

# THE PRODUCTION OF METHANOL AND GASOLINE

Methanol is made from methane (natural gas) in a series of three reactions:

- Steam reforming:  $\text{CH}_4 + \text{H}_2\text{O} \xrightleftharpoons{\text{Ni}/800^\circ\text{C}} \text{CO} + 3\text{H}_2 \quad \Delta_r H = +206 \text{ kJ mol}^{-1}$
- Water shift reaction  $\text{CO} + \text{H}_2\text{O} \xrightleftharpoons{\text{Ni}/800^\circ\text{C}} \text{CO}_2 + \text{H}_2 \quad \Delta_r H = +206 \text{ kJ mol}^{-1}$
- Synthesis  $2\text{H}_2 + \text{CO} \xrightleftharpoons{\text{Cu-Zn}} \text{CH}_3\text{OH} \quad \Delta_r H = -92 \text{ kJ mol}^{-1}$

Thus overall:  $\text{CO}_2 + \text{CO} + 5\text{H}_2 \xrightarrow{\text{Cu-Zn}} 2\text{CH}_3\text{OH} + \text{H}_2\text{O} + \text{heat}$

The methanol thus formed may be converted to gasoline by the Mobil process. First methanol is dehydrated to give dimethyl ether:



This is then further dehydrated over a zeolite catalyst, ZSM-5, to give a gasoline with 80%  $\text{C}_5^+$  hydrocarbon products.

The Methanex plant and sites in Taranaki are described.

## INTRODUCTION

Methanol or methyl alcohol ( $\text{CH}_3\text{OH}$ ) is a colourless liquid with a boiling point of  $65^\circ\text{C}$ . Methanol will mix with a wide variety of organic liquids as well as with water and accordingly it is often used as a solvent for domestic and industrial applications. It is most familiar in the home as one of the constituents of methylated spirits.

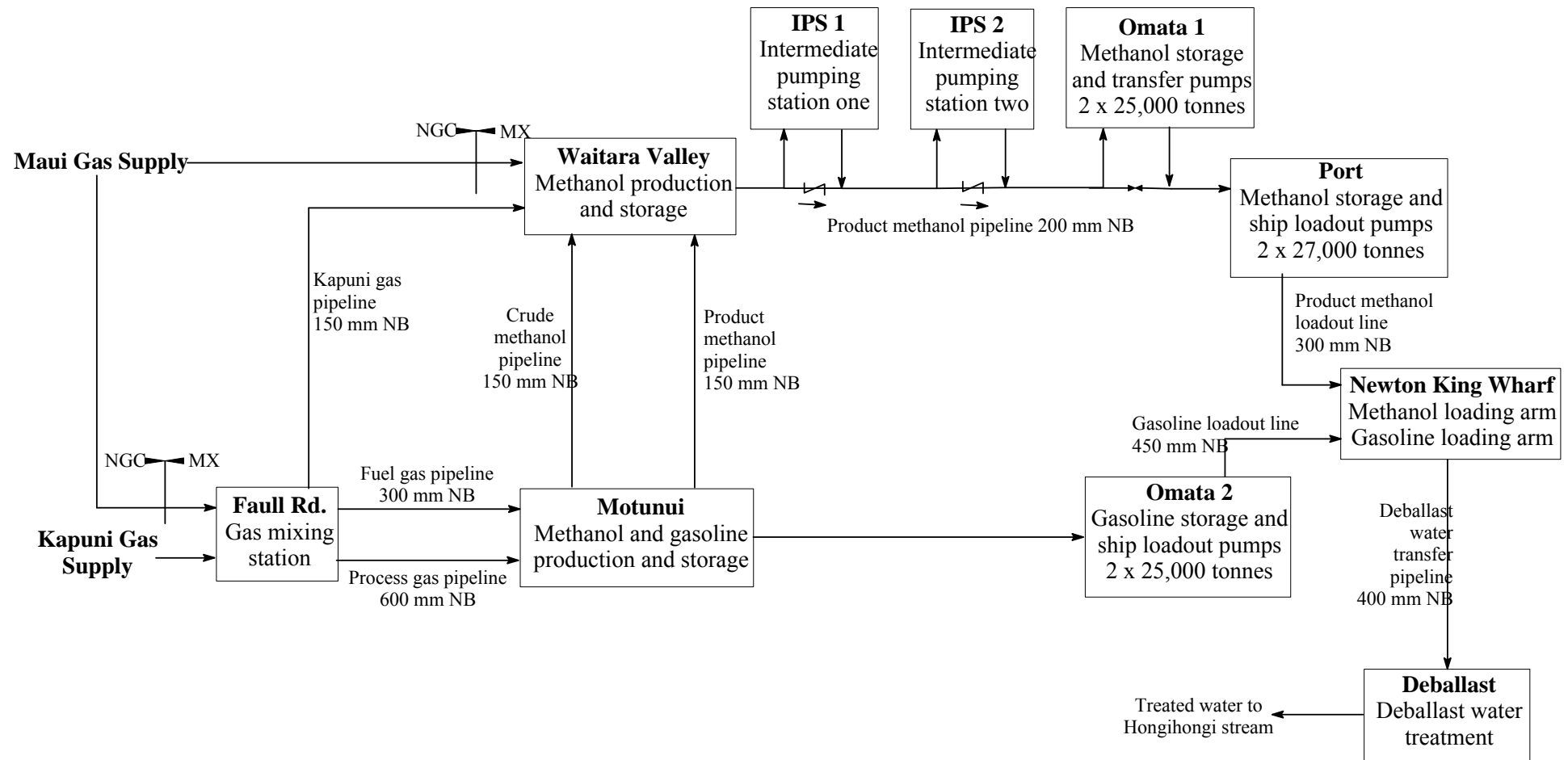
Methanol is the raw material for many chemicals, formaldehyde, dimethyl terephthalate, methylamines and methyl halides, methyl methacrylate, acetic acid, gasoline etc.

Methanol and gasoline are produced from Kapuni and Maui natural gas (methane) by Methanex New Zealand Ltd around Waitara and New Plymouth in North Taranaki. Methane is steam reformed to make syngas (hydrogen and carbon monoxide), and this in turn is used to make methanol some of which can be used in methanol to gasoline (MTG) production. For economic reasons the MTG plant was taken out of production in late 1996, but could be recommissioned if the economic situation warranted it.

In this article the overall layout and production steps at the Methanex plants will be described, followed by sections on the chemistry of methanol and gasoline production.

## THE METHANEX PLANTS

Methanex owns two methanol plants, the stand alone plant at Waitara Valley which came on stream in 1983 and which can produce 1500 tonnes per day of crude methanol and distil 3000 tonnes per



**Figure 1 - Flow schematic of Methanex NZ production and storage facilities**

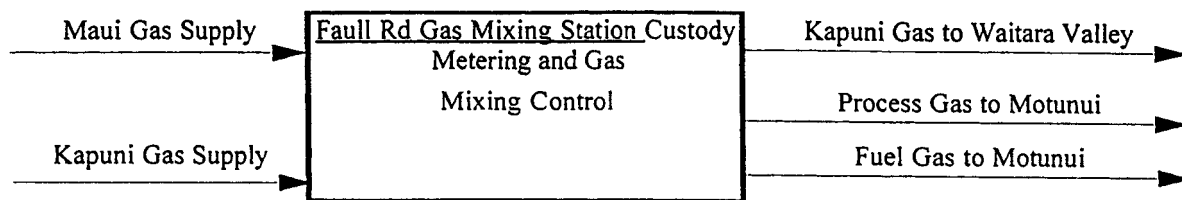
day of crude methanol into product methanol, and the Motunui site plant which also produces gasoline. Here crude methanol is produced in two Davy McKee designed methanol plants, each with a capacity to produce 2600 t/d of crude methanol. Crude methanol generally has a water content of 18% w/w, and contains small quantities of by-products from methanol synthesis. This crude can then be used directly in the MTG process, or piped to the Waitara Valley site and distilled to give product grade methanol.

### Production and storage facilities

The flow relationships of natural gas supply, crude methanol, product methanol, and gasoline are shown in **Figure 1**.

### Faull Road gas mixing station

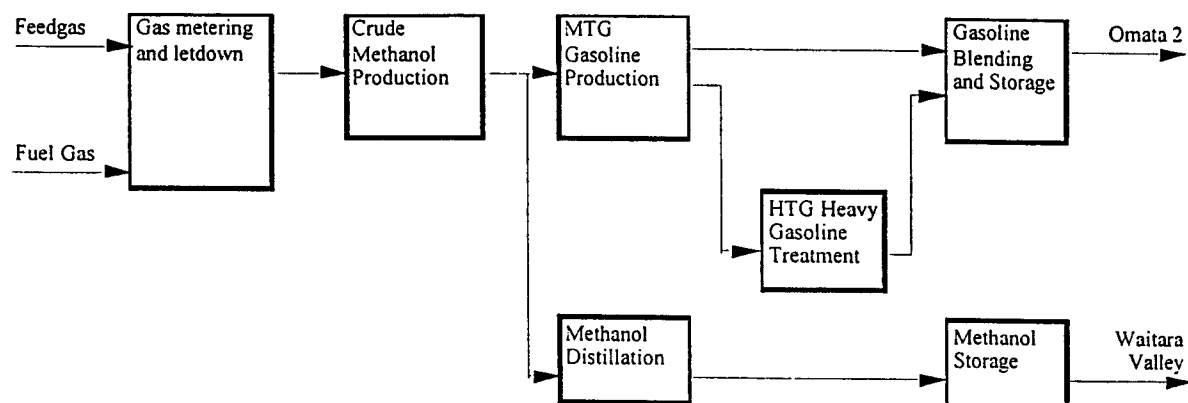
The purpose Faull Rd gas mixing station is to carry out custody metering and control the mixing of Maui gas (low CO<sub>2</sub> content) and Kapuni gas (high CO<sub>2</sub> content) as the process gas supply for the Motunui plant with a CO<sub>2</sub> content of 16%. The plant is operated for Methanex by the Natural Gas Corporation NCG). **Figure 2** outlines the process.



**Figure 2 - Block diagram of Faull Rd gas mixing station**

### Motunui site

Motunui produces 5200 tonnes per day of crude methanol. This can be converted to either gasoline by the MTG process, or product methanol with distillation. Up to 25% of the crude methanol can be exported to Waitara Valley for distillation into product methanol. **Figure 3** outlines the processes.

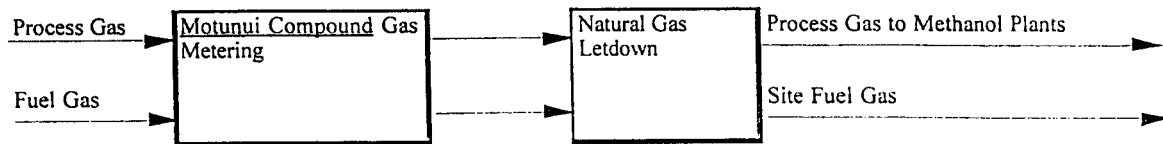


**Figure 3 - Block diagram for the overall process at Motunui.**

### Gas metering and letdown

The process gas and fuel gas from Faull Rd is metered at Motunui for custody transfer and meter checking, and then letdown to the required process pressures to be used in the plant.

**Figure 4** outlines this.

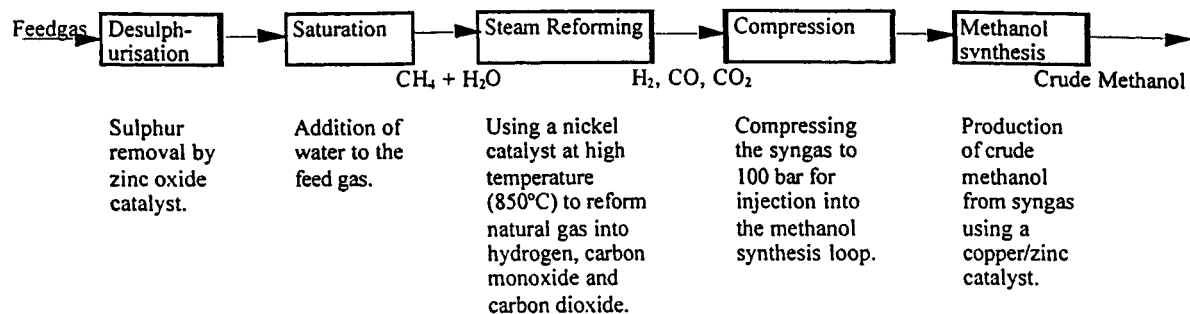


**Figure 4 - Gas metering and letdown**

### Crude methanol production

Crude methanol is produced in two Davy McKee designed methanol plants, each with a capacity to produce 2600 t/d of crude methanol. Crude methanol generally has a water content of 18% w/w, and contains small quantities of by-products from methanol synthesis.

**Figure 5** outlines the manufacturing process at Motunui.



**Figure 5 - The crude methanol manufacturing process at Motunui**

### Methanol to gasoline (MTG) production

Gasoline can be produced from methanol using a process developed by Mobil, which uses ZSM-5 Zeolite catalyst. The plant consists of five identical trains for conversion, and has a maximum design capacity of 2200 tonnes per day of product gasoline. **Figure 6** outlines the process.

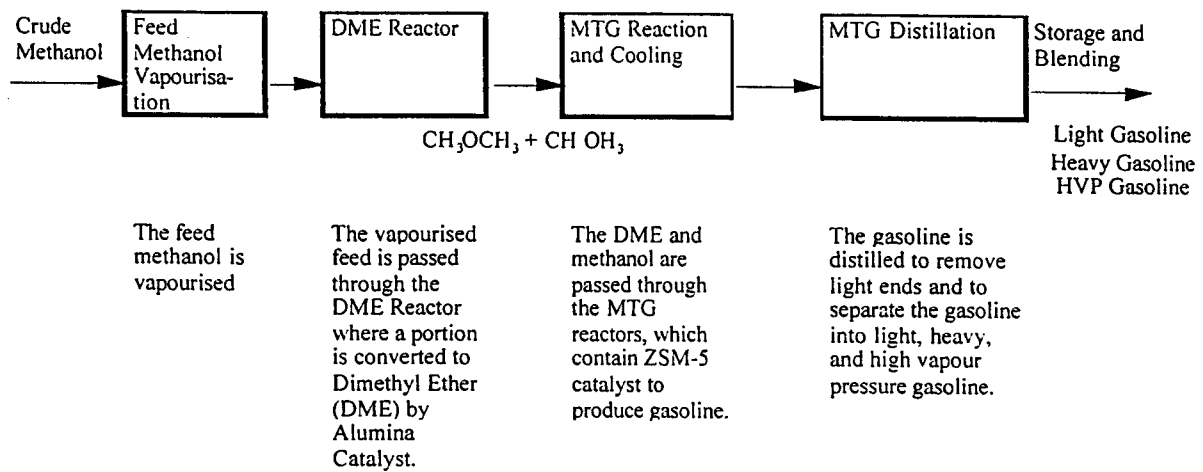
### Heavy Gasoline Treatment (HGT)

The gasoline produced by the MTG process contains Durene, a substance with a high melting point (79°C). The Durene produced by the MTG process is more than that permitted under product gasoline specifications. The Durene content is reduced by treating the heavy gasoline produced in MTG, in the Heavy Gasoline Treatment plants prior to blending into product gasoline. **Figure 7** outline the process.

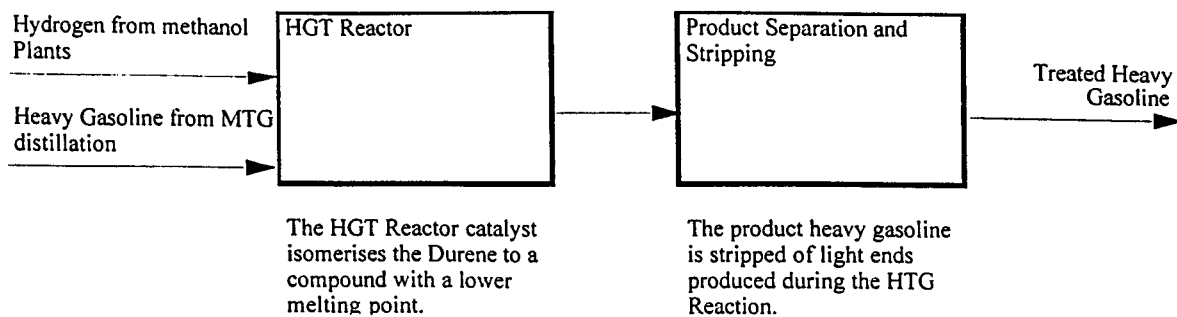
### Gasoline Blending and Storage

The separate gasoline components of light gasoline, heavy gasoline, and high vapour pressure gasoline are all stored in intermediate storage facilities.

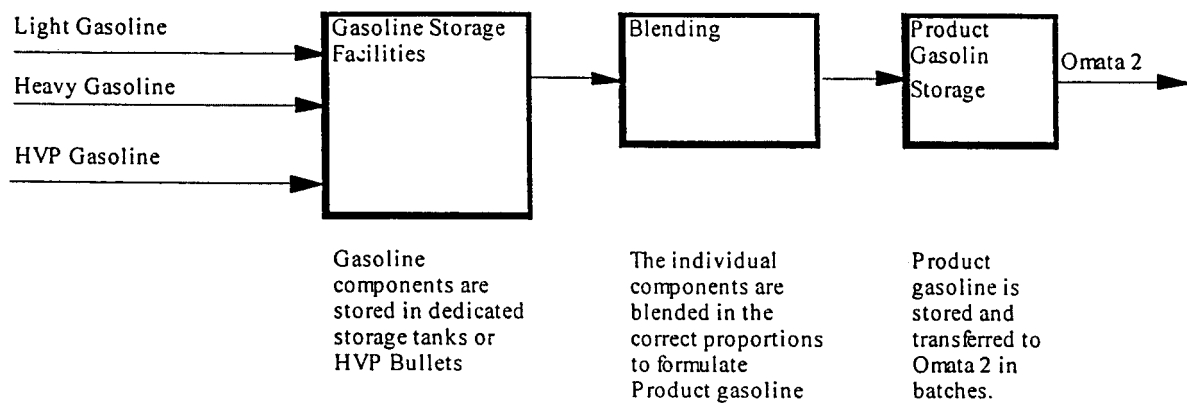
Gasoline of product specification is then produced by the controlled blending of these components



**Figure 6 - The gasoline manufacturing process**



**Figure 7 - The heavy gasoline treatment process**

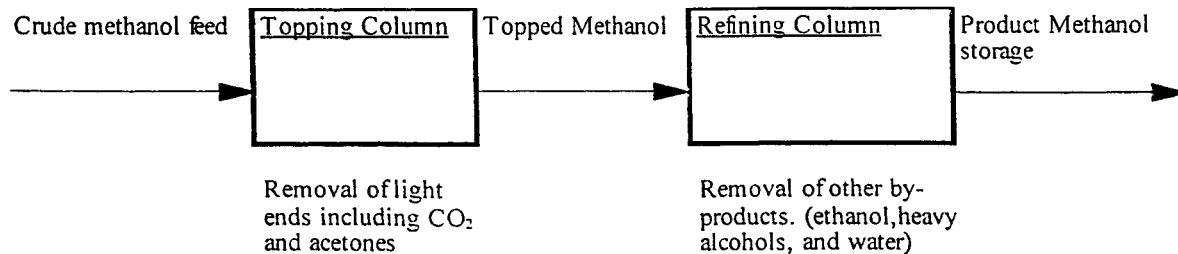


**Figure 8 - Blending and storing gasoline**

in the correct proportions. The product is then transferred by pipeline to the Omata 2 storage facility for storage and load-out to ships. **Figure 8** represents these processes.

### *Methanol Distillation*

Crude methanol can be distilled, to remove Water and by-products formed during methanol synthesis, into product methanol. This is done at Motunui in Distillation III and IV, which are both rated at 2000 t/d of production. **Figure 9** shows the process.



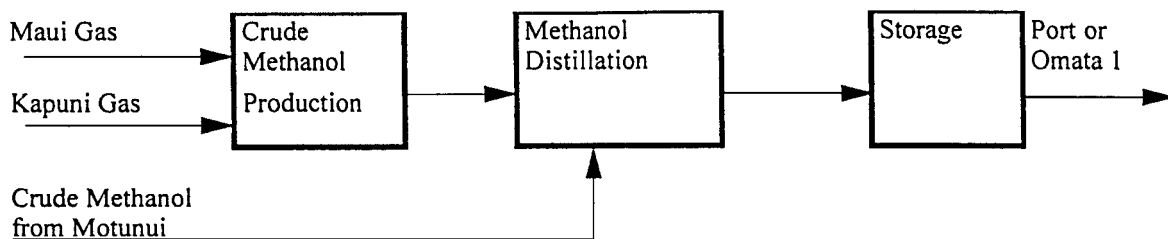
**Figure 9 - The methanol distillation process**

The product methanol is stored in rundown tanks initially for quality checking, and then transferred by pipeline to Waitara Valley, for transfer to Omata 1 or the port.

### **Waitara Valley**

The Waitara Valley methanol plant can produce 1500 t/d of crude methanol and distil 3000 t/d of crude methanol into product methanol in Distillation I and II.

The additional crude methanol to match distillation capacity is transferred from Motunui via the crude methanol pipeline for distillation at Waitara Valley. The overall process at Waitara Valley is shown in **Figure 10**.



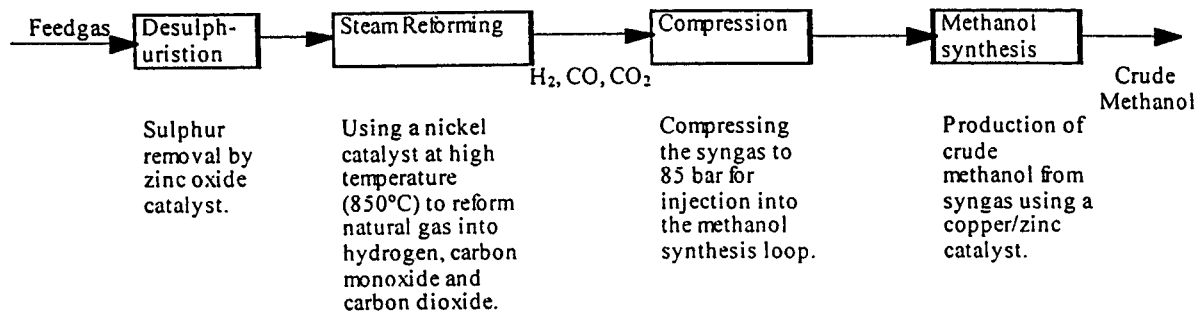
**Figure 10 - Overall process at Waitara Valley**

The methanol manufacturing process is very similar to that used at Motunui and is shown in **Figure 11**.

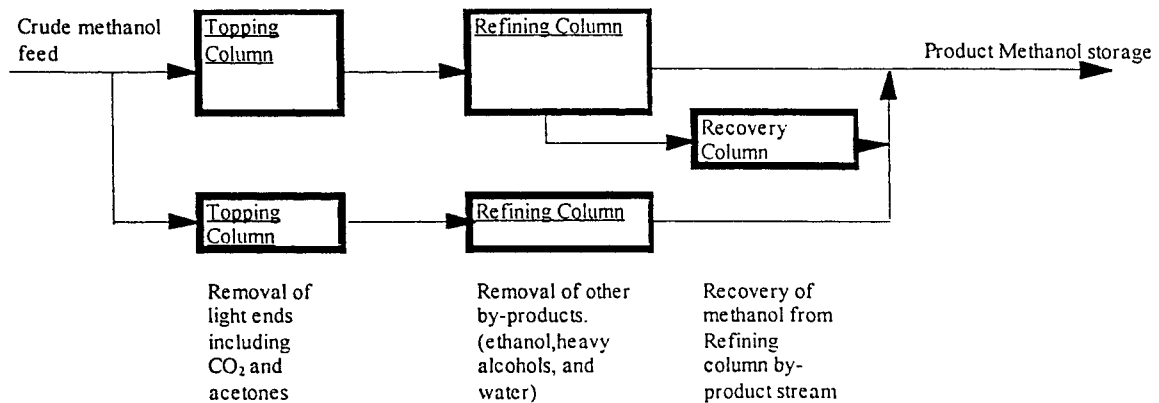
The crude methanol is then distilled in either Distillation I or Distillation II as shown in **Figure 12**. The plant distillation designs vary, with Distillation I incorporating a three tower design, and Distillation II using a two tower design.

### **Pipelines**

The Methanex facilities utilise a number of underground pipelines for the transfer of products between the plants, and to the Port for shipment. See **Figure 1**.



**Figure 11 - Methanol manufacturing process at Waitara Valley**



**Figure 12 - Distillation at Waitara Valley**

*Process Gas Pipeline (600 mm NB)*

To supply mixed gas feedstock to Motunui from Faull Rd Gas Mixing Station.

*Fuel Gas Pipeline (300 mm NB)*

To supply Maui gas for fuel gas to Motunui from Faull Rd Gas mixing station.

*Waitara Valley Kapuni Gas Pipeline (150 mm NB)*

To supply Kapuni gas to Waitara Valley from Faull Rd.

*Crude Methanol Pipeline (150 mm NB)*

To transfer crude methanol from Motunui to Waitara Valley.

*Motunui - Waitara Valley Product Methanol Pipeline (200 mm NB)*

To transfer product methanol from Motunui to Waitara Valley, for storage and onward transfer to the Port or Omata 1.

*Product Methanol Pipeline (200 mm NB)*

This pipeline is used to transfer all product methanol produced at Waitara Valley and Motunui, to the Port and Omata 1. The pipeline requires the use of two intermediate pumping stations to transfer the required volumes.

Product methanol from Omata 1 is transferred to the Port using the section of Product Methanol Pipeline located between the two sites.

### *Product Gasoline Pipeline (250 mm NB)*

This pipeline is used to transfer product gasoline from Motunui to Omata 2 for storage and subsequent ship load-out.

### *Gasoline Load-out Line (450 mm NB)*

The product gasoline is loaded onto ships by transferring the gasoline from Omata 1 directly to the gasoline loading arm on the Port Taranaki Newton King Wharf.

## **Pumping stations**

### *Intermediate Pumping Station 1 (IPS 1)*

At higher flows, between 270-360 m<sup>3</sup>/h, in the Product methanol Pipeline, IPS 1 is required to boost the pressure in the pipeline in order to maintain the required flowrates.

IPS 1 consists of four pumps, which operate in parallel, to increase the pressure of the product methanol from 6 bar to 40 bar. The intermediate pumping station can be by-passed when it is not required for use. IPS 1 is an unmanned site and is operated from Waitara Valley

### *Intermediate Pumping Station 2 (IPS 2)*

At maximum pipeline flowrates in the Product Methanol Pipeline (360-430 m<sup>3</sup>/h), IPS 2 is required, in addition to IPS 1, in order to boost the pressure and maintain the required flowrate. IPS 2 is an unmanned site and is operated from Waitara Valley.

## **Storage**

### *Omata 1 Product Methanol Storage*

Product methanol can be diverted from the 200 mm NB Product methanol pipeline to storage at Omata 1.

Omata 1 consists of two 25,000 tonne fixed roof storage tanks and three transfer pumps. The facility is remotely operated from the Port. The pumps are used to transfer methanol from the Omata 1 storage tanks to the Port storage tanks, using the Product methanol pipeline.

### *Omata 2 Gasoline Storage*

Omata 2 is used for the storage of Product gasoline prior to ship load-out.

The facility consists of two 25,000 tonne floating roof tanks and two ship load-out pumps. One of the floating roof tanks is being converted to dual use, with a vented fixed roof and internal floating roof, allowing it to be used for either gasoline or methanol. It is currently to be returned to gasoline service.

The ship load-out pumps transfer the gasoline directly to the gasoline ship load-out arm on the Port Taranaki Newton King -wharf, via the 450 mm NB Gasoline load-out line.

### *Port Storage and Load-out Facilities*

The Port storage facility is used for the storage of product methanol prior to loading onto ships. The facility consists of two 27,000 tonne fixed roof tanks, and four ship load-out pumps. The load-out pumps transfer methanol to the methanol shiploading arm on the Newton king Wharf, via the 300 mm NB load-out line.



The gasoline and Methanol ship loading arms have been included as part of the Port facilities for the risk assessment.

### **Deballast Facility**

The deballast facility is used to treat ballast water from ships. The ballast water contains small quantities of oil from ship storage tanks. The deballast facility separates the oil from the water, and then discharges the water into the nearby Hongihongi Stream. The recovered oil is returned to crude oil storage

The facility consists of a deballast water storage tank, a small recovered oil storage tank, and an API separator and dissolved air flotation unit.

## **THE METHANOL PRODUCTION PROCESS**

The main process area of the plant can be divided into three sections as shown in **Figure 5**:

- Reforming
- Compression and Synthesis
- Distillation

In addition, a number of support utilities are required, including a conventional water treatment plant, an ion-exchange demineralizer to produce higher quality water for boilers, a package boiler, a cooling water system, an inert gas system, an instrument air system and an electricity generator.

### **Reforming**

The term "steam-hydrocarbon reforming" refers to the endothermic reaction between steam and methane (or any other alkane) which produces carbon monoxide, carbon dioxide and hydrogen. The reaction is carried out in a furnace at high temperatures over a nickel catalyst inside tubes. Fired burners supply heat for the endothermic reaction:



Under these conditions, the water gas shift reaction also occurs to a small extent:



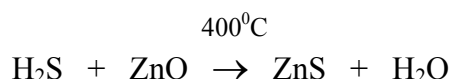
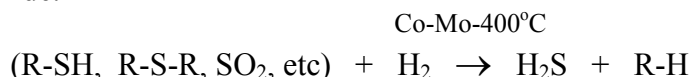
Thus the products of the reforming reaction ("synthesis gas") include carbon oxides and hydrogen as well as unreacted methane, nitrogen, and steam. They leave the furnace at over 800°C. Heat is recovered from this stream as it is cooled to 32°C.

The recovered heat is used to generate high-pressure steam; heat boiler feed water, and to supply heat to the distillation section. Some heat, which cannot be recovered, is rejected to the atmosphere (air coolers) and the cooling water system. After cooling, steam in the reformed gas is condensed and recycled to water treatment.

Waste flue gases leave the furnace at over 1000°C. In order to increase plant efficiency and decrease thermal pollution, the flue gas is used to generate and superheat high pressure

steam, preheat the reactants (steam and hydrocarbons), and heat the combustion air to the furnace. The flue gas leaves the stack at 150°C.

Maui gas is considered almost sulphur-free but, as sulphur in only trace amounts is a poison to the reformer catalyst, a sulphur removal system is included in the process as a precautionary measure. Desulphurization of the hydrocarbon feedstock is carried out at 400°C. It is mixed with a small amount of hydrogen-rich purge gas from the converter and passed over a cobalt-molybdenum catalyst that converts any thiols, sulphides and carbonyl sulphides to hydrogen sulphide H<sub>2</sub>S. It then passes through a zinc-oxide bed where the H<sub>2</sub>S is absorbed by the zinc oxide.



### Compression and Synthesis

The "synthesis gas" from the reformer is then compressed in a centrifugal compressor. A turbine which draws its power from the high pressure steam system drives this compressor. Extraction steam from the turbine is used in the reforming reaction and drives other turbines in the process.

The compressed synthesis gas enters the converter reactor containing copper zinc and catalyst and the synthesis reaction occurs, according to the equation:



This reaction is highly exothermic and this excess heat is used to heat boiler feed water and to pre-heat reactant gas.

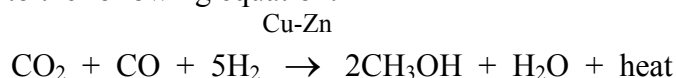
Since the reaction is exothermic, low temperatures favour conversion to methanol. On the other hand, the rate of reaction increases with increasing temperature. Pressure will also affect the position of the equilibrium, with increasing pressure favouring methanol formation. The final conditions used involve a copper oxide based catalyst at about 5 MPa (50 atmospheres) pressure and about 270°C.

As carbon monoxide is used up in the methanol synthesis reaction the water gas shift reaction reverses producing more carbon monoxide:



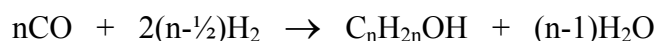
These reactions combine to produce approximately 40% conversion of carbon oxides to methanol each pass through the reactor. On leaving the reactor the gas mixture is cooled and methanol and water condense out. The remaining gas is returned to the circulator, mixed with incoming compressed synthesis gas and recycled through the methanol converter.

Hence, the overall reactions by which methanol is produced from synthesis gas may be summarised into the following equation:



A feature of the steam reforming reaction and the methanol synthesis reaction is that for every three moles of hydrogen gas produced in the steam reformer, only two moles are used in the recycled gas being returned to the methanol converter and the mixture must be purged to remove this excess. At present this purge is used as fuel in the reformer, but the potential for using hydrogen as a feedstock for other reactions (e.g. production of ammonia, reduction of iron sands) should be noted.

It should also be noted that although the converter catalyst is highly specific in producing methanol, some side reactions occur which produce higher alcohols (ethanol, propanol, butanol) and alkanes. These may be summarised:



The crude methanol and water produced in the converter are reduced in pressure in a let-down "flash" vessel. Gas from this vessel is recycled to the furnace as fuel. The crude is then sent to "in process storage".

This crude methanol contains a large range of impurities which have to be removed to produce methanol of chemical grade quality. The technique used for purification is distillation.

### **Distillation**

The distillation system consists of an extraction column, a refining column, and a recovery column.

The first step is the removal of the volatile impurities and dissolved gases - these include carbon dioxide, carbon monoxide, hydrogen, nitrogen, acetone, ethers, esters and volatile alkanes up to decane - which are carried out in the extraction column. The temperature in this column is kept as low as possible to prevent significant methanol loss by evaporation.

The bottom of the extraction column provides the feed for the refining column. The feed is vapourised and enters the refining column about a third of the way up the column. Methanol is now the most volatile component and it leaves the top of the column with a purity of 99.99%. This is product methanol.

A mixture of ethanol and methanol is purged from the column (about half way up) and is sent to the recovery column for further treatment. Propanol and other higher alcohols are purged off (at quarter height) and pumped to the 'tails' tank. Quantities of these alcohols are so small that it is not economic to recover them and they are added to the reformer fuel gas stream and burned. Essentially pure water is drawn from the bottom trays and pumped to waste.

As it is very difficult to separate methanol from ethanol, a third column (the recovery column) is completely allocated for this purpose. The feed for this column is the purge from the refining column described above. High purity methanol leaves the top of the column, combines with the refining column product, and is pumped to the storage tanks. From there it is transferred by pipeline to two 27 000 tonne capacity storage tanks at Port Taranaki in New Plymouth for subsequent export. The 'bottoms' of the recovery column are pumped to the 'tails' tank and subsequently used as fuel for the reformer.

### **Utilities**

The main process areas require the following utilities:

- A package boiler which generates steam at intermediate pressure. This is essential for plant start up and useful as a steam pressure controller during steady operation.
- A conventional water treatment plant to treat water abstracted from the Waitara River. All the water is clarified and some is further treated by filtration.
- An ion-exchange demineralisation plant. This plant removes ions from filtered river water, so that less than 0.1 mg/L of impurities remain. Returning turbine and process condensate streams are also treated here before joining with demineralised water to become boiler feedwater.
- A cooling water system which cools various areas in the plant and is in turn cooled by evaporation of some of the warm water returning from the process in cooling towers.
- An inert gas (nitrogen) supply and distribution system. Nitrogen is required during the plant start up before steam and natural gas are introduced to the reformer. It keeps some coils in the flue gas section cool while warming up and drying out the refractory in the reformed gas boiler. It is also used for pressure control in some areas, and is a back-up for the instrument air system.
- An instrument air compressor and distribution system. Instrument air is required to operate most of the control valves in the plant. It also serves as a source of air which is used for plant maintenance.
- An electricity generator is required to maintain supply to essential process areas in the event of failure of the main supply to the plant.

The complete process is designed to make most efficient use of resources any recycling of waste streams is carried out wherever possible. This has the added benefit of minimising the volumes of waste to be discharged from the plant.

The product methanol is stored in rundown tanks initially for quality checking, and then transferred by pipeline to Waitara Valley, for transfer to Omata 1 or the Port.

### **METHANOL TO GASOLINE - THE MOBIL PROCESS**

The Methanol to Gasoline (MTG) process was developed by Mobil in the early 1970's. In 1979, the New Zealand government decided to employ the Mobil MTG process as an alternative in reducing the dependence on imported crude oil. A plant was built at Motunui with a production of about 14 000 barrels per day of unleaded gasoline, having an octane rating of 92 to 94.

The MTG plant was the first commercial synthetic gasoline plant using new technology developed since the Second World War. The gasoline coming out from the plant can be shipped to the Marsden Point refinery for blending into the New Zealand gasoline pool. The

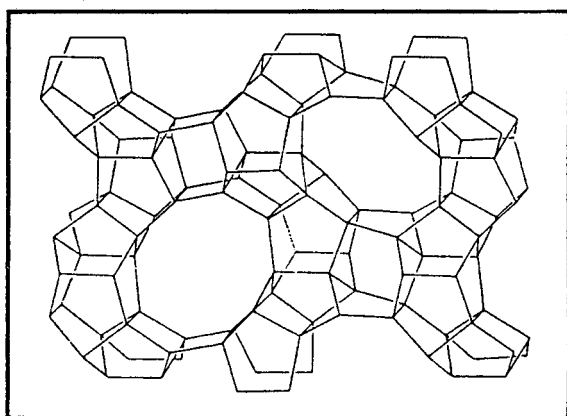
methanol requirement for this process comes from the two 2,200 tonnes (water free basis) per day methanol plants.

### Catalyst

In the 1970's, Mobil synthesised a new zeolite catalyst, which became a key element in the MTG process. Zeolites are porous, crystalline materials with three dimensional framework composed of  $AlO_4$  and  $SiO_4$  tetrahedra.

This catalyst, known as ZSM-5 (**Figure 13**) can convert methanol to hydrocarbon products which are similar to the gasoline fraction of conventional petroleum.

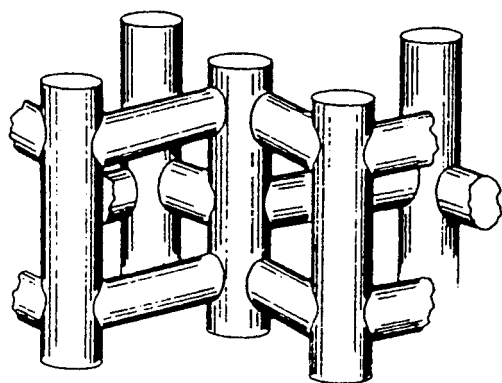
ZSM-5 has an intermediate pore diameter about  $6\text{\AA}$  and a unique channel structure. There are two sets of intersecting channels present: elliptical, 10-membered ring channels present and near circular (sinusoidal) channels. It is this unique combination of channel shapes and sizes that make ZSM-5 so efficient and special in MTG conversion, producing gasoline range molecules ( $C_4 - C_{10}$ ) with practically no hydrocarbons above  $C_{10}$ . In other words, ZSM-5 catalyst produces the right kind of shape and size selectivity properties suitable for gasoline synthesis. These selectivities also give ZSM-5 a reputation for high resistance to deactivation. Hence, a novel route to gasoline from either coal or natural gas can be achieved.



A line diagram of the ZSM-5 structure. The lines are drawn between the positions occupied by the silicon or aluminium atoms.



A scanning electron-microscope photograph of ZSM-5 crystals 1300 times normal size (courtesy of G. Walker, Physics and Engineering Laboratory, DSIR).



An impression of the channel structures in ZSM-5. The zigzag channels are almost round, and about 5.5 angstroms in diameter, and the straight channels are oval and about 5.2 by 5.6 angstroms.

**Figure 13 - Representation of the ZSM-5 catalyst**

## Operational processes

A schematic layout for the Motunui plant is shown in **Figure 6**.

The natural gas is first desulphurised and saturated before entering the reformer furnace where it reacts with steam to produce synthesis gas of hydrogen, carbon monoxide (and carbon dioxide). The synthesis gas coming out from the reformer is cooled compressed reheated then sent to the methanol converter. The crude methanol produced contains about 20% of water. The feed gas desulphurization facilities are included to protect the reformer and methanol catalyst from sulphur poisoning. H<sub>2</sub>S is removed by ZnO pellets contained in a reactor vessel

There are three stages involved in the MTG process

- Petrol synthesis
- Distillation
- Heavy Petrol treating

Catalyst regeneration is also an essential part of the MTG process

### *Petrol synthesis*

The crude methanol is initially preheated, vapourised and then superheated to between 300-320<sup>0</sup>C in a series of heat exchangers. The vapour is then sent to the dimethyl ether (DME) reactor containing a dehydration catalyst (alumina) where approximately 75% of the methanol is partially dehydrated to an equilibrium mixture of DME, water and methanol.



The reaction is rapid, reversible and exothermic. About 20% of the total heat produced is liberated in this step.

The mixture (at the temperature between 400-420<sup>0</sup>C) is then mixed with recycle gas and passes to the conversion reactors. The recycle gas, composed mainly of light hydrocarbons, CO<sub>2</sub> and H<sub>2</sub> serve to absorb the heat of reaction. In the conversion reactor which contains ZSM-5 catalyst DME is further dehydrated to give light alkenes which oligomerize (ie. undergoing chain growth by joining two or more alkene molecules together) and cyclise to give the final products with the liberation of the remainder of the heat.

The mixed effluent is cooled, by generating medium pressure steam by preheating the methanol feed and recycle gas, by air and water. It contains approximately 94 weight percent (w/w %) of hydrocarbons and 56 w/w% of water, the expected stoichiometric ratio. The conversion is essentially 100%. About 85-90% of the hydrocarbon products can be used as gasoline the remainder is fuel gas. Small amounts of CO, CO<sub>2</sub> and coke are formed as by-products. Coke is defined (in simple terms) as the reaction product that is deposited on the surface and fills the pores of the catalyst. This process leads to the deactivation of the catalyst.

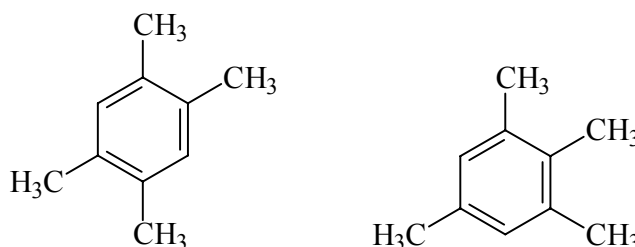
The recycle gas, water and hydrocarbons then goes to the product separator. The water is normally recycled to the reformer saturator, the recycle gas returns to the compressor and liquid hydrocarbons are sent to the distillation section.

### Distillation

The MTG hydrocarbon is refined in three distillation columns. A portion of the lighter and more volatile hydrocarbons dissolved gases and some water is removed by the first column. The second column removes the remaining light hydrocarbons, which are cooled to form LPG. It also recovers a high vapour pressure petrol blending component. The petrol is then split into light and heavy fraction in a splicer column. The light petrol is stored. The heavy fraction is sent to the treating facility.

### Heavy Petrol treatment

Heavy petrol produced in the MTG process contains a component known as durene (1,2,4,5-tetramethylbenzene) which has a high melting point (79°C). The concentration of durene is reduced in the heavy petrol treating section, by converting to low melting point petrol components, e.g. isodurene (1,2,3,5-tetramethylbenzene) with melting point of -23.7°C.



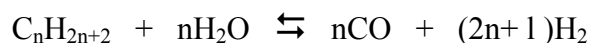
### Product composition

The composition of the synthetic gasoline is quite similar to conventional high quality gasoline. The products from the MTG process are summarised below:

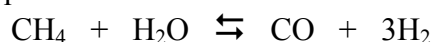
Hydrocarbon product	w/w %	Gasoline composition	w/w %
Light Gas	1.4	Highly branched alkanes	53
Propane	5.5	Highly branched alkenes	12
Propene	0.2	Napthenes (cycloalkanes)	7
Isobutane	8.6	Aromatics	28
n-Butane	3.3		
Butenes	1.1		
C <sub>5</sub> <sup>+</sup> Gasoline	79.9		

### Chemistry of reactions

The steam reforming process can be represented by the general equation:

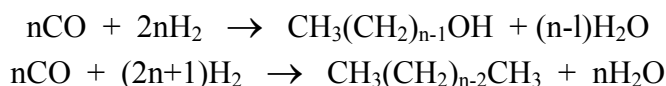


where C<sub>n</sub>H<sub>2n+2</sub> is any alkane and n is a positive integer. For natural gas, which is almost entirely methane, the above equation becomes:

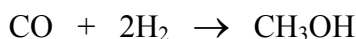


Hence, synthesis gas is formed which can be used for methanol synthesis.

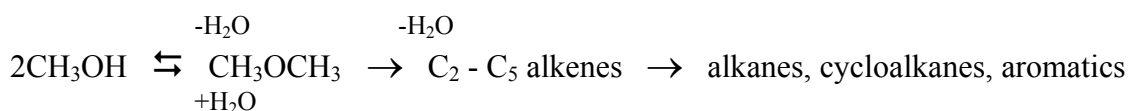
The reaction of the synthesis gas can give a range of products e.g.



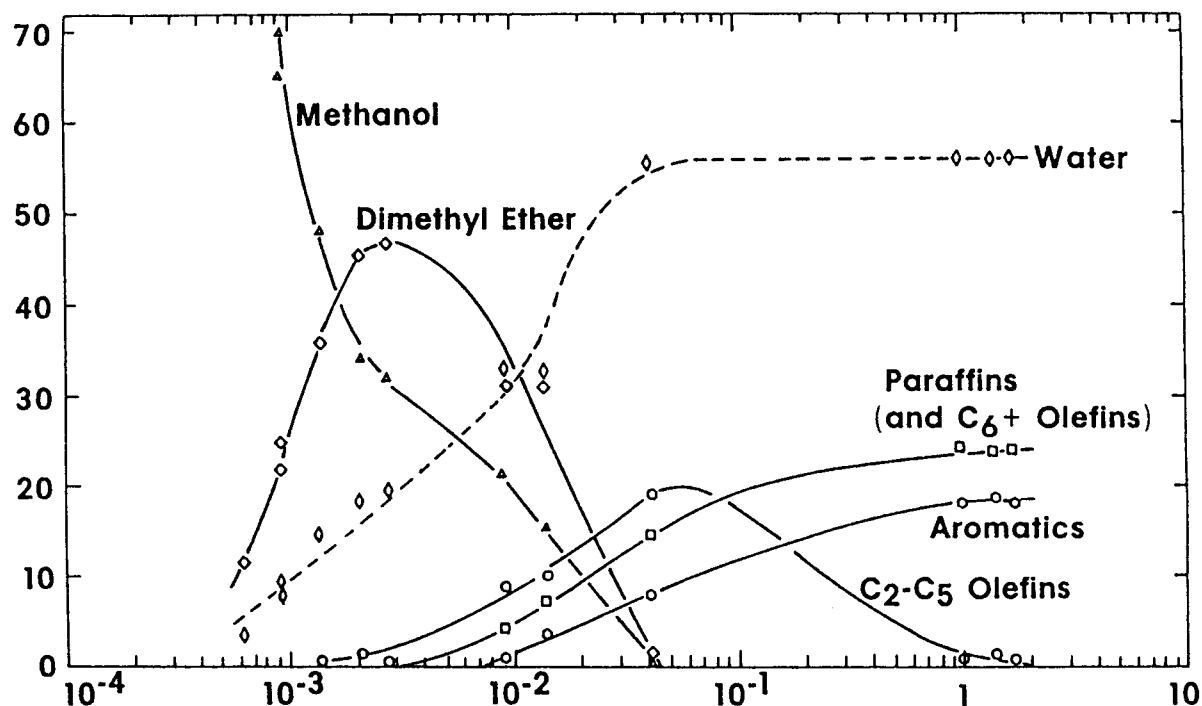
Hence, methanol synthesis requires proper choice of catalyst, which gives high selectivity for methanol. From above if  $n=1$ , then:



The chemistry involved in the MTG process is quite complex. A simplified reaction scheme (proposed by Chang and Silvestri) is shown below.



**Figure 14** shows the product selectivity measured over a wide range of space time (contact time). The contact time measures the time of contact between the catalyst and the reactant molecules. At shorter contact time (in the order of  $10^{-3}$  hr), water and DME are the main products obtained. When the contact time is increased, the yield of DME reaches a maximum after which it decreases, since DME now has more chance to further dehydrate to give  $\text{C}_2$ - $\text{C}_5$  alkenes. With further increase in the contact time, alkanes/ $\text{C}_6+$  alkenes and aromatics are obtained.



**Figure 14 - Product time plot of products in w/w% against space time in hours**

The MTG process is a selective catalytic conversion. The rate limiting step is the conversion of DME to alkenes, a reaction step that appears to be autocatalytic. The catalytic conversion of methanol relies on the action of protonic (Bronsted acid) sites, ie. the hydroxyl groups of the zeolitic structure. The condensation of methanol molecules to DME is thought to involve the



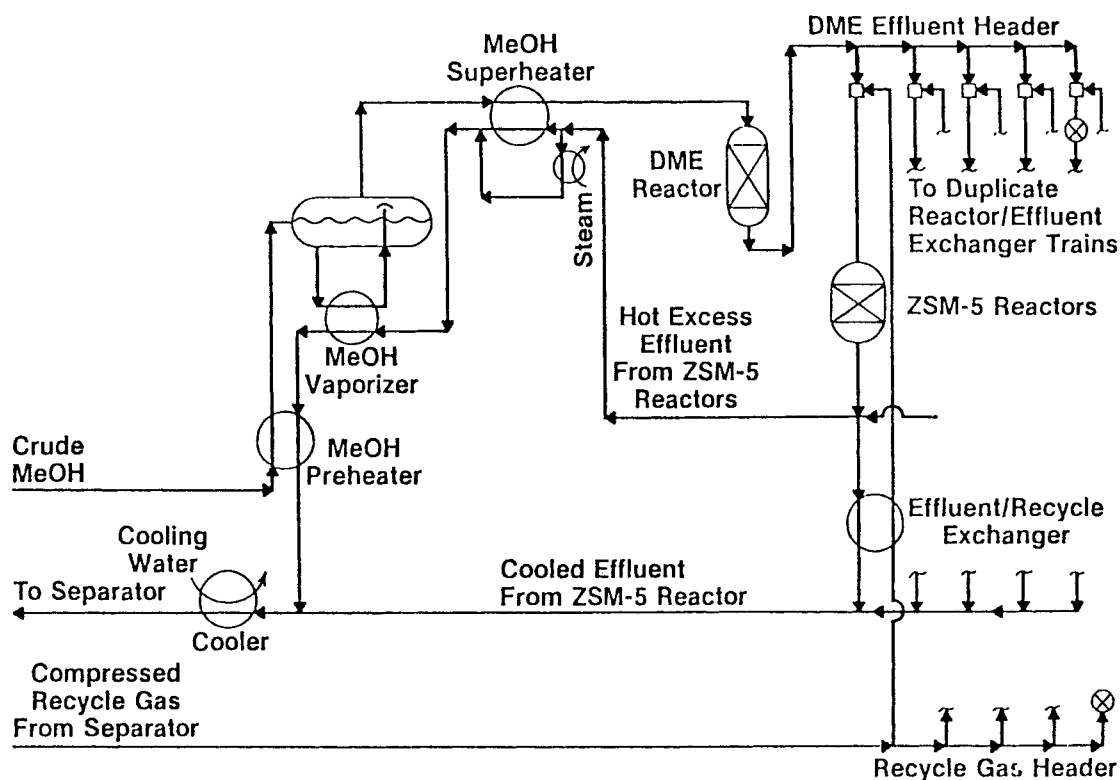
formation of surface methoxy group formed by the protonation and subsequently removal of water. The second step, i.e. the oligomerization of alkene molecules probably involves carbocation intermediates, by protonation of alkene double bonds.

### **Constraints of the MTG process**

- The MTG process is highly exothermic, producing heat at 1740 kJ/kg of methanol consumed. The principal problem in reactor design is thus heat removal, which is important. The recycle gas then provides a good absorbent for the heat of reaction.
- One of the undesirable products in the MTG process is durene, which causes carburettor "icing" because of its high melting point. The synthetic gasoline contains higher concentration of durene (about 3-6 wt. %) than is normally present in conventional gasoline (about 0.2-0.3 wt. %). Durene can be isomerized to give isodurene by the process discussed above to reduce its concentration in the synthetic gasoline. However, durene can potentially be used as a feed stock in the polymer industry.
- Catalyst aging is an inevitable problem in catalysis. There are two types. The first is reversible aging caused by coking. The coked catalyst, hence, requires regeneration every three or four weeks. Coke is burned off with a heated air-nitrogen mixture. Operation of the MTG process is kept continuous by using multiple reactors (**Figure 14**). The Motunui plant uses five swing reactors, with one undergoing off-line regeneration at any given time while the other four are run in parallel for MTG. The second type is irreversible, caused by steam (a reaction product), which leads to dealumination and loss of crystallinity. It can be minimized by operating at low temperatures and pressures.
- In fixed-bed reactors, especially with fresh catalyst, the reaction only occurs over a relatively narrow band of the catalyst bed. As coke deposits first deactivate the front part of the bed, the active reaction zone moves down the bed along the flow of the reactants. This phenomenon is known as band aging, which finally allows the reactant to break through the bed unconverted.
- The major products of the MTG process are hydrocarbon and water. Therefore, any unconverted methanol will dissolve in the water and be lost unless a distillation step is added to the process for recovering the methanol. Thus, essentially complete conversion of methanol is highly preferred.
- The principal disadvantage of the Mobil process is its inability to directly produce diesel and jet fuel. Both diesel and jet fuel are composed of linear, long chain alkanes which the ZSM-5 catalyst does not produce. Jet fuel for example is made up of mainly C<sub>9</sub>-C<sub>14</sub> alkanes with maximum at about C<sub>11</sub>. Diesel is made up of mainly C<sub>10</sub>-C<sub>16</sub> alkanes with maximum around C<sub>14</sub>.

### **Advantages of the process**

- The synthetic gasoline is free of sulphur and nitrogen.
- The overall energy efficiency of the MTG process including processing energy is high, about 92-93%. The energy balance is extremely favourable, 95% of the thermal energy of the methanol feed is preserved in the hydrocarbon product. The remaining 5% is liberated as heat of reaction. However, if one includes the thermal efficiency for the methanol synthesis process from natural gas (~60%), then the overall energy efficiency (natural gas to gasoline) is about 50-60%.
- The product meets or exceeds existing gasoline specifications.
- Methanol conversion is virtually complete. Gasoline yield high.



**Figure 15 - Flowsheet of the MTG process section**

- The feed (methanol) for the MTG process can be made from the wide variety of sources, namely natural gas, coal, biomass etc. In fact, the MTG process will convert most types of alcohol to gasoline, although methanol produced from either natural gas or coal will probably continue to be the most economic feedstock.

## ROLE OF THE LABORATORY

The role of the laboratory is to analyse all process streams. This involves analysis of natural gas, process gas, cooling water, boiler feed water, waste water and methanol. It is the laboratory's task to ensure that these streams are within their specification. On the basis of the analytical results, process conditions can be changed and optimised

Gas streams are analysed continuously with on-line gas chromatography and at regular intervals with the laboratory gas chromatography. For each gas stream different programs are used to ensure complete separation and detection of the individual components

Methanol is frequently sampled at various stages of the process and undergoes a series of physical and chemical tests

Cooling water and boiler feed water are analysed several times a day for pH, hardness, chloride, phosphate etc. to ensure their corrosive properties are minimal

All plant waste effluents are regularly analysed and checked to see that they meet environmental restrictions and conditions

## **ENVIRONMENTAL IMPLICATIONS**

The production of methanol from natural gas poses only limited pressure on the environment. Only one product is manufactured (methanol) which is a compound of relative low toxicity. A special methanol sewer collects any methanol wastes spilled on the plant site. This waste is burned in the reformer as fuel .

A storm pond collects rainwater from the plant and is analysed for methanol and other contaminants prior to discharge to the river.

Rewritten by John Packer from the two articles of volume 2, compiled by P. Kooy (Petrolgas - Waitara Valley) and Dr C M Kirk (Taranaki Polytechnic - New Plymouth) with information supplied by Clare Wrinkles of Methanex New Zealand Ltd.