

# JM

# Low temperature methanation:

Operating experience and something unexpected!

Sam Van Den Broeck – Yara Sluiskil  
Martin Fowles – Johnson Matthey

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## Introduction

**Yara International ASA is a leading chemical company that converts minerals, energy and nitrogen from the air into essential products for farmers and industrial customers.** One of the biggest sites is located in Sluiskil, the Netherlands. Daily ammonia production of 4950 MTPD is accomplished by Units C, D and E. All three have a Brown & Root purifier design, with molecular sieves and a cryogenic purifying unit in between the methanator and the synthesis gas compressor.

The methanation process as a final synthesis gas purification step within an ammonia plant is well known, however this paper describes recent operating experience that has been gained following a project in which a new methanation catalyst charge was installed to operate at a lower inlet temperature, operating at 210-220°C (410-428 °F), significantly lower than the norm of around 290-310°C (554-590 °F).

In this project, carried out in the 1225 MTPD unit C plant, the main benefits from the low temperature operation were the operation of the inlet/outlet heat exchanger well below the Nelson curve for C-0.5 Mo steel and an improved plant efficiency due to a saving of HP steam, previously used to trim the inlet temperature.

The start-up and operating experience for what is considered as a novel operating window in the ammonia industry will be reviewed. In reviewing the operating experience, we included our observations of some unexpected side reactions (formation of higher hydrocarbons by Fisher-Tropsch reactions) across the reactor, the understanding behind the reactions and their impact on the plant process.

## Why choosing low temperature methanation?

The drivers behind the choice for a low temperature catalyst in ammonia unit C were twofold. First aim was operation of the inlet/outlet heat exchanger well below the Nelson Chart for C-0.5 Mo steel. Second goal was the improved plant efficiency due to of HP steam savings on the trim heater.

### Nelson curves

Steels exposed to hydrogen at elevated temperatures and pressures may suffer from hydrogen cracking or blistering (also called high temperature hydrogen attack or HTHA). Hydrogen atoms diffuse into the steel and react with carbon to form methane. These molecules are larger than hydrogen atoms and therefore become trapped in the

steel, building up local high pressure at grain boundaries and inclusions, leading to possible blistering or internal cracking of the steel. Alloying the steel with Cr and Mo avoids failures by making stable carbides, more resistant to methane formation.

Nelson curves describe the operating limits for steels in hydrogen service to avoid the abovementioned decarburisation and fissuring.

In the first edition of API Publ. 941 (1970), the operational boundary of C-0,5 Mo-steel in hydrogen service was described by a separate Nelson curve, well above the one for carbon steel.

Twenty-seven hydrogen attack incidents in the safe area of the Nelson curves, however, forced the API to down rate C-0.5Mo to the same curve that applies to for carbon steel (4th Edition of API RP 941, 1990).

Yara's internal material recommendation MR-002 recommends to maintain a safety margin of 30 °C below the Nelson curves at any time. For the unit C methanator inlet/outlet heat exchanger E-307, the maximum outlet temperature dictated by the Nelson curve is 300 °C (572 °F). However, the exchanger operated from 1970 to 2007 right on or slightly above the Nelson curve. Therefore, at possible occasions, 100 % ultrasonic testing (UT) was performed to check for cracks on the main welds of the pressurised shell (i.e. longitudinal, circumferential, butt welds and man hole welds). In addition, during each turnaround, a replica test was performed. However, no cracks were revealed during these investigations.

When the temperature of the inlet/outlet exchanger is decreased by 50 °C by application of a low temperature methanator, the exchanger clearly moves into the safe area of the current Nelson curves.

### Energy efficiency improvement

After the revamp of the CO<sub>2</sub>-removal system in 1996 (conversion from Vetr<sup>®</sup>Coke to aMDEA), the CO<sub>2</sub> slip at the exit of the unit C bulk absorber decreased significantly to a value lower than 0,1 %. As a consequence, methanator feed-effluent exchanger E307 could not raise the methanator inlet temperature anymore up to 290 °C (554 °F). The trim heater E-308 was used at its full capacity, consuming 4-5 ton/h (8,8-11,0 MLb/h) of 100 bar (1450 psi) steam. This is shown in Figure 1.

By installing a low temperature methanator catalyst, less duty is required from trim heater E-308, as shown in Figure 2. A gain in 100 Bar (1450 psi) steam consumption of 2-3 ton/h (4,4-6,6 MLb/h) is obtained, depending on the temperature rise over the methanator catalyst.

This corresponds to an improvement of the energy efficiency of unit C of 0,15 GJ/MT (0,142 mmBTU/MT).

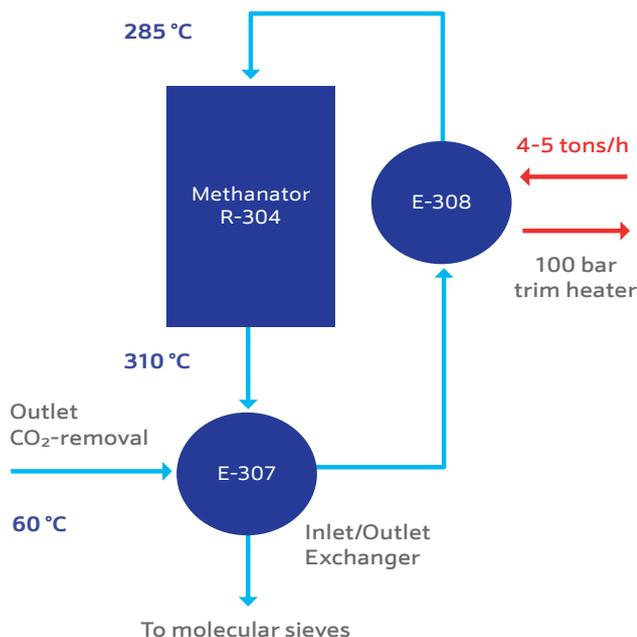


Figure 1: Classic methanation

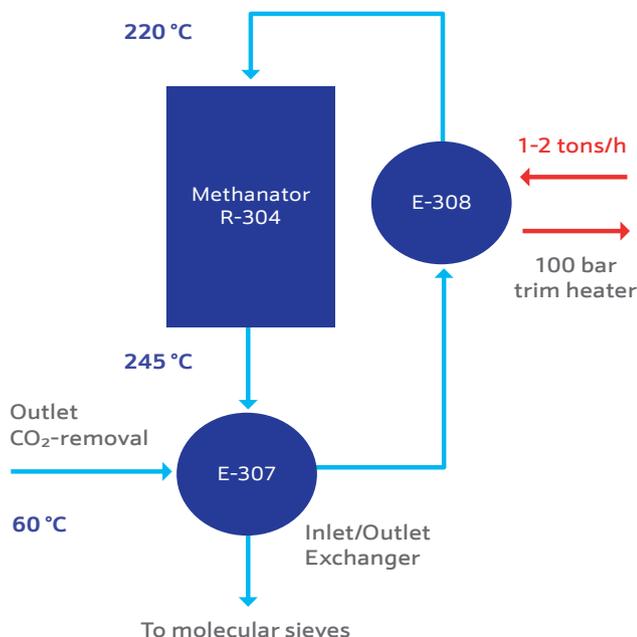
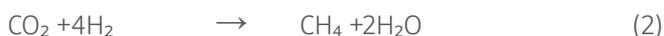
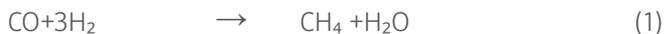


Figure 2: Low temperature methanation

## Low temperature methanation

### Methanation

In classical ammonia production, methanation is the final stage of purification of the synthesis gas after CO<sub>2</sub> removal that reduces carbon oxides to trace levels. Carbon oxides are poisonous for ammonia synthesis catalysts, so methanators ensure long ammonia synthesis catalyst lifetime.



The reactions are strongly exothermic. Reaction 1 gives a temperature rise of 74 °C for each 1 % of CO converted, reaction 2 provokes a rise of 60 °C for each 1 % of CO<sub>2</sub> converted. The reactions are governed by kinetics and are not equilibrium limited. CO is methanated first; CO<sub>2</sub> only reacts when CO concentrations are down to 200-300 ppm, which makes CO<sub>2</sub> the favourable compound to assess methanator performance.

Higher conversion over the Nickel catalyst is promoted by high pressures and high temperatures. So in normal plant designs, a methanator is typically run at around 290-310°C (554-590 °F) to ensure a CO<sub>2</sub> slip below the standard of 5 ppm (normal 1-2 ppm). To our knowledge, not many methanators are run at temperatures below 250 °C (482 °F). For low temperature methanation (220 °C or 428 °F), a higher overall activity is needed, so increased Ni content and effective Ni surface area is considered to be necessary. In the Unit C case, a **KATALCO** 11-4 catalyst with 35 wt% of Ni was installed.

Operating at temperatures below 200 °C (392 °F) is not recommended, because of the potential of nickel carbonyl formation in this temperature region.

### Outlet specifications

In a typical Brown & Root (or KBR) design, a cryogenic unit is placed in front of the synthesis gas compressor to adjust H/N-ratio and to remove methane. At cold box temperatures of about -175 °C (-283 °F), compounds such as H<sub>2</sub>O, NH<sub>3</sub> and CO<sub>2</sub> cause freezing of the cryogenic unit. Therefore, molecular sieves are used to remove traces of H<sub>2</sub>O, NH<sub>3</sub> and CO<sub>2</sub> downstream the methanator. The maximum allowable inlet concentration of CO<sub>2</sub> at the inlet of the molecular sieves is only 10 ppm, as described in the design specification. A higher CO<sub>2</sub>-slip from the low temperature methanator would cause an outage of the plant due high-pressure drop in the cold box caused by CO<sub>2</sub> freezing within it.

As unit C is a Brown & Root plant (see figure 3), the CO<sub>2</sub> slip from the methanator is even more crucial than in a traditionally designed plant. In this light, the target was set at max. 1 ppm of CO/CO<sub>2</sub> slip at start-of-run.

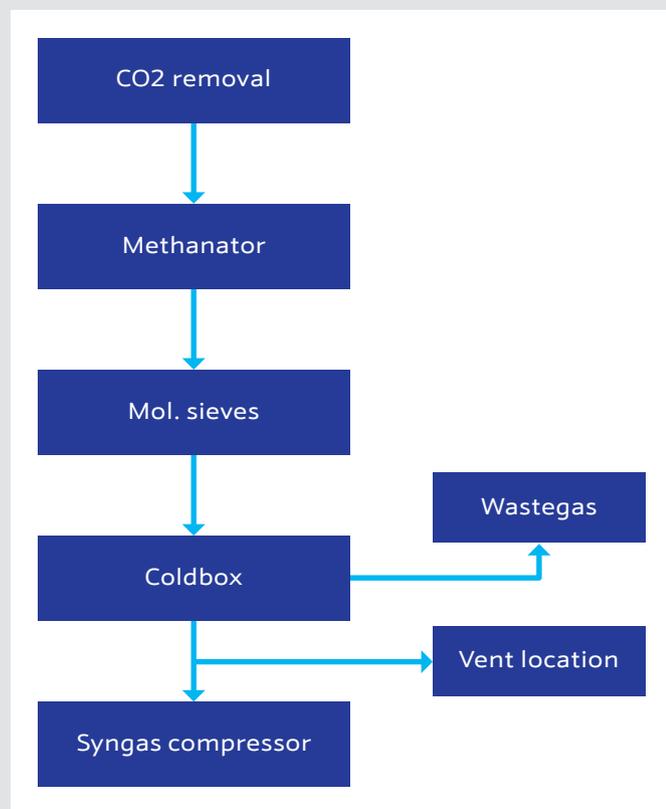


Figure 3: Overview Brown & Root synthesis gas purification

## Operating experience

The top 30 % of the catalyst bed was filled with pre-reduced KATALCO 11-4R catalyst. The remaining part was loaded with conventional KATALCO 11-4 catalyst.

### Reduction & Start-up

The reduction was carried out in different stages as recommended by Johnson Matthey Catalysts with their technical support to help to ensure:

- that the risk of nickel carbonyl formation was minimised, and
- to ensure that the catalyst was fully reduced and achieved the maximum catalyst activity.

Although favourable for the formation of nickel carbonyl, the procedure was carried out at 20 bar (290 psi) plant pressure. In normal start-up procedures, the partial pressure of CO is kept as low as possible by keeping the syngas compressor vent wide open and cracking the feedgas valve upstream.

In Figure 4, the development of the CO and CO<sub>2</sub> slip is indicated at the outlet of the methanator. One notices that after only 4 hours into the reduction, no CO<sub>2</sub> slip could be detected by lab analysis.

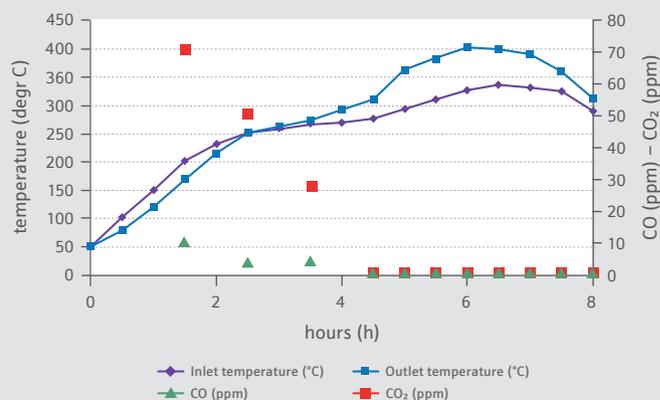


Figure 4: Low temperature methanator reduction

### Performance

At start-up, it was proven that the CO/CO<sub>2</sub> slip was lower than 1 ppm at 210 °C (410 °F). Afterwards, the temperature was set at 220 °C (428 °F). After 18 months of continuous operation, the CO/CO<sub>2</sub> slip is still lower than 1 ppm.

## Unexpected side reactions

### Higher hydrocarbons formation

Unexpectedly, detailed analysis of the synthesis gas leaving the methanator revealed the presence of higher hydrocarbons (ethane, propane, butane, pentane).

Analyses confirmed the higher hydrocarbons did not originate from the high temperature shift, as shown in Table 1.

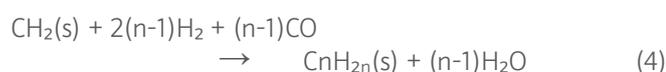
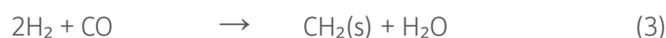
Outlet	C <sub>2</sub> H <sub>6</sub> ppm	C <sub>3</sub> H <sub>8</sub> ppm	C <sub>4</sub> H <sub>12</sub> ppm	C <sub>5</sub> H <sub>12</sub> ppm
HTS	<1	<1	<5	<5
Methanator	7	<1	0,04	0,007

Table 1: Initial analyses (220 °C / 428 °F) exit HTS and inlet methanator

After 1 year of operation, hydrocarbon formation continued on the same level. For completeness, it was checked that other hydrocarbons, such as ethylene and benzene, these were not formed above 1 ppb level.

### Fisher-Tropsch reactions

The formation of higher hydrocarbons on the methanation catalyst can only be explained by the occurrence of the Fisher-Tropsch reaction. The Fisher-Tropsch process is a catalyzed chemical reaction in which carbon monoxide and hydrogen are converted into hydrocarbons of various forms. In general terms, the reaction is a chain growth process described by the following equations:



In this path, the formation of a C1 intermediate is the first step in the formation of higher hydrocarbons (Reaction 3). Depending on the catalyst and the conditions, the C<sub>1</sub> intermediate can readily desorb from the surface of the catalyst resulting in the formation of methane (Reaction 5). The reaction observes fits classic Fisher-Tropsch theory with stepwise hydrocarbon chain growth occurring (Reaction 4) with CH<sub>2</sub> as the monomer species. Plotting the occurrence of distribution of the different C<sub>n</sub> chain lengths formed (Reaction 6) gives an Anderson-Schultz-Flory distribution (Figure 5), the linear nature of this plot is typical for Fisher-Tropsch reactions.

Typical catalyst materials used for the commercial application of the Fisher-Tropsch reaction (synthetic fuel production) are iron and cobalt. Ni has a much higher selectivity for the methanation reaction, although some authors (see reference 1) report the formation of higher molecular weight hydrocarbons at temperatures less than 280 °C (536 °F).

As in conventional Fisher-Tropsch synthesis, lower temperatures favor C<sub>2+</sub> formation. Yara confirmed this observation in practice, after 1 year of low temperature operation. Results, at different inlet and outlet temperatures of the methanator are summarized in Table 2.

In/outlet Temp °C	C <sub>2</sub> H <sub>6</sub> ppm	C <sub>3</sub> H <sub>8</sub> ppm	C <sub>4</sub> H <sub>10</sub> ppb	C <sub>5</sub> H <sub>12</sub> ppb
215/241	8.4	<1	60	11
225/253	6.7	<1	40	9
235/262	6.7	<1	30	6
245/272	6.3	<1	23	5
255/282	3.7	<1	18	5

Table 2 Temperature dependency of FT-reactions

In all cases the selectivity to methane is very high (> 98%), and the extent of chain growth is very low. Looking at the data, it seems that the formation of C<sub>2+</sub> molecules over a nickel catalyst is negligible at temperatures higher than 280 °C (536 °F). However, although the data is limited, the C<sub>2</sub>-C<sub>5</sub> product yield seems to follow an Anderson-Schultz-Flory distribution across the range of temperatures investigated (see Figure 5). It is concluded that, even at the highest temperatures investigated, the product distribution is determined by the relative rates of methane desorption and the rate of chain growth, rather than subsequent hydrogenolysis of any higher hydrocarbons formed in the Fischer-Tropsch reaction.

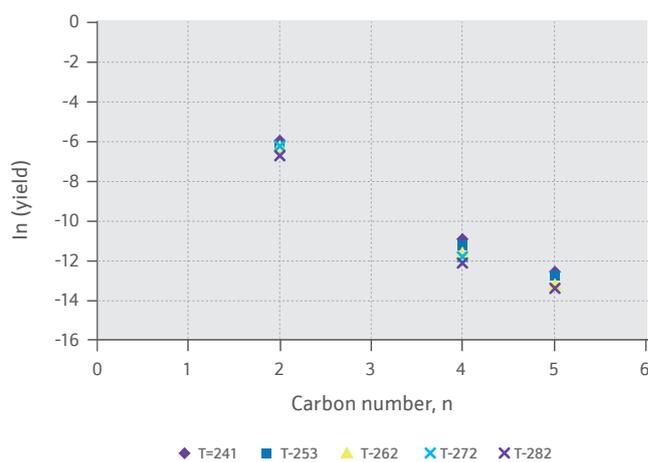


Figure 5 Anderson-Schultz-Flory Plot

### Impact on the ammonia production process

In the Brown & Root process (Figure 3), the methanation step is succeeded by a drying step of the synthesis gas, using molecular sieves (UOP 13X). Analyses show that ethane and propane are not absorbed, whilst butane and pentane are (see table 3). In the regeneration step of the sieves, butane and pentane traces end up in the primary reformer fuel gas.

Outlet	C <sub>2</sub> H <sub>6</sub> ppm	C <sub>3</sub> H <sub>8</sub> ppm	C <sub>4</sub> H <sub>10</sub> ppb	C <sub>5</sub> H <sub>12</sub> ppb
Meth.	8.4	<1	60	11
Mol. sieves	8.2	<1	<5	<5

Table 3: Analyses outlet Methanator and Mol. Sieves at 215 °C (419 °F)

## Sieves

Ethane and propane are entering the cold box. At the cryogenic temperatures of -175 °C (-283 °F), both components are liquefied in the rectification column and removed as waste gas (after evaporation). This waste gas is sent to the primary reformer as fuel gas. Malfunctioning of the cold box would cause minor ethane slip to the synthesis loop, without further consequence.

Luckily, the molecular sieves remove butane and pentane, because both components have the potential to freeze out in the cold box.

## Summary & Conclusions

Following conclusions can be drawn after the operation of a methanation catalyst at temperatures of 220 °C (428 °F):

- Due to operation with the new catalyst charge at low temperatures, C-0.5 Mo steel equipment is now operating with a safer margin below the Nelson Curve.
- An energy gain of up to 0,15 GJ/MT (0,142 mmBTU/MT) is realised by 100 bar (1450 psi) steam savings.
- At 210-220 °C (410-428 °F), it is achievable in practice to run with a CO/CO<sub>2</sub> slip below 1 ppm with a high percentage Nickel catalyst. This has been proven for a runtime of over 18 months, but is expected to last much longer.
- Higher hydrocarbons are formed to a certain extent by Fisher-Tropsch reactions. These reactions occur over the Ni catalyst at temperatures below 280 °C (536 °F). The rate of formation increases with decreasing temperatures.
- In traditional ammonia plant designs, the higher hydrocarbons would end up in the synthesis loop purge. In a Brown & Root design, ethane and propane are captured in the cryogenic purification unit. Butane and higher hydrocarbons are captured by the molecular sieves.

## Acknowledgements

The author thanks shift supervisors Etienne de Schepper and Theo van Deurzen for their eagerness to try this new operation mode. Johnson Matthey is thanked for their technical support in helping to select and start-up of this catalyst, as well as the detailed information on the Fisher-Tropsch reactions.

## References

1. Fisher-Tropsch Selectivity of Ni/Al<sub>2</sub>O<sub>3</sub> Catalysts  
G A Hadjigeorghiou & J T Richardson Applied Catalysis, 21(1986) 11-36 Elsevier Science Publishers

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Billingham, UK  
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