

Impact of high CO₂ content in natural gas

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Summary

Most of the production of bulk chemicals like ammonia and methanol uses natural gas as feedstock and fuel. Especially the reforming process requires a high amount of energy and the chemical products are themselves energy, which makes the production of these molecules highly energy intensive. For these reasons, the CO₂ emissions from methanol and especially ammonia production are significant.

CO₂ is considered as a greenhouse gas (GHG) and with today's fossil fuel consumption, the impacts on climate changes are apparently bigger than anticipated. At Haldor Topsoe, we work hard to improve plant efficiency by utilising the natural resources in the best and most efficient way.

What is the impact on the ammonia and methanol plants in case the natural gas contains more and more CO₂?

This paper will go through how the CO₂ can be utilised to produce methanol or ammonia, and also co-production of ammonia and methanol. It will show how the overall CO₂ foot print can be reduced for the same production capacity.

Key words: High CO₂ content, ammonia, methanol, urea, IMAP™.

1. Ammonia and urea production

For the ammonia plant, the additional CO₂ would normally not add any value because CO₂ is just considered as an inert costing some energy to remove. In worse cases with additional CO₂, the reformer and/or the CO₂ removal section will become bottlenecks and the ammonia plant capacity will be reduced from current level. This will of course have an important impact on the business for plant owners.

In case of urea production then it can be beneficial to go from a lean natural gas to a natural gas containing more CO₂, because the ammonia and CO₂ production can be better balanced. With lean natural gas there would typically be too low carbon content so to balance ammonia and CO₂ production to produce urea some excess hydrogen will be used as fuel to reduce the ammonia production. By adding CO₂ more ammonia and urea can then be produced. There will of course be an upper limit for the CO₂ content before it becomes a problem for existing am-

monia/urea plants being designed for lower CO₂ content. When the limit is exceeded then it will end up in the same situation as for the ammonia plant, where bottlenecks in the reformer and/or CO₂ removal section limit the production capacity.

In order to mitigate the plant bottlenecks, we have to bring in additional energy resources not containing carbon. This is an opportunity to actually reduce the ammonia/urea plant's CO₂ footprint for the same urea production.

Reference is made to Figure 1, which is a block diagram for an ammonia to urea plant. By having too much CO₂ in the feedstock, the plant capacity will be reduced and CO₂ will be vented. This can be mitigated by introducing electrolysis producing hydrogen and oxygen for the ammonia process. By powering the water electrolysis unit with renewable energy, a partial energy substitution is made for natural gas by renewable energy. The hydrogen product from the electrolysis will then be used to balance the CO₂ and ammonia production to prevent any CO₂ venting. Overall the CO₂ emissions will be reduced because less fuel firing will be required for the primary reformer.

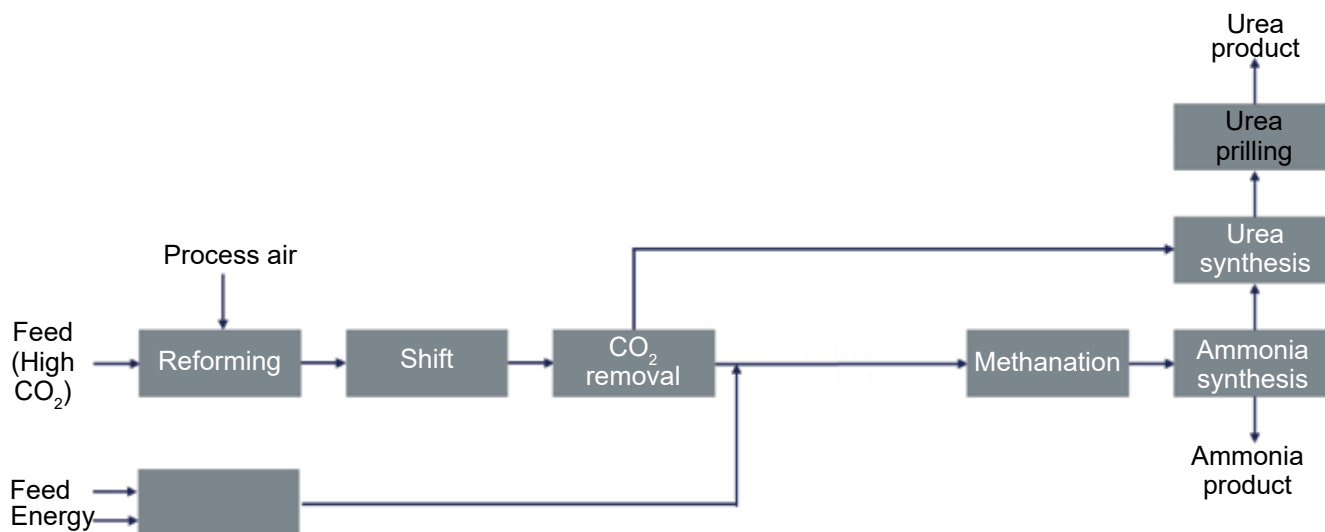


Figure 1. Ammonia to urea with addition of hydrogen

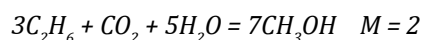
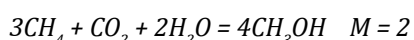
The optimum content of CO₂ in the feedstock for an ammonia/urea plant is depending on the composition of the natural gas. If it is lean gas then it is good to have a few percent, say up to 5% of CO₂. Whereas, if the gas is heavy, it is desirable not to have CO₂ at all in the gas. It is about balancing carbon and hydrogen in the syngas production.

When there is a very high CO₂ content in the gas, it is still practical to balance it with hydrogen produced from electrolysis. However, in order not to make too big changes to the existing plant, up to 10% of the hydrogen could come from electrolysis. An estimate of maximum CO₂ content would be around 20% depending on what the plant is initially designed for.

There is no doubt about water electrolysis being the future reforming. Presently, in many regions the power from a reliable grid is still more expensive than the equivalent energy from natural gas. There will be a lot of factors for the given plant, influencing at what cost the power should be available before revamp with electrolysis is economical feasible. A good rule of thumb is when the price ratio is one between gas and power. In Asia, the production cost of renewable power is lower than the cost of natural gas.

2. Methanol production

Together with CO and hydrogen, CO₂ is one of the reactants for methanol production. This means it can be an advantage to have a high CO₂ content in the natural gas feedstock. The below equations show the optimal amount of CO₂ content can be up to 25% for methanol production.



For syngas production from natural gas reforming, we typically distinguish between three different designs of reforming.

- One step reforming is the simplest as only a fired tubular reformer is required. For a low CO₂ containing feed gas, this will typically give a syngas being over-stoichiometric in hydrogen, which gives a high purge rate from the loop. This purging results in having a fuel gas to the reformer being rich in hydrogen. The syngas is less reactive due to high CO₂ to CO ratio.

- Two-step reforming consists of a primary reformer and an oxygen fired secondary reformer. With this design, the syngas composition can be adjusted by steam-to-carbon ratio and oxygen amount to give a stoichiometric syngas having a module of 2.0. The reactivity of the syngas is higher than that for one step reforming, resulting in smaller methanol reactors and typically lower specific energy consumption.

- Autothermal reforming (ATR), or with Topsoe terminology SynCOR™, is without a primary reformer and consists of only an oxygen fired reactor, giving typically a slight under-stoichiometric syngas composition. This requires recovery of hydrogen from the loop purge gas in order to make a stoichiometric syngas in the loop. This design gives the highest reactivity of the syngas because the CO to CO₂ ratio is the highest.

The Table 1 summarises the syngas module for the three different reforming designs and if they are suitable for either CO₂ import for injection or simply high CO₂ content in the feedstock.

Table 1. Comparison of reforming designs for methanol production

Reforming	Syngas Module	Suitability for CO ₂ import	Capacity gain CO ₂ import
One-step	Over stoichiometric	Very	10 - 20%
Two-step	Ideal module	NA	NA
ATR	Sub stoichiometric	NA	NA

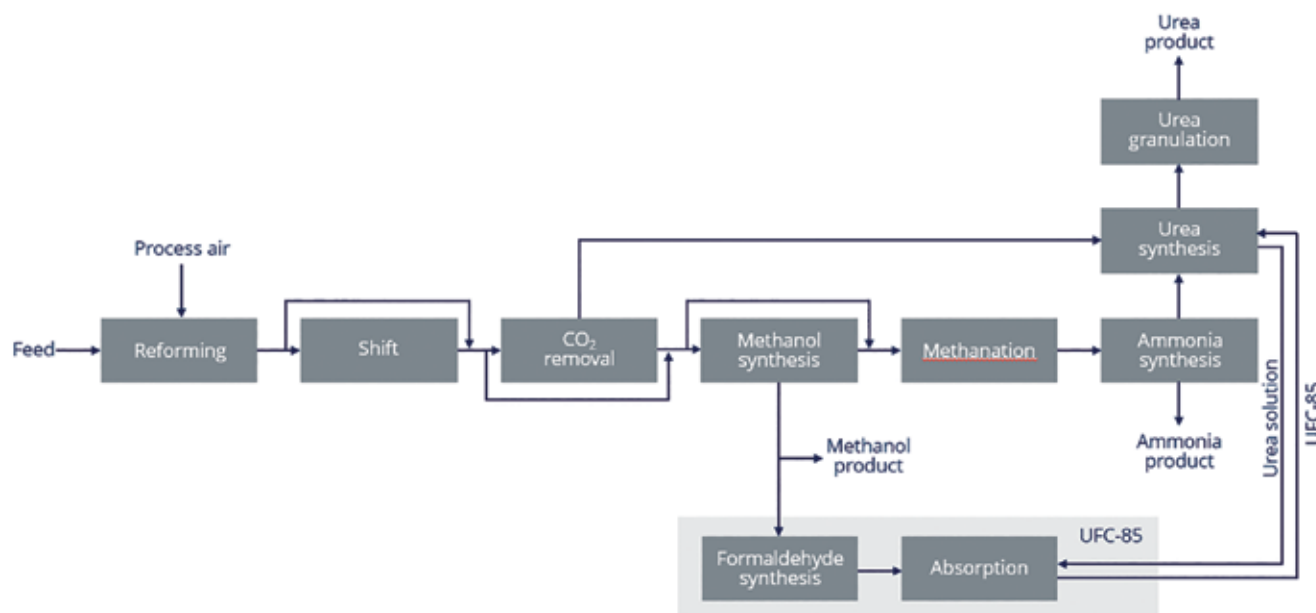


Figure 2. IMAP ammonia+™ process design

As it can be seen, the one-step reforming is very suitable for feedstock with high CO₂ content to compensate for the typical over-stoichiometric syngas module.

3. IMAP™

Today, Topsoe’s IMAP™ (integrated methanol & ammonia process) portfolio consists of 3 different process solutions: IMAP ammonia+™, IMAP methanol+™ and IMAP urea+™.

IMAP ammonia+™ is an ammonia plant with an in-line methanol synthesis, where the methanol capacity can vary from 0 - 35%. IMAP methanol+™ is a methanol plant having an ammonia synthesis downstream operating at similar pressure as the methanol synthesis. This is a very cost-effective co-production plant because it is the simplest process with very limited flexibility on product split being around 80/20 methanol/ammonia. IMAP urea+™ is the most flexible product split on three products: ammonia/urea/methanol. It can be designed with the required product split flexibility, and it will typically require higher investment compared to the other two IMAP solutions.

In the following, the process solution of an IMAP ammonia+™ plant will be described. The technology is

equally suitable for grassroots plants as well as revamps, where a methanol synthesis unit is added to an existing ammonia plant. The IMAP ammonia+™ solution is typically configured to provide a product flexibility ranging from 100% ammonia and up to 35% of the capacity being substituted by methanol. If only ammonia is needed, the methanol unit is simply by-passed.

The block diagram in Figure 2 summarises the different process steps to co-produce ammonia and methanol for downstream granulated urea.

3.1. Advantages of IMAP™ co-production

The choice of the ammonia and methanol co-production concept can be an important strategic decision providing added value to plant owners. It should be considered in cases where opportunities exist, such as import substitution or local off-takers of methanol and/or UFC-85.

A urea granulation plant requires UFC-85 as coating material for granulated urea. The co-production process is a convenient way to supply the UFC-85 plant with methanol produced locally. Specific opportunities exist in remote areas or cold sites where, due to high viscosity of

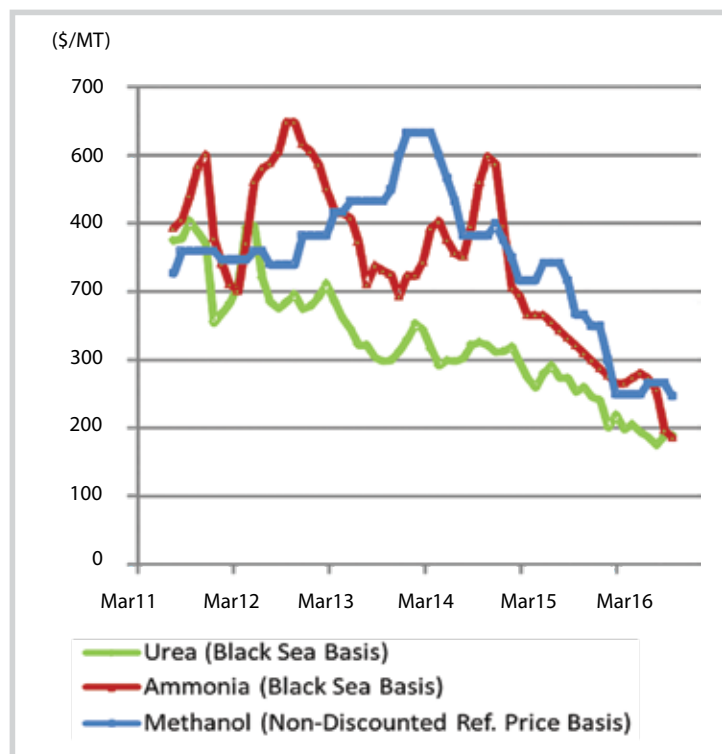


Figure 3. Market product price

Table 2. CAPEX comparison

	Two stand-alone units	Ammonia+™
#reforming units	2	1
#syngas compressors	2	1
NG consumption index	102	100
Relative investment cost index	115 - 125	100

UFC-85, it is difficult to procure and transport UFC-85 or methanol as an imported chemical.

As an alternative to two stand-alone ammonia and methanol plants, an IMAP™ co-production facility offers the advantage to produce multiple products without the often prohibitive cost of installing and operating a second plant. Diversifying the product portfolio offers plant owners the possibility to maximise their profits by meeting changing market needs as they arise and as prices fluctuate, as seen in Figure 3.

At a point, when having high CO₂ content in the natural gas feedstock for IMAP plants, it would be beneficial to have an electrolysis unit to compensate for less hydrogen production from the reforming to keep the full flexibility of the plant.

By powering the water electrolysis unit with renewable energy, a partial energy substitution is made for natural gas by renewable energy. Overall the CO₂ emissions will be reduced because less fuel firing will be required for the primary reformer.

3.2. Estimated savings for IMAP

The below table is showing a comparison of CAPEX for IMAP ammonia+™. The specific energy consumption per ton of products is very similar for IMAP as for stand-alone plants.

4. Conclusions

High CO₂ content in natural gas feedstock can impact negatively on existing ammonia and methanol plants resulting in capacity reduction or higher energy consumption. For existing plants as well as for new plants, the high CO₂ content can be addressed for all technologies discussed above and will always depend on the given case. In Topsoe, we have a long tradition designing for all kinds of natural gas composition, and for revamping existing plants to handle major changes in the feedstock composition.

One of the latest design options is the use of renewable energy for substitution of natural gas via introduction of electrolysis. This will reduce the overall CO₂ footprint of the ammonia and methanol as well as for IMAP plants.

The most mature electrolysis technology is the alkaline electrolysis and has been proven for approximately 100 years. It provides hydrogen and oxygen purity suitable for use in ammonia and methanol production.

Topsoe's way of utilising electrolysis in the process for ammonia and methanol plants is patent pending.