

JM

Methanol synthesis revamps

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1. Introduction

Johnson Matthey (JM) is a leader in sustainable technologies and a market leader in the development of catalyst and process technology in the ammonia, methanol and formaldehyde industries. With a heritage in ammonia dating back to the first decade of the 20th Century, Johnson Matthey (JM) currently offers a range of high-performance catalysts, leading edge technologies and diagnostic services to our customers. Johnson Matthey's range of **DAVY™** technologies offers design, licence and commissioning expertise. The combined skills and experience of catalysts and process design is ideally suited to the development of innovative syngas flowsheets.

Johnson Matthey has been developing and selling formaldehyde **FORMOX™** technology and catalysts since the late 1950s and has supplied more than 20 million MTPA (as 37wt%) capacity to a wide range of customers. To put this into context, global demand in 2015 was about 45 million MTPA. By carrying out both catalyst and technology development in the same organisation, any catalyst development can easily be implemented in the flowsheet and vice-versa. Johnson Matthey typically acts as an engineering and procurement contractor during the project phase and assists during erection and commissioning. After start-up Johnson Matthey continue to support plant operation with an extensive technical support program.

Johnson Matthey has continuously improved the formaldehyde catalyst and technology and today our customers produce more than four times as much formaldehyde in the same size reactor as in the early 1960s. This increase in production also comes with a considerably improved yield, less than half the power consumption and more than double the steam generation.

The integration of the ammonia and methanol processes into a single flowsheet can exploit the common upstream syngas generation unit operations. There is a history of methanol and ammonia coproduction from a common feed. Methanol synthesis has even been used as a carbon oxides removal stage in the flowsheet to produce ammonia from coal. Developments in ammonia production technology from naphtha and natural gas meant that a single stream ammonia production was more economic than the historic coproduction concepts.

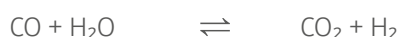
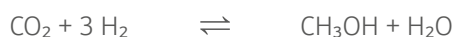
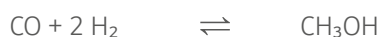
Either downstream use of methanol in an ammonia complex, or changeable market conditions can now make the flexibility of a single process to produce both ammonia and methanol attractive. Through the combination of industry proven technologies, the synergies between

ammonia and methanol production can be maximised. This allows the environmental impact of the twin productions to be minimised, and the operating costs and energy consumption of the coproduction scheme to be optimised.

2. Methanol Coproduction

2.1 Methanol synthesis

The reactions involved in the synthesis of methanol from syngas are as follows:



The synthesis of methanol is favoured by high pressure, moderate temperature, high levels of carbon dioxide and low levels of water.

The methanol industry today is almost entirely based on low pressure methanol technology and high performance catalysts developed by ICI, and continually improved by Johnson Matthey since its acquisition of the business. Johnson Matthey has licensed over 100 grassroots methanol plants using their leading technology, and the skills and experience in catalysis and process design within JM lend themselves to the development of novel revamps for the synthesis of methanol on ammonia plants.

The requirement for carbon oxides in the feed for the methanol synthesis section means that there are various locations within an ammonia process for the coproduction of methanol which make use of the residual carbon oxides in the process. The selection of location for a coproduction retrofit is mainly dependent on the desired methanol production rate since this dictates a required level of CO and CO₂ in the feed but is assessed on a case by case basis.

2.2 Operation

Johnson Matthey's high performance and stable activity **KATALCO™** methanol synthesis catalyst allows methanol production to be carried out at low temperatures that minimise the formation of by-products such as high alcohols, hydrocarbons, aldehydes and ketones.

Reduction of the methanol synthesis catalyst can be considered similar to that of the low temperature shift catalyst, and it is possible to design for the use of the existing reduction gas system.

2.3 Coproduction using syngas inlet high Temperature Shift

2.3.1 Flowsheet

In general, for cases requiring a relatively high production rate of methanol, the carbon oxides level upstream of the high temperature shift (HTS) are most attractive. In this flowsheet, the syngas from the secondary reformer waste heat boilers on the ammonia plant is passed through a desaturation stage to reduce the water content and then heated to methanol synthesis temperatures. A fraction of the CO and CO₂ is converted to methanol in a suitable once-through methanol converter. The product methanol is recovered in a crude state and sent to a distillation section for refining to product specifications. The unreacted syngas is passed through a saturation stage to return the removed water to the stream and reheated to the HTS inlet temperature before returning to the ammonia plant. This is illustrated in Figure 1.

2.3.2 Benefits

Advantages of a retrofit in this form are that there is a single break in and return point to the existing ammonia plant and has little impact on the operation of the existing equipment.

A once through methanol synthesis system allows the capital cost of the equipment to be kept at a low, reasonable value. The nature of the upstream process on the ammonia plant means that there is a high level of nitrogen in the feed syngas which results in very high flowrates, and therefore high equipment costs, for circulating systems. The configuration also allows for continual operation of the ammonia plant without the methanol section running and for simple start up of the methanol section in parallel to the ammonia plant.

A benefit of installing the methanol synthesis retrofit upstream of the HTS is that any additional CO slip from the methanol section as a result of methanol synthesis catalyst deactivation can be accommodated in the existing shift section. Therefore, any loss of production of methanol is offset by the increase in ammonia production as a result of the increased hydrogen produced in the shift section. The increase in carbon dioxide exit the shift section is removed in the existing CO₂ removal stage.

The once through system is designed such that operation is as simple as possible, and the plant with the retrofit in place can be operated with existing staffing levels.

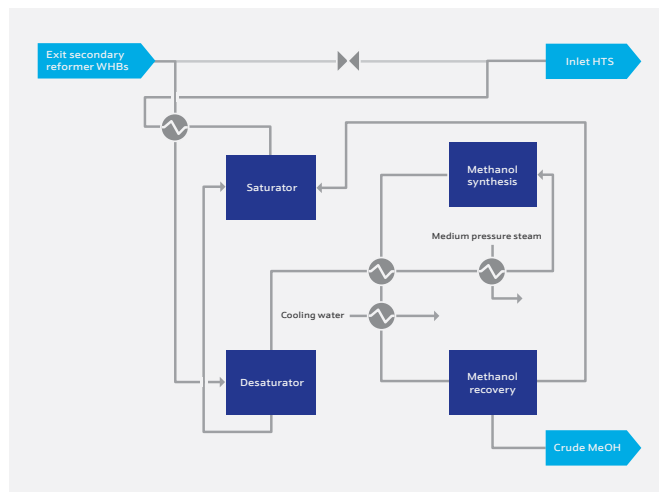


Figure 1: Block diagram showing methanol synthesis retrofit using syngas exit the secondary reformer as the feed.

2.3.3 Ammonia Plant Impact

Since the synthesis of methanol consumes hydrogen which would otherwise be used in ammonia synthesis, it is necessary to adjust the operation of the existing ammonia plant to maintain a 3:1 H:N ratio in the syngas being fed to the ammonia synthesis loop. The operation of the reforming section can be adjusted such that the syngas leaving the methanol synthesis retrofit is suitable for ammonia conversion.

The front end of the ammonia plant can also be updated to accommodate some of or all the reduction in ammonia rate associated with the introduction of the methanol synthesis retrofit.

The synergies between the production of ammonia and methanol can be maximised via close collaboration and integration between the design of the methanol synthesis retrofit and the adaptation of the existing ammonia technology. The global strategic alliance agreement between Johnson Matthey and KBR to license ammonia-methanol coproduction processes combines JM's methanol production process and KBR's proprietary PURIFIER™ ammonia process. KBR's PURIFIER technology provides a method of optimising the syngas composition downstream of the methanol synthesis retrofit.

Collaboration between the technology providers can exploit the synergies between the two technologies and reduce the environmental impact of the plant and its OPEX through shared utilities and lower energy consumption. The interconnectivities between the processes and the design of the methanol synthesis retrofit in close collaboration with the ammonia technology allows for flexibility to optimise production between ammonia and methanol.

2.4 Coproduction using syngas exit CO₂ Removal

2.4.1 Flowsheet

For cases requiring a lower production rate of methanol, the syngas exit the CO₂ removal stage can be used. Here, there are low levels of CO and carbon dioxide following the shift and CO₂ removal sections, so the maximum methanol capacity is limited. The syngas typically has a water content that is low enough to not require a desaturation stage. The syngas from the overhead of the CO₂ removal column is heated to methanol synthesis temperatures. The CO and carbon dioxide is converted to methanol in a suitable once-through methanol converter. The product methanol is recovered in a crude state and sent to a distillation section for refining to product specifications. The unreacted syngas is returned to the ammonia plant. This is illustrated in Figure 2.

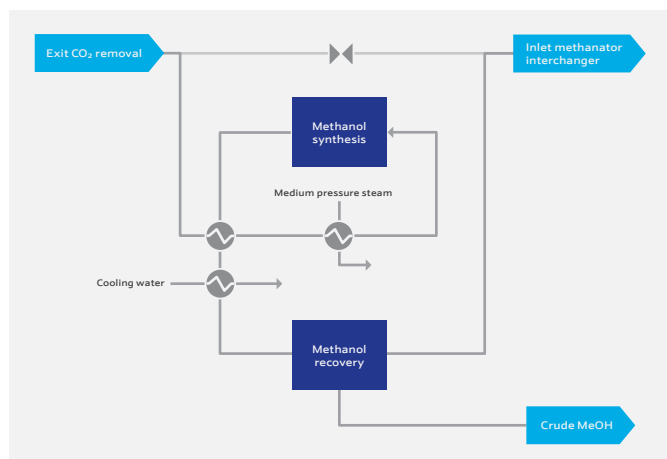


Figure 2: Block diagram showing methanol synthesis retrofit using syngas exit the carbon dioxide removal section as the feed.

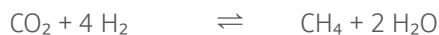
If there are insufficient carbon oxides in the ammonia plant syngas exit the CO₂ removal stage, but the required production rate is not so high as to make the scheme using syngas inlet the HTS attractive, it is possible to make small modifications to the ammonia plant to increase the methanol production rate.

To increase the CO content exit the CO₂ removal stage, a portion of the plant flow can be bypassed around the low temperature shift (LTS) converter. Alternatively, the operation of the CO₂ removal section can be adjusted to increase the slip of carbon dioxide.

2.4.2 Benefits

Advantages of the retrofit in this form are that there is a single break in and return point to the existing ammonia plant and has little impact on the operation of the existing equipment. The bypass configuration allows of continual operation of the ammonia plant without the methanol section operating and for simple start up of the methanol section in parallel to the ammonia plant.

Downstream of the CO₂ removal section, the carbon oxides are considered a contaminant since they act as a poison in the ammonia synthesis converter, and carbon dioxide can form ammonium carbamate via reaction with ammonia. Therefore, any carbon oxides in the process are converted to methane in the methanator. The methanation process consumes hydrogen via the reactions:



This hydrogen consumed via methanation cannot then be used in the synthesis of ammonia. Since the conversion of CO and CO₂ to methanol consumes less hydrogen than the corresponding methanation reactions, the net effect of introducing the methanol synthesis retrofit is to reduce the hydrogen consumed to convert the residual carbon oxides. This allows for a higher flow rate of hydrogen to the ammonia synthesis section, and if the synthesis loop and associated equipment is capable, allows for an increase in the production of ammonia.

Note that increasing the CO or carbon dioxide at the feed to the retrofit section via a partial bypass of the LTS or modification of the CO₂ removal section will increase the carbon oxides slip from the methanol synthesis section. These carbon oxides consume hydrogen in methanation and will reduce the potential ammonia production rate. Eventually, the increased slip will offset the benefit on hydrogen consumption of synthesising methanol over methanation.

The once through system is designed such that operation is as simple as possible, and the plant with the retrofit in place can be operated with existing staffing levels.

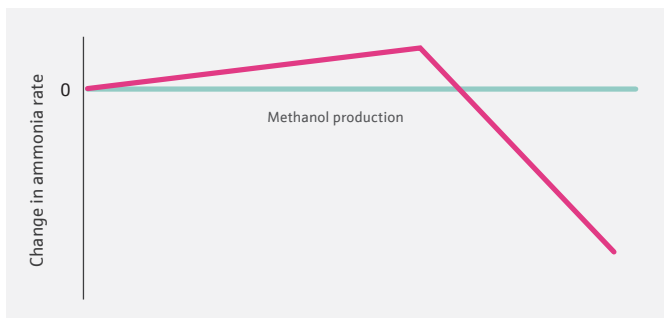


Figure 3: Effect of production rate of methanol synthesis retrofit installed downstream of CO₂ removal stage on potential ammonia production rate.

For significantly higher required methanol production rates, this illustrates how a retrofit using syngas exit the CO₂ removal stage is less suitable than one using syngas exit the secondary reformer.

2.4.3 Ammonia Plant Impact

There is a lesser impact on the ammonia plant for a retrofit using syngas exit the CO₂ removal stage since the methanol synthesis is using a smaller flow of CO and carbon dioxide than that upstream of the shift section.

As discussed above, there may be a benefit to ammonia production as a result of the methanol synthesis retrofit. For cases requiring higher CO and carbon dioxide in the feed, the ammonia production may be reduced. Some, or all, of this reduction in rate may be accommodated by uprating the ammonia plant syngas generation section, and an assessment of the optimal technology configuration can be made on a case by case basis in close collaboration with the ammonia technology provider.

A reduced exotherm over the methanator as a result of lower CO and carbon dioxide levels in the methanator feed means that additional heating will be required to achieve the methanator inlet temperature. The effect of the increase in heating required can be mitigated with collaboration between ammonia and methanol technology providers and the optimal integration of the flowsheets.

3. Integrated UFC

3.1 Introduction

Urea formaldehyde concentrate (UFC) is used to condition a granular urea product and some prilled urea products. UFC is added to the urea product in small quantities, which renders a standalone production facility for an individual urea producer unfavourable economically. Therefore, urea producers typically import purchased UFC from third party distributors.

UFC producers would normally purchase a methanol feedstock at market value, which includes the margins of the methanol producers. The imported UFC cost also allows for the third-party producer's margins, and the cost of transportation to the urea producer. This raises the opportunity for significant savings to a urea producer were it possible to manufacture the necessary UFC on the ammonia-urea complex.

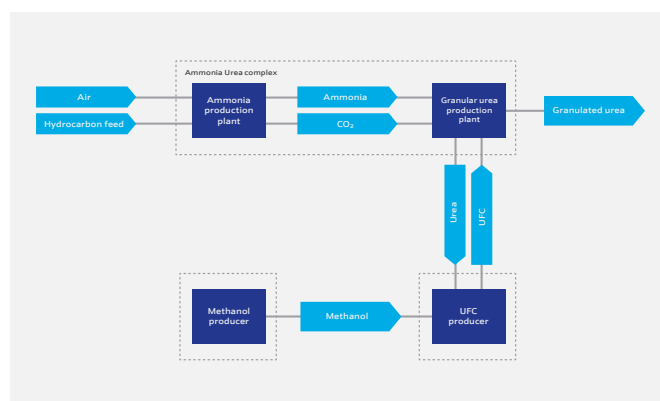


Figure 4: Standard arrangement of ammonia, urea and UFC technologies showing battery limits and transportation requirements between sites.

The interconnectivities between the production of ammonia, urea and formaldehyde can be exploited to offer a retrofit to existing ammonia plants to produce UFC for conditioning the urea product. In the iUFC™ process, formaldehyde is produced via the oxidation of methanol, and methanol can be produced using a retrofit as described in section 2 above. The modest capital costs of a well-designed retrofit section can allow the savings of in-house UFC production over purchased UFC to be realised.

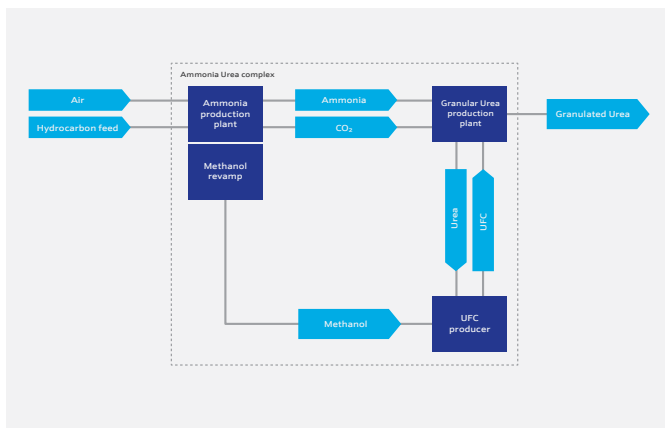


Figure 5: Arrangement of technologies using Johnson Matthey integrated UFC flowsheet

3.2 UFC production

3.2.1 Flowsheet

Production of formaldehyde and UFC uses well established technologies. Johnson Matthey **FORMOX** employ mixed oxide catalyst technology due to its superior yield, high steam production and because it makes it possible to produce UFC-85 directly in the same plant.

Formaldehyde is produced via the partial oxidation of methanol with air as an oxidising agent:



The product stream from the formaldehyde synthesis reactor is sent to a water absorber column. The formaldehyde is absorbed into the water, the water condensed, and any unreacted air is recycled to the formaldehyde synthesis reactor. A purge stream is taken from the recycle gas which is released to the atmosphere after treatment in an emission control system to convert the trace methanol, formaldehyde and CO to carbon dioxide and water. The formaldehyde in the absorbed water is absorbed into a urea solution to produce a UFC product at the required concentration. This is illustrated in Figure 6.

3.2.2 Integrated UFC production

Standard Johnson Matthey **FORMOX** plants are designed with flexibility in mind and either UFC-85 or formaldehyde can be produced on the same plant. The plant can also be configured to produce UFC concentrations other than 85%.

When retrofitting an ammonia urea complex for the integrated production of UFC, the UFC plant can be designed to operate with crude methanol. This allows for

capital and operating cost savings in the distillation of the crude methanol product from the methanol synthesis retrofit. Further integration is also possible and can be offered on a case by case basis.

The integration of the UFC plant and the methanol synthesis retrofit on the ammonia plant can integrate the utility requirements to optimise the operating costs of the two processes.

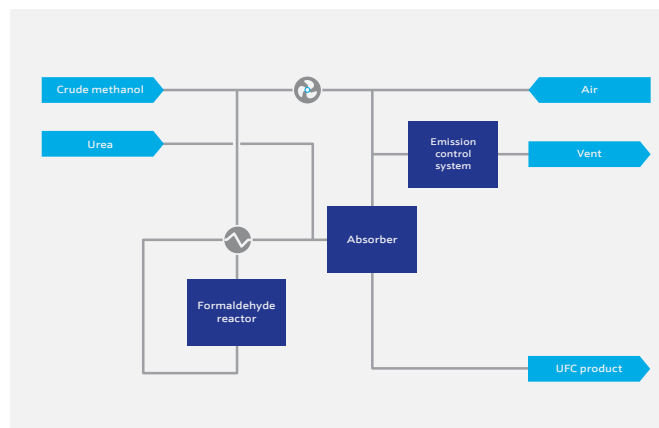


Figure 6: Block diagram showing UFC production plant using crude methanol as a feed

3.3 Benefits

As discussed above the main benefit of the iUFC process is the reduction in the cost of UFC since the integrated process eliminates the premium of the third-party producer for methanol or UFC and the transport costs. The operating costs for the UFC process are minimal in comparison to the ammonia-urea complex. The potential savings are assessed on a case by case basis and can be maximised by optimising the integration of the iUFC process. Typically, the savings are of the order of the purchase cost of the UFC.

Typically, the required rate of methanol production for an iUFC process means that the methanol synthesis retrofit using the syngas exit the CO₂ removal stage is most appropriate. Therefore, the benefits as outlined in section 2.2 are also applicable here. The flexibility of the methanol synthesis retrofit means that there is no impact on ammonia plant reliability and standard storage designs can be provided for intermediate storage of crude methanol to accommodate catalyst changes in the methanol and formaldehyde synthesis systems.

Conclusions

Johnson Matthey's market leading methanol technology can offer methanol synthesis retrofits to ammonia plants to maximise savings while offering the highest levels of safety, flexibility and reliability. Close collaboration with ammonia technology providers, and a global strategic alliance agreement with KBR combines market leading technologies to maximise the synergies between ammonia and methanol production.

Methanol coproduction retrofits can be used as part of an iUFC retrofit using Johnson Matthey **FORMOX** technologies to produce formaldehyde and UFC using crude methanol produced on the ammonia plant. This offers a new method of producing UFC for urea producers which offers significant cost savings over importing purchased UFC.

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