PRODUCTION OF SYNTHETIC GASOLINE AND DIESEL FUEL FROM NON-PETROLEUM RESOURCES

By:

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In late 1985, the New Zealand Gas-to-Gasoline Complex was successfully streamed producing high octane gasoline from natural gas. The heart of this complex is the Mobil fixed-bed Methanol-to-Gasoline (MTG) section which represents one of several newly developed technologies for production of synthetic gasoline and diesel fuels. All of these technologies are based on production of methanol by conventional technology, followed by conversion of the methanol to transportation fuel.

The fixed-bed (MTG) process has been developed and commercialized. The fluid-bed version of the MTG process, which is now also available for commercial license, has a higher thermal efficiency and possesses substantial yield and octane number advantages over the fixed-bed. Successful scale-up was completed in 1984 in a 100 BPD semi-works plant in Wesseling, Federal Republic of Germany. The project was funded jointly by the U.S. and German governments and by the industrial participants: Mobil; Union Rheinsche Braunkohlen Kraftstoff, AG; and Uhde, GmbH.

This fluid-bed MTG project was extended recently to demonstrate a related fluid-bed process for selective conversion of methanol to olefins (MTO). The MTO process can be combined with Mobil's commercially available olefins conversion process (Mobil-Olefins-to-Gasoline-and-Distillate, MOGD) for coproduction of high quality gasoline and distillate via methanol. This MTO process was also successfully demonstrated at the Wesseling semi-works with this project being completed in late 1985.

The key to all these processes (MTG, MTO, and MOGD) is Mobil's unique family of shape selective zeolite catalysts. It

is this shape selectivity which in MTG/MTO inhibits coke-forming reactions and in MOGD allows production of a high quality diesel range (C_{10}-C_{20}) iso-olefinic product, which is then hydrogenated to the corresponding iso-paraffins (Figure 1).

A simplified schematic of the combined MTO/MOGD process is shown in Figure 2. Methanol is fed to the MTO unit where it is converted stoichiometrically to hydrocarbons and water byproduct. The hydrocarbons are separated into MOGD light olefin feed, an ethene rich fuel gas, and an aromatic gasoline stream which is routed to final product blending. MTO light olefins are fed to the MOGD unit along with an MOGD gasoline recycle stream. MOGD product is then separated into raw distillate, gasoline, and small fuel gas and LPG streams. The raw distillate is hydrotreated at mild conditions to take full advantage of its cetane number potential. To improve liquid yield an optional alkylation unit can also be employed to react produced isobutane with light olefins.

The combined process is highly flexible and can be operated to meet seasonal variation in fuels demand (Table 1). The D/G ratio can be adjusted between zero and about 1.5 while maintaining overall single pass gasoline plus diesel yield above 90 wt % of hydrocarbons. Octane number of the finished gasoline exceeds 92 R+O (Research, unleaded). Distillate cetane number is about 50 and is essentially independent of feedstock and D/G mix.

MTO reaction chemistry is nearly identical to that of MTG. In the simplified MTG reaction scheme (Figure 3), methanol is equilibrated to a methanol-dimethyl ether-water mixture, and then dehydrated further to a mixture of C_5^- olefins. The light olefins react reversibly to heavier olefins, which convert further to aromatics and paraffins. In contrast to MTG, MTO process conditions are selected to maximize olefins yield. A small amount of highly aromatic gasoline is also produced. The light olefin fraction is an excellent feedstock for the MOGD unit.

The MTO initial process step preferentially converts methanol to light olefins and a lesser amount of aromatic gasoline having an octane number of greater than 98 R+O. Yield of C_3^+ olefins is 50-75 wt % of hydrocarbon, depending on process conditions.

A fluid-bed reactor configuration (Figure 4) is preferred as it permits steady-state operation at maximum olefin selectivity and complete methanol conversion. The exothermic heat of reaction can be recovered by immersing heat exchange coils

directly in the catalyst bed. Overall thermal efficiency of the MTO reactor section is estimated to be 95-96%.

The second step of this route is the MOGD process. This process reacts light olefins to the final gasoline and diesel product. In this process, gasoline and diesel selectivity is greater than 95% of the light olefin feed, and gasoline/diesel product ratios have been produced ranging 0.12 to >100. Because of the catalyst shape selectivity, most products are methyl branched iso-olefins. In the C_5-C_{10} range, branched iso-olefins have good octane rating. In the C_{10} to C_{20} range, after hydrogenation, isoparaffins have good diesel fuel properties.

Figure 5 shows the schematic flow for a commercial MOGD plant. The preferred process flow generally uses four fixed-bed reactors, three on line and one in regeneration. The three on line are in series with inter-reactor coolers and liquid recycle to control the heat of reaction. The olefinic feed is mixed with a recycle stream and passes through the three reactors. After exiting the last reactor, fractionation is used to generate a gasoline-rich stream for recycle to the reactors. This recycle helps control the heat of reaction.

MOGD distillate and gasoline mode product yields are shown in Table 2 for comparative purposes. The charge stock, propene/butenes ($C_3^=/C_4^=$), represent the main olefinic components of MTO product. As shown $C_3^=/C_4^=$ yielded 79% diesel, 18% gasoline and only 3% light gas. Of the nonolefins in MTO product, all saturated compounds (paraffins and cycloparaffins) will pass through MOGD unreacted and thus can be left in the feed. Of the range of potential olefin feeds, $C_2^=$ to $C_{10}^=$, all give distillate and gasoline. Gasoline mode MOGD yields are also shown. If desired, a single MOGD plant can be designed to shift from gasoline to distillate mode to accommodate shifts in product demand.

Table 3 shows representative MOGD distillate product properties (after hydrotreating) compared with U.S. industry standards. As diesel, the paraffinic MOGD fuel is low density but is an exceptionally good blending stock due to its low pour point and negligible sulfur content. Vehicle testing has also shown straight MOGD diesel to perform similarly to conventional diesel fuel.

Because of its essentially pure iso-paraffinic structure, the MOGD product makes excellent Jet Fuel, meeting or exceeding all commercial and military specifications (Jet A, A-1, U.S. Military JP-4, -5 and -7).

Large Scale Testing

In late 1981, a large scale MOGD test run was made in a Mobil refinery. The test run used commercially produced zeolite catalyst in refinery scale equipment and was carried out successfully for 70 days.

The unit was a commercial wax hydrofinisher modified to duplicate a prototype design using 3 MOGD reactors. Charge stock was a mixture of propane/propene/butanes/butenes (62% olefins) pumped directly from an FCC unit. The test run had four objectives: demonstrate all modes of operation in commercial scale equipment, demonstrate controllability in a large multireactor adiabatic unit, demonstrate catalyst regenerability, and provide sufficient distillate product for fleet testing. All objectives were met, and over the 70-day run, product yields and selectivities were the same as found in our pilot plant; thus, demonstrating MOGD could be scaled up for commercial application.

The MTO process has presently been scaled up successfully in a 100 BPD fluid-bed semi-works in Germany. The 100 BPD plant was started up February, 1985 after completing modifications required to enable extended operation at MTO conditions. Plant operation was terminated in November 1985 after a successful six months on-stream program. Product yields and catalyst performance were similar to those obtained in a 4 BPD pilot plant at Mobil's Paulsboro Laboratory, under the same conditions. With completion of the 100 BPD MTO program, large scale testing is completed for both steps of the MTO/MOGD process route, completing development of a novel and efficient route to synthetic gasoline and diesel.

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Table 1

MTO/MOGD PRODUCT YIELDS

Distillate/Gasoline Ratio	0.8
Product Yield, Wt %	
LPG	4.4
Gasoline	52.9
Diesel	42.7
	100.0
Product Quality	
Gasoline, R+O	94.4
M+O	80.6
(R+M)/2	87.5
Diesel Cetane Number	50.0

Table 2

MOGD PROCESS YIELDS
$C_3^=/C_4^=$ FEED

	Max Distillate Mode	Gasoline Mode
C_1-C_3	1	4
C_4	2	5
C_5-165°C Gasoline	18	-
165°C$^+$ Distillate	79	-
C_5-200°C Gasoline	-	84
200°C$^+$ Distillate	-	7

Table 3

MOGD PRODUCT QUALITY

	MOGD Product	Industry Standards
Diesel Fuel		
Specific Gravity, 15°C	.79	.84-.88
Pour Point, °C	<-50	-7
Cetane Number	50	45
Sulfur, Wt %	<.002	0.5 max
Viscosity, cs @ 40°C	2.5	1.90-4.1
Jet Fuel		
Freeze Point, °C	<-60	-40
Aromatics, Vol %	4	25 max
Smoke Point, mm	28	18 min
JFTOT, °C	343	260

Figure 1

SHAPE SELECTIVE REACTION PATH

MTG/MTO

Methanol → C_{10}^- Paraffins, Olefins, Aromatics

$nCH_3OH \rightarrow (CH_2)_n + nH_2O$

MOGD

Light Olefins ⇌ Gasoline ⇌ Distillate

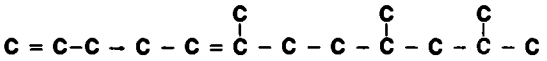

Figure 2

MTO/MOGD PROCESS SCHEMATIC

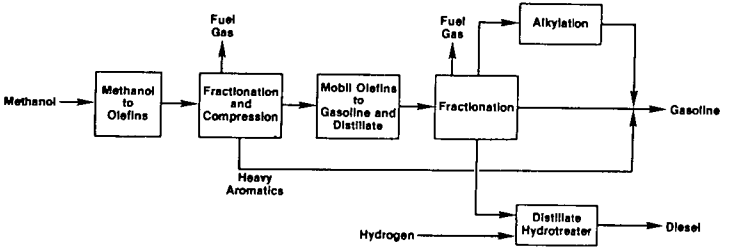

Figure 3

REACTION PATH

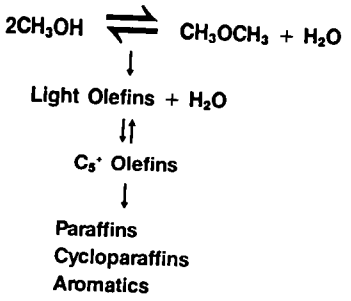

Figure 4

100 B/D FLUID-BED MTO PLANT

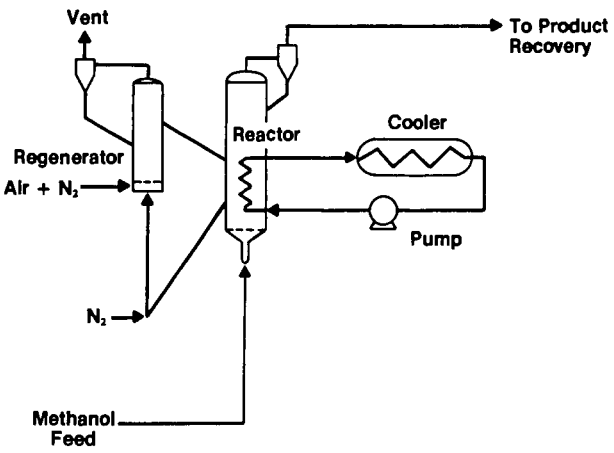

Figure 5

MOGD PROCESS FLOW
Max Distillate Mode