JM

UFC manufacture for urea production

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Reprint from Nitrogen & Syngas 2016

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Inspiring science, enhancing life

Formaldehyde in the form of UFC-85 is used as an additive in the manufacture of solid urea. Formaldehyde is synthesised from methanol which is normally purchased on the open market and is priced accordingly. In most cases, the quantity of UFC-85 that is required by any individual site is too small to justify investment in small scale methanol production and in a UFC-85 plant. Johnson Matthey's skills in catalyst design, along with ammonia, methanol and formaldehyde process technology development have been used to create a new and cost effective method of synthesising small quantities of UFC-85 which allows a urea producer to make significant savings when compared to the alternative of open market purchases.

Introduction

Johnson Matthey is a leader in catalyst and process technology development for 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.

Today's methanol industry is based almost entirely around the low-pressure technology and catalysts developed and commercialised by ICI in the late 1960s. Since the acquisition of this business, Johnson Matthey has continued to adapt and improve methanol technology.

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 **FORMOX**™ formaldehyde 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 (flowsheet) 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 **FORMOX** catalysts 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 production and use of these three chemicals is linked. Carbon dioxide, a by-product of the synthesis gas generation process for ammonia manufacture, can be usefully combined with product ammonia to synthesise urea, an important fertiliser and chemical product. Solid urea is manufactured as prills or granules and formaldehyde (in the form of urea-formaldehyde concentrate or UFC) is used to condition granular, and sometimes prilled, urea. One of the most commonly used grades of UFC is UFC-85, a mixture of 60% formaldehyde, 25% urea and the balance water. Formaldehyde is produced from the oxidation of methanol, which in turn is produced from synthesis gas.

Generally, the formaldehyde additive required for urea conditioning is purchased from a third party as the small quantities required for an individual ammonia/urea plant are below the economic limit that would justify investment in a stand-alone formaldehyde plant along with the associated methanol plant.

As a result, urea producers tend to purchase UFC-85 from third parties whose cost structure is based on the purchase (or opportunity cost) of methanol at market price which is normally at a considerable premium to the cost of the raw materials used to synthesise the methanol. The cost of the UFC-85 is then further increased due to transportation

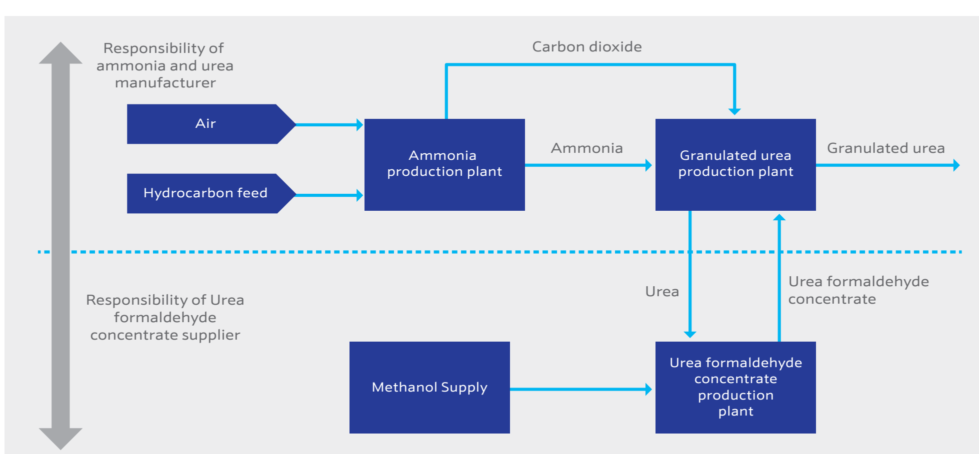

Figure 1: Standard arrangement of technologies

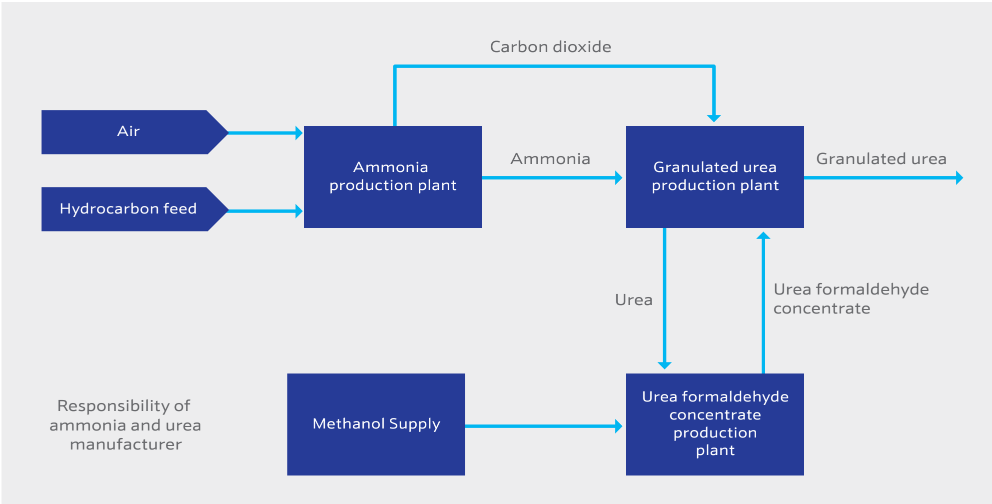

Figure 2: Arrangement of technologies when utilising the Johnson Matthey integrated flowsheet

costs, the need to cover supplier overheads and return on investment criteria.

If an ammonia-urea producer could manufacture sufficient UFC-85 to meet their own needs in a plant that required only modest CapEx, using feedstock which otherwise only had fuel value and that could be operated with existing staffing levels, significant savings could be realised compared to the alternative of purchasing the UFC-85.

Flowsheet development

Using the knowledge and experience available across Johnson Matthey, a novel scheme, which is the subject of patent applications, has been developed whereby the ammonia, methanol and UFC-85 production plants have been combined to provide reliability of supply as well as capital and operating cost savings.

The scheme uses the residual carbon oxides in the synthesis gas generated on the existing ammonia plant to produce methanol. This methanol can then be used to produce UFC for the urea plant. The bulk of the syngas remains and is then passed to a standard ammonia synthesis loop to produce the ammonia for urea production.

The scheme described here is proposed as a retrofit to existing ammonia-urea plants. However, it could also be conveniently applied to a new build project.

Co-production of ammonia and methanol

The first step in the integration of the three technologies is to produce methanol and ammonia on the same plant.

There are a multitude of flowsheet concepts for integrating ammonia and methanol production. Whilst some have been commercialised, others remain conceptual. This integration is possible as the syngas generation sections of ammonia and methanol flowsheets share many of the same unit operations and features, such as natural gas purification and steam reforming.

However, the purpose of the majority of the previously proposed co-production schemes was the bulk production of both ammonia and methanol. For example, ICI's METHAMM flowsheet would have been capable of producing 1100 mtpd of ammonia and 2200 mtpd of methanol.1

In the flowsheet considered in this paper for the provision of methanol for UFC-85 production the methanol requirement is much lower than the ammonia production rate. For example, a typical 2200 mtpd ammonia plant produces enough carbon dioxide to allow around 3500 mtpd of urea to be manufactured. Depending on the specific design of urea plant the UFC-85 requirement for this amount of granulated urea is 20-30 mtpd. To produce this much UFC-85 requires 14-21 mtpd of methanol. Therefore, existing co-production schemes for ammonia and methanol are not best suited to this application

Methanol synthesis

The reactions involved in methanol synthesis are as follows:

$$CO + 2H_2 \rightleftharpoons CH_3OH \quad \Delta H = -90.64\ kJ/mol$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \quad \Delta H = -49.67\ kJ/mol$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad \Delta H = -41.47\ kJ/mol$$

In commercial methanol production plants, the preferred conditions for methanol synthesis are:

- High pressure
- Moderate temperature
- Sufficient CO_2 to synthesise the desired quantity of methanol

Based on this, there are three options to make methanol with syngas from the ammonia plant, as shown in Figure 3. The first (shown blue) uses gas from upstream of the shift section, the second (shown green) uses syngas

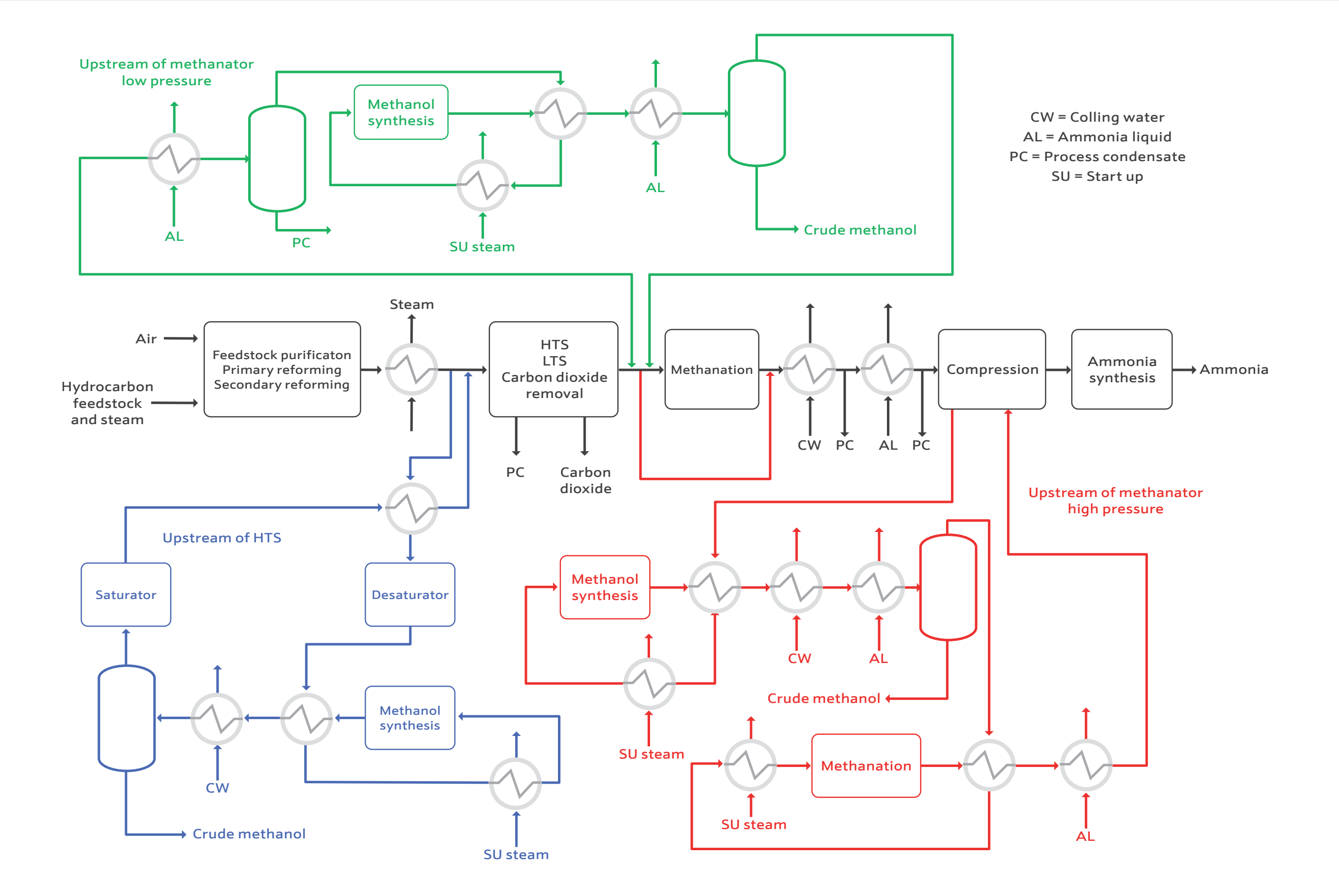

Figure 3: Ammonia-methanol integration options

from upstream of the methanator at the synthesis gas compressor suction pressure and the third (shown red) uses higher pressure syngas at an interstage pressure of the compressor, still upstream of a methanator.

Upstream of HTS

In this flow scheme, the secondary reformer effluent is cooled and passed through a desaturator before being heated to methanol synthesis temperatures and fed to the converter. The product gas from the converter is cooled and the crude methanol separated. The unreacted gas from the separator is then re- saturated and heated back to the HTS inlet temperature before re-joining the standard flowsheet.

Upstream of methanator – low pressure

In this flow scheme, the syngas that has passed through the shift section and the carbon dioxide removal system is heated before being fed to a methanol converter. The effluent from this converter is cooled and the crude methanol separated from the unreacted synthesis gas. The gas from the separator is then fed to the existing methanator feed/effluent interchanger and methanator.

Upstream of methanator – high pressure

In this flow scheme, the synthesis gas that has passed through the shift section and the carbon dioxide removal system is fed to the first stage of synthesis gas compression. The relatively high pressure synthesis gas is then heated before being fed to a methanol converter. The effluent from this converter is cooled and the crude methanol separated from the unreacted synthesis gas. The gas from the separator is then fed to a new high pressure methanation section.

Composition of produced methanol

The Johnson Matthey integrated **FORMO**X process allows formaldehyde to be produced from crude methanol. However, if the water content of the crude is too high, it is not possible to make UFC-85 without a concentration step (typically distillation). Products with a lower concentration of urea and formaldehyde can of course be made. The correct selection of methanol synthesis location within the ammonia plant allows crude methanol to be generated which has a concentration high enough to avoid the need for an energy consuming and capital intensive distillation system

	Catalyst Volume	Saturator / Desaturator	Distillation	New High Pressure Methanator
Upstream of High Temp Shift	High	Yes	Yes	No
Upstream of methanation at compressor suction	Highest	No	No	No
Upstream of methanation at compressor interstage	Lowest	No	No	Yes

Table 1: Comparison of options for methanol-ammonia integration flowsheet positions

Option summary

The first option requires a complex saturator and desaturator system and distillation of the crude methanol before it can be used on a UFC plant. Although the carbon oxide content is low in the second option, there is still sufficient residual carbon oxide present to produce the amount of methanol required for UFC production

JM integrated flowsheet

Ammonia plant

The Johnson Matthey integrated flowsheet uses the residual carbon oxides downstream of low temperature shift and carbon dioxide removal to produce methanol. The choice between low pressure (compressor suction) and high pressure (compressor interstage) is assessed on a case by case basis.

In both cases, syngas is first chilled to remove moisture and then heated in a feed/effluent interchanger before entering a methanol synthesis reactor. The gas leaving the reactor is cooled in the feed/effluent interchanger before being chilled to remove the crude methanol which is let down in pressure and sent to storage or to the UFC-85 plant. The remaining gas passes through a methanator before being compressed to ammonia synthesis loop pressure.

Bypass option

The production of methanol is limited by the amount of residual carbon oxides present in the gas stream exit the carbon dioxide removal system. In most cases this produces sufficient methanol to meet the UFC demand for an associated urea plant.

However, if the UFC and therefore the methanol requirement are higher than this limit allows, Johnson Matthey can design the flowsheet to incorporate a bypass around one or more of the HTS, the LTS and/or the CO_2 removal system to increase the carbon oxide concentration inlet the methanol reactor. It is important to choose the correct bypass location to minimise water formation in the methanol synthesis section to avoid the need for a crude methanol distillation column.

If using the bypass to synthesise more methanol, there will either be a reduction in ammonia make, or the feed rate of natural gas will need to be increased accordingly.

Urea formaldehyde concentrate (UFC-85) production

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.

The main principle is to partially oxidise methanol in the presence of air to form formaldehyde and water. The gas mixture of formaldehyde, water and air is separated in an absorption column in which water is condensed and the formaldehyde is absorbed into the water. UFC is produced when formaldehyde is absorbed into a urea solution which is fed to the column. The oxidation process consumes oxygen; hence oxygen needs to be provided to the process and oxygen lean gas has to be removed. The oxygen lean gas contains traces of formaldehyde, methanol and carbon monoxide and is passed over a noble metal catalyst incinerator (emission control system or ECS) in which trace impurities are converted to carbon dioxide and water.

Ammonia and UFC plant integration

Standard Johnson Matthey **FORMOX** plants are designed with flexibility in mind and either UFC-85 or formaldehyde can be produced on the same plant. However, if the plant is only required to produce UFC-85, it is possible to reduce capital cost by replacing the second stage of the absorption tower with a gas cooler/condenser.

The plant can be configured to produce UFC concentrations other than 85%

The UFC plant can be designed to operate with crude methanol. Although operating with crude methanol is uncommon, it is not a new concept. Further integration is also possible and is offered on a case by case basis. An integrated UFC plant flow sheet is shown in Figure 4.

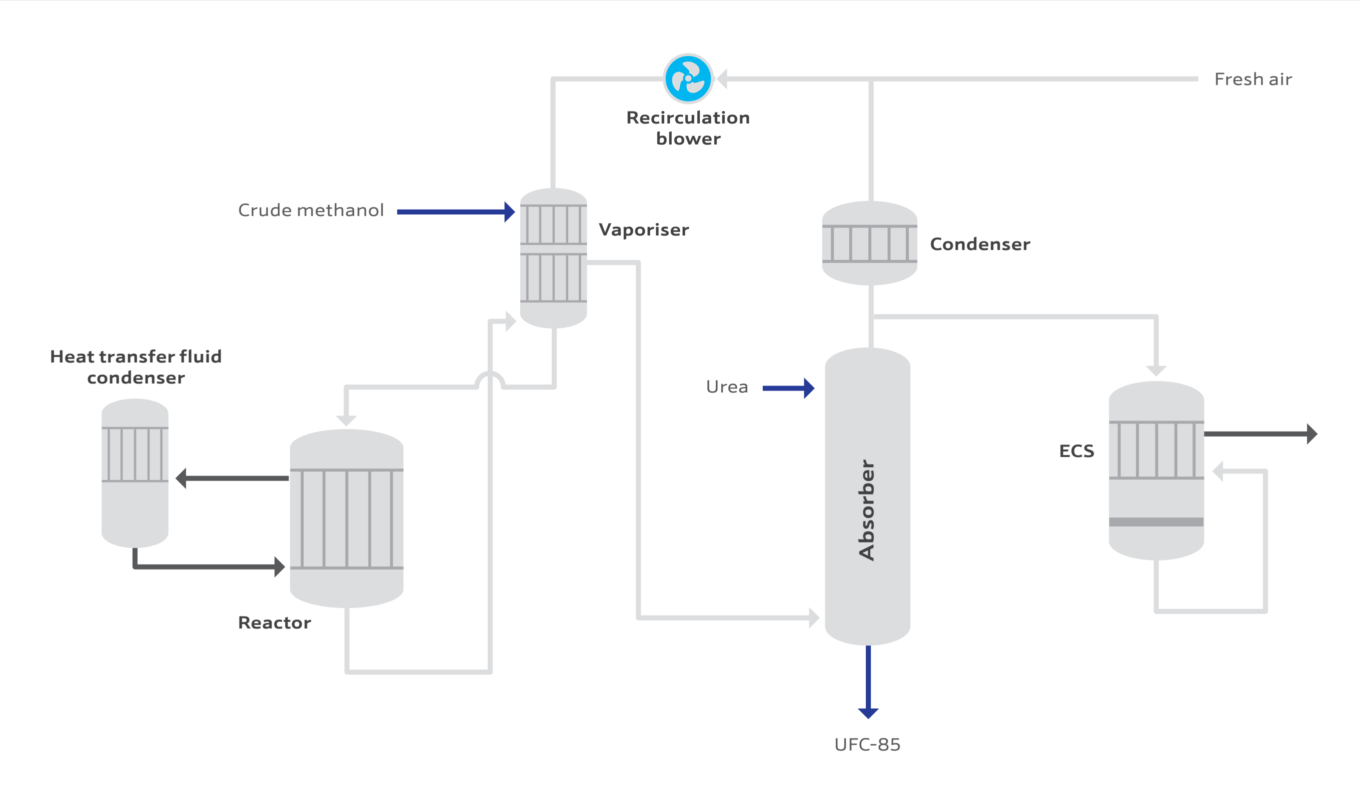

Fig. 4: Integrated UFC flowsheet

Operation

Ammonia plant catalyst

The methanol synthesis section of the plant uses the **KATALCO**™ 51-Series of methanol synthesis catalysts. The high and stable activity of this 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 and start-Up

The reduction of methanol synthesis catalyst is similar to the reduction of low temperature shift catalyst. Natural gas or nitrogen can be used as carrier gas and the reductant may be pure hydrogen or synthesis gas. Once the catalyst is reduced, synthesis feed gas can slowly be introduced to the bed and methanol produced.

Operational considerations

Despite the inclusion of a chiller to maximise separation of methanol from the gas stream it is inevitable that there will be methanol and other by-products in the feed to the methanator. Johnson Matthey's proven **KATALCO** 11-Series catalysts reduce their concentration to levels suitable for the ammonia synthesis loop.

The methanol synthesis section can be isolated from the rest of the ammonia plant. This means that the ammonia plant can be started up using existing methods and the syngas which is generated during normal operation can then be used to reduce and start-up the methanol synthesis section.

The Johnson Matthey scheme is designed to avoid issues associated with the reaction of ammonia with carbon dioxide to form ammonium carbamate and the reaction of ammonia with methanol to form trimethylamine.

The final change that may be encountered due to the addition of a methanol synthesis section is that the hydrogen recycle to the front end of the plant could now contain carbon oxides. As a result a nickel- molybdenum hydrodesulphurisation catalyst such as **KATALCO** 61-1T may be recommended.

UFC-85 plant

The UFC plant is of a proven standard design used in plants worldwide with minor adjustments to reduce capital cost by integration with the ammonia complex. However the capacity is lower than that of a normal Johnson Matthey **FORMOX** plant to match the UFC requirement for an individual complex.

Occasional UFC-85 plant shut-downs are required to replace the catalyst. The catalyst lifetime is dependent on the plant operating rate, but will be a minimum of 8 months. The change-out duration is around 5 days.

The UFC plant can be configured either to consume urea solution generated on the adjacent urea plant or to consume solution generated by dissolving solid urea.

Crude methanol and UFC storage

The crude methanol storage system will follow standard, proven designs. In retrofit cases the urea plant would be likely to have an onsite UFC storage tank and this could be used to store UFC produced in the new UFC plant.

Benefits

Running costs

The major benefit of the Johnson Matthey integrated flowsheet is the reduction in the cost of purchasing methanol or UFC-85. The operating costs of the UFC-85 plant itself are minimal.

The range of potential savings that can be achieved using the Johnson Matthey scheme on a standard 2000 mtpd ammonia plant making around 3200 mtpd granulated urea are shown in Figure 5 below.

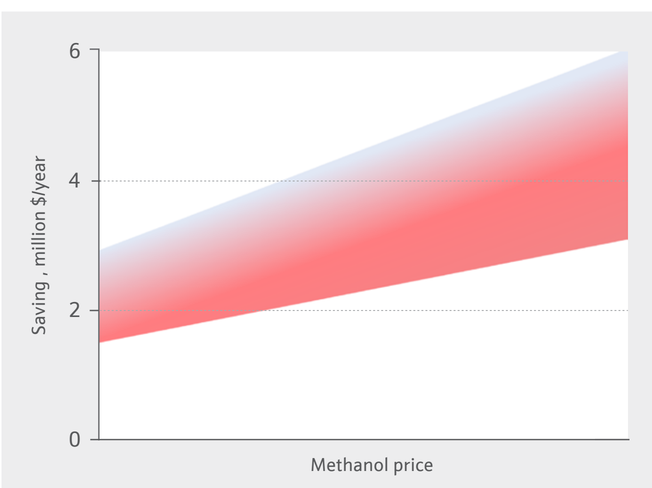

Figure 5: Expected savings with varying methanol price on a 2000 mtpd ammonia plant using JMs integrated flowsheet

The figure uses a range of recent methanol prices for the assessment of savings. The lower range of savings in the figure relate to customers who already have UFC production facilities on site and would save only the cost of importing methanol to their UFC plant. The upper range relates to customers who import UFC so are paying additional a margin to the UFC producer and additional transportation costs. Further operational savings can be achieved but vary case by case.

Capital costs

The capital cost of the process is competitive when compared to the alternative of purchasing UFC-85 at prices which reflect those of traded methanol.

Flexibility and reliability

As the methanol synthesis unit can bypassed, there is no impact on ammonia plant reliability. Instantaneous methanol/UFC unit capacity and intermediate storage tank size allows sufficient inventory to be built up to cover a formaldehyde catalyst change without affecting ammonia or urea production.

Synthesis gas and ammonia loop

In the case of a retrofit of an existing plant, the hydrogen content in the synthesis gas to the ammonia loop is increased and the methane content is reduced. This means that the retrofit may allow an increase in ammonia make or an improvement in efficiency.

$$CO + 2H_2 \rightleftharpoons CH_3OH \quad \text{Methanol production}$$

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \quad \text{Methanation}$$

As shown by the reaction equations above, the production of methanol from carbon monoxide uses less hydrogen per mole of carbon oxide removed than the methanation reaction. Therefore, as some of the residual carbon oxides are removed by producing methanol it means that there are less carbon oxides in the methanator feed so less hydrogen is consumed overall than in a standard flowsheet. The second effect is that because the methanator has less carbon oxides to convert there is less methane produced which results in a lower methane content in the loop.

On a typical 2200 mtpd ammonia plant using the Johnson Matthey integrated flowsheet, the natural gas feed to the primary reformer can be reduced while still achieving the same production rate of syngas and ratio of hydrogen to nitrogen in that syngas. This also reduces the firing required on the primary reformer and gives a total natural gas saving of around 250 Nm^3/h or 0.4% of the standard flowsheet.

Crude methanol usage

The flowsheet allows the use of crude methanol in the UFC-85 plant. This means that no complex and energy intensive distillation systems are required, making this flowsheet much simpler to operate. It also reduces the capital cost of the plants compared to stand-alone units that could be supplied.

Conclusions

Johnson Matthey has combined it's knowhow in ammonia, methanol and formaldehyde production to deliver an innovative new way of producing UFC-85 which will generate significant cost savings when compared to the alternative of purchasing UFC-85 from third parties.

The scheme, which is the subject of patent applications, is now offered commercially.

References

1 "Ammonia or Methanol: The choices", K.J. Elkins, Paper 9, IMTOF 1995, San Francisco

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