

Special Design for Methanol Plants

Frank C. Brown
Manager of Process Technology & Consulting
Jacobs Engineering
United Kingdom

Abstract

In this paper the author examines 7 different routes for making methanol using ICI Katalco Technology in non standard flowsheets. Six of these use synthesis gas either originally produced to make something else or produced as by-products in other production processes. Each of these is considered in some detail and the most appropriate ICI approved reactor is selected. The economic criteria for the processes are also discussed. A seventh novel process using a mixture of catalyst and adsorbent is also described. Apart from this latter process all of the others are considered to be currently viable small scale production schemes, particularly where the product is to be used local to the plant. In most cases a major contributor to the low installed cost is the use of a low pressure once through reactor system without any compressor or circulator. Where this scheme is required to make a higher output, a more conventional higher pressure scheme may still be economic.

Introduction

At the moment the large base load plant of 2500 t/d to 3000 t/d would appear to be completely dominant. ICI technology is used in the majority of these plants including several partly or wholly designed by Jacobs. We expect this trend to continue with single stream plants in the range 2500 - 4000 t/d becoming the norm in cheap gas areas.

All of this production has led to methanol being a widely traded commodity since, apart from some MTBE units, most of these plants have few or no local consumers. Consequently the final buying price of methanol is made up of the ex works price, plus two shipping costs and a trader's margin. These can result in the near tripling of the ex works price before it gets into the storage tanks of the user.

Many smaller methanol users have thought that it might be possible to break this chain and make their own smaller quantities of methanol. For example to make about 100 t/day of Urea formaldehyde resin only requires 35 t/day of methanol. While making 12,000 bbl/day of MTBE needs about 550 t/d and 3000 bbl/day the size of a refinery unit only needs 135 t/d. One thought that is never too far from the minds of these parties is the knowledge that for about 6 months the market price of methanol soared to \$600/t causing many to have to sell their derivative products at a loss.

Other people have developed flowschemes which produce by-products which are themselves methanol feedstocks. The leading concept is that of Bio Clean Fuels Inc who take CO₂ from ethanol fermentation and hydrogen from isobutylene manufacture and convert them into methanol which along with the ethanol is reacted with the isobutylene to make MTBE and ETBE.

We shall now look at the following 7 scenarios in more detail:

1. Methanol from fermentation CO₂ and dehydrogenation H₂
2. Methanol from CO₂ and Hydrogen from ammonia, urea plants
3. Methanol co-production on ammonia plants
4. Methanol co-production on hydrogen plants
5. Methanol and electric power co-production
6. Additional syngas production for more ammonia and methanol
7. A completely new process

Fermentation CO₂ and Dehydrogenation H₂ Fig.1

Bio Clean Fuels employed Jacobs Engineering to produce, using ICI technology, a Process Package for a methanol unit in Canada.

The parent of this company owns a patent for the combined production of MTBE and ETBE using organic and LPG feedstocks with some natural gas usage.

In this project the methanol plant is fed with the CO₂ produced by fermentation of grain and with the impure hydrogen from the isobutylene dehydrogenation unit. These two feeds are cleaned up and then passed straight to the methanol loop. The heavier hydrocarbons are then purged

off and mixed with some natural gas and steam reformed in a small furnace which is about 1/3 of the size of one for a totally natural gas based plant.

Since the front end is much smaller than the loop it is not possible to use the loop heat in a feedstock saturator or for BFW heating. This led to the choice of the ICI Linde steam rising reactor which perfectly suits this situation. The 34 bar steam produced is then used throughout the complex as well as in the Primary Reformer.

An alternative scheme where the H₂ was totally purified then mixed with the CO₂ was also considered. Since this does not produce enough methanol additional methanol would need to be imported. All CO₂ using processes require a CO₂ compressor. However, this process also needs a hydrogen compressor. In places like Canada where electricity is cheap this process involves less specific capital than a stand alone natural gas based plant of the same size and close to that of a larger plant. It is however seen as an economic way of converting locally derived feedstocks of LPG, Natural Gas and surplus grain into transport fuels of great environmental benefit.

Methanol from CO₂ and Hydrogen from Ammonia Urea Plants Fig.2

Many producers of Urea sell it to companies making urea formaldehyde resins and would like to share in the better returns this product gives compared with fertiliser sales. Jacobs produced a design for one urea producer to make 35 t/d of methanol. Since this was to be made into formaldehyde no distillation was needed thus saving a lot of money.

The hydrogen equivalent to 40 t/d of ammonia is taken from the purge gas hydrogen recovery unit. CO₂ equivalent to about 70 t/d Urea is extracted from the CO₂ compressor. The methanol loop is extremely simple operating at 50-60 bar if a PRISM unit is being used. CO₂ at 150 bar is used to circulate the loop gases using an ejector. If a cryogenic unit is employed then the loop will operate at 40 bar. The best reactor for this loop is a simple ICI tube cooled design. Only a gas gas exchanger, a loop cooler and a separator are additionally required at pressure. The methanol is stripped to remove dissolved gas before going direct to the formaldehyde reactor.

The operator of a 1350 t/d ammonia plant exporting 80 t/day of ammonia and 2200 t/d of Urea would, on introducing this scheme, only make 2130 t/d of Urea with about 40 t/d of ammonia available for export along with 75 t/d of urea formaldehyde resin.

This is a special version of the plant discussed in the next section to co-produce ammonia and methanol.

Methanol Co-production on Ammonia Plants

Where 10-30% of the ammonia syngas is to be converted into methanol then a much more radical conversion is required and unless the methanol is to be converted immediately into formaldehyde, a distillation unit will also be required.

Both synthesis and distillation sections are likely to be required. The exact scheme will depend upon the situation and the amount of methanol required. Where the methanol production is

within the capacity of the early stages of the syngas compressor then one designer prefers to make the methanol at an intermediate stage of the compressor. Generally however there is a requirement that the combined total of methanol and ammonia output should be greater than that of the original maximum ammonia output. In the case where the original ammonia production is also to be maintained and where the syngas compressor is already limiting then there has to be either a low pressure once through or partly recycled reactor system or a small higher pressure loop with its own compressor.

Where a low pressure once through system is to be used it is generally the case that up to 20% of the syngas can be turned into methanol. A flow scheme of the type shown in figure 3 is used. Gas is taken from after the Secondary Reformer, cooled, desaturated and then passed through the methanol synthesis section. Before being resaturated the gas is cooled and washed free of all methanol. After resaturation the steam to dry gas ratio can be adjusted by steam addition if necessary before the gas enters the existing HT CO shift reactor.

If more methanol is required then more gas will have to be passed through the reactor or the reaction has to be conducted at higher pressure. To make 20-30% of the syngas into methanol then a low head compressor can be installed after the desaturator and gas can be recycled from after the methanol wash column to the suction of this compressor. Another advantage of installing this low head compressor is that it can completely overcome the pressure loss of all the new equipment.

Once more than 25% of the syngas is to be made into ammonia then the synthesis should be conducted at high pressure (60 to 100 bar). Between 20 and 30% of syngas to methanol the total output should be between 5-10% greater than the original ammonia output. At the very highest total outputs the air flow to the secondary reformer may have to be greater than that needed for ammonia synthesis. In this case part of the methanol loop purge is returned to the CO shift while part is put through a membrane to remove the excess nitrogen before being returned to the entry to the CO₂ removal system.

Which is the best scheme to use will require careful study which takes into account the client's requirements and the margin present at all parts of the ammonia plant. Jacobs have done this exercise for two clients and have selected the independent high pressure loop with its own compressor and circulator. In both cases around 25% of the syngas was to be made into methanol.

In the low pressure once through system where the conversion is small (10-15%) then either a single adiabatic bed or two adiabatic beds with intercooling can be employed. The methanol reactor is likely to be half-way in size between the HT and LT CO shift reactors. In the higher throughput cases either the ICI tube cooled reactor or the ICI Linde steam raising reactor can be employed. These two reactors would also be the preferred types for a higher pressure loop.

Since the methanol production removes syngas the ammonia syngas compressor and the ammonia loop are debottlenecked with the saturator desaturator system. However, to make methanol and ammonia in greater quantity than the original ammonia production then the front end must be debottlenecked.

Front End Debottlenecking

Reformer tubes must be replaced every so often and it is expedient in this case to install larger tubes. If the plant is still running on cylindrical single hole catalyst then the old or new tubes can be filled with multihole or shaped catalyst like ICI 57-4 and 25-4. If Urea production is to be maintained then not only must methanol production be limited but the syngas quantity must be increased. If the tube change is accompanied by an outlet header change then the outlet temperature can be increased. This will compensate for the lower nitrogen admission in the Secondary Reformer.

It is often the case that new tube materials and catalysts result in the potential for more syngas production than can be compressed and synthesised into ammonia. In this case the excess syngas can be made into methanol using the once through low pressure system. However, the once through system will introduce extra pressure drop where the total syngas production has been increased and ammonia production maintained. This has to be accommodated by increasing the front end pressure and the reformer tube outlet temperature increased sufficiently to compensate. This may put a strain on the process air compressor which has to be run faster to produce the higher head.

Hydrogen and Methanol Co-production Fig.4

Many hydrogen plants are located in refineries where MTBE is also manufactured. A PSA hydrogen plant has a reformer very similar to that of a methanol plant consequently the reformed gas can be directly taken to methanol synthesis. Where natural gas is the feedstock then the gas is very hydrogen rich and the methanol reactor outlet gas is sent to the PSA unit to recover its hydrogen value. Unfortunately in most refineries the requirement for hydrogen is continually increasing as the operator digs deeper into the barrel. However, existing hydrogen plants can be debottlenecked using a scheme developed by Jacobs using the ICI gas heated reformer.

For 25% extra output the primary reformer outlet gas is diverted through the shell side of the gas heated reformer. For 50% or more output then a small oxygen secondary reformer is added. If a 50,000 Nm³/hr hydrogen plant is expanded to 75,000 Nm³ by this technique then about 200 t/d of methanol and 56,000 Nm³/h of hydrogen are produced after adding the methanol section. Since the methanol reaction removes most of the additional carbon oxides then the PSA unit only has to cope with the increased quantity of CH₄ which is more easily adsorbed.

The methanol reaction is carried out on either all of the make gas or on part of it. Where only part is required to make the desired production rate then the balance of the gas is put through the HT CO shift reactor which is operated in parallel with the methanol reactor. On new plants the methanol reactor can replace the HT CO shift completely. It is also advantageous on new plants to operate the reformer above 30 bar as this improves the methanol conversion. The stream going to the methanol reactor is completely cooled to separate the water vapour before it is reheated to enter the preferred steam raising type of reactor.

With this technology there should be ample methanol to convert all the iso olefines to fuel additives. If in future hydrogen demand increases further then the operator could either make

less methanol or further debottleneck the reformer with more oxygen and maybe another gas heater reformer.

Jacobs did complete the process design of a combined hydrogen and methanol plants from scratch for an Indian client. Due to a change in the financial circumstances of the client it did not proceed beyond the front end package.

Methanol and Electric Power Fig.5

Jacobs are confident that much electricity in the future will be produced in integrated gasification combined cycled plants. Our own Clean Power Generation Process has an overall efficiency at present between 43 and 46% using coal and heavy fuel oil feedstock. At the same time sulphur and NOx emissions are negligible.

The fuel gas after desulphurisation is a good feedstock for either hydrogen, methanol or ammonia co-production. One advantage of making methanol is that the expensive front end can be run at a steady rate and the surplus gas at low electrical demand periods made into methanol. At high electrical demand periods the methanol can be burnt to make more power in an open cycle gas turbine.

If the methanol is made in a once through reactor then only 1 to 2% of the carbon molecules are converted to methanol. By re-configuring this to a loop then up to 10% of the carbon molecules can be converted without having to use a CO shift system. For a 500 MW power station using coal or heavy fuel oil as feedstock then methanol production will lie between 150 and 1500 t/d. A more likely scenario is to make either 150 t/d once through or 400 t/d with some recycle.

If 400 t/d is burnt at 50 t/hr in a gas turbine combined cycle then the power of the station could be boosted by 200 MW at periods of high demand for a 10-15% reduction in output at slack periods. Alternatively if only 150 t/day is made which is burnt at 50 t/hr in a simple gas turbine then about 140 MW extra can be made for 3 hours. This would result in either a reduction of 3% in main turbine power or the front end needing to be 3% larger.

Additional Syngas for More Ammonia and Methanol

One operator in India had debottlenecked their heavy fuel oil based ammonia plant's gas production section as far as possible. However, the ammonia loop and the Urea plant still had more capacity to increase output. This plant also extracted some syngas to make 70 t/day of methanol in a small ICI technology loop.

Jacobs Indian subsidiary, Humphreys & Glasgow, have supplied this client with a new natural gas based steam reformer producing syngas equivalent to 200 t/d of ammonia or methanol. Half of the syngas is sent to a CO shift unit, cooled and then compressed into the ammonia plant while the other half is sent to the methanol loop where it now makes 100 t/d of methanol.

A Completely New Process Fig.6

A few years ago Jacobs invented a novel methanol process for making small to medium quantities of methanol. This process which was only experimentally operated at bench scale

worked by defeating normal restraints on the equilibrium conversion. This was achieved by adsorbing the methanol as it was synthesised.

In this process ICI's latest methanol synthesis catalyst is mixed with a Union Carbide molecular sieve adsorbent in a pair of cyclic isothermal reactors operating at 25 to 40 bar. The Linde steam raising reactor is likely to be very suitable for this duty. Once the adsorbent in one reactor is saturated then a second reactor is switched in and the loaded reactor is depressurised. Since the gas coming off is almost entirely methanol it is easily condensed at about 2 bar.

This process would be very suitable for operation with once through low pressure sources of syngas. Since the equilibrium is completely altered all of the carbon would be reacted away if sufficient hydrogen is present.

At the operating temperature of methanol synthesis the molecular sieve in the reactor absorbed between 5 and 7% of its mass as methanol. To make 75 t/day two vessels holding about 10 M³ of adsorbent and 2 or 3 M³ of catalyst each would be required.

If this process was used on an ammonia plant in a co-production scenario then only sufficient syngas for almost 100% conversion to methanol would be required. The tail gas would contain mainly hydrogen and nitrogen. This gas could either be used as fuel or put back into the ammonia plant at the entry to the methanator.

The drawbacks of the process is that the reactors are proportionally larger than normal and are subject to cyclic fatigue. In a PSA plant this is accommodated by making the vessel as simple as possible with the minimum connections to reduce stress raising points. In the cooled reactor adsorber there are inevitably more connections so the design analysis has to be even more thorough.

The Economics of Local Production

The feature of the examples given which is most obvious is their size. The largest plant produces about 400 t/d of methanol. By reducing the equipment in the scope of the plant the capital charges per tonne are reduced till they are similar to that of a large world scale unit.

A new 2500 t/d methanol plant can be erected in a cheap gas country for \$250-300 million, including all utilities, tankage, export facilities and local infrastructure. This means that the specific cost per daily tonne is between \$100,000 and \$120,000. On this basis a plant producing 200 t/d should not cost more than \$20-24 million. The transport cost of \$30-50/t can then be used to subsidise the production cost difference between cheap remote gas and more expensive imported gas. Generally local gas at under \$2.5/10⁶ BTU (\$10 per Gcal) NCV will result in an economic product.

It is our experience that the once through processes without expensive compressors can get the capital cost below \$100,000 per daily tonne at any size down to 60 t/day/ Above 300 t/d with a pressurised loop then it is probable that a simple motor driven compressor will still permit economic operation provided cheap electricity is available.

Summary

I hope to have shown in this paper that smaller quantities of methanol can be produced economically in plants where part of the investment is borne by another product. In particular it has been shown how Urea producers can extend their business to resins, refiners can back integrate to make the other feedstock for MTBE and TAME and the electricity producer of the future can control his peak demand by making methanol during slacker periods. Most of these producers will be looking to meet demands that they have on site. Ammonia producers who decide to co-produce methanol may be thinking of trading some of the product to nearby resin producers.

By limiting investment costs and keeping operating and transportation costs under their own control these special production situations are likely to grow and prosper as some consumers prefer to break their dependence on the major traders.

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References

- 1) Keith Elkins
- 2) Jim Abbott