanol to Gasoline Technology
- EMRE provides a basic engineering design package for Licensees to perform engineering design and construction
- ExxonMobil Catalyst Technologies provides catalysts for the MTG Process
- EMRE Provides assistance as needed of EPC, Start-up and ongoing operations support
The World’s First Commercial Scale Gas to Liquid Plant