

# Air Products' Ammonia Cracking Process

*Report prepared for the MER (EIA) Committee for the Air Products Rotterdam Renewable Hydrogen Facility project*

## 1. Introduction

The Rotterdam Renewable Hydrogen Facility (RRHF) will feature the implementation of Air Products' ammonia cracker design (sometimes called an ammonia dissociator or ammonia reformer). This is a hydrogen production unit designed to convert ammonia into a hydrogen stream and purify it further into a product suitable to power a fuel cell, or for other end uses as needed.

Ammonia has been determined by Air Products to be the preferred way to transport hydrogen over long distances in the near to mid-term, particularly where shipping by sea is required. Ammonia has a higher energy density than liquid hydrogen or LOHC (Liquid Organic Hydrogen Carrier – an organic liquid that can capture and then release hydrogen molecules). While ammonia is already safely shipped in large volumes (18-20 million tons per year worldwide <sup>(1)</sup>), liquid hydrogen ships are only in early stages of development and although LOHC can be shipped in conventional oil tankers, the infrastructure to extract the hydrogen from LOHC has yet to be commercialised.

## 2. Existing Ammonia Cracking Landscape

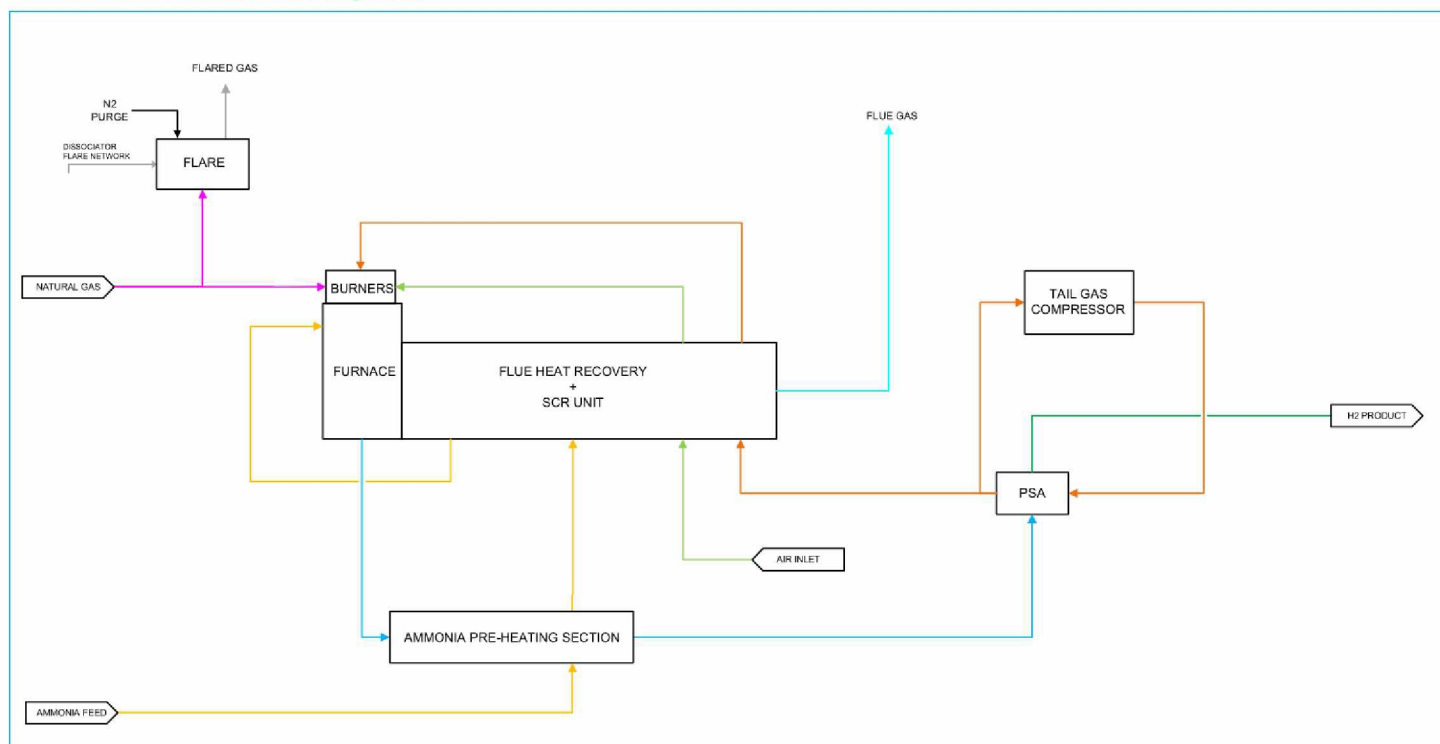
Up until recently, most commercially available ammonia crackers have been small electric-based furnace solutions at a production capacity ranging from 1 to 2 t/d hydrogen. These commercial units usually produce a forming gas ( $H_2$  and  $N_2$  mixture) for various industrial applications and rarely include any additional steps to produce hydrogen at high purities. The design focus for these units is conversion and as such they operate at high temperature and low ammonia feed pressure. This operational philosophy is not compatible with a process required for low carbon hydrogen production, which would require a higher pressure to feed the downstream process. The electric based furnace solution currently employed in commercially available small-scale crackers is not compatible with the low Carbon Intensity requirements of low-carbon hydrogen. These commercial offerings have poor thermal efficiency which results in increased Carbon Intensity of the hydrogen product, as these small-scale solutions typically lack heat integration and require compression of the hydrogen product to reach pressures required for utilisation.

In addition to these small crackers, there have been five large ammonia crackers built in the 1980s, the largest of which is still operating in Argentina. That cracker runs periodically and can produce over 500 t/d hydrogen. This type of cracker was not designed with the efficiency required for a low carbon process, and cannot be replicated to make low carbon hydrogen, particularly as the hydrogen produced was not purified after cracking but rather combusted. That cracker was also designed to process fully anhydrous ammonia, i.e. without any water content, whilst modern crackers need to handle commercial ammonia which always contains a small amount of water (typically 0.2 to 0.5 wt%) to mitigate the risk of corrosion cracking in storage tanks. Large scale production units capable of producing fuel cell grade purity hydrogen in large quantities have been designed and evaluated as part of academic studies and several companies have now designed and engineered their own solutions and are in the process of developing pilot units.

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<sup>(1)</sup> [Will the Ammonia Shipping Market Boom? \(maritimeoptima.com\)](https://maritimeoptima.com)

### 3. Process Description



In the Air Products' cracker design, ammonia is pressurised to around 40 bar before being fed through a series of heat exchangers, which pre-heat and vaporise the ammonia, before entering the reaction section at an elevated temperature of 500 to 600°C. The ammonia is reacted endothermically to produce nitrogen and hydrogen in catalyst-filled reactors. The core of the production unit consists of catalyst-filled tubes inside a fired furnace, which is similar in design concept to a Steam Methane Reformer (SMR). The catalyst facilitates the ammonia to hydrogen reaction. Additional heat exchangers are in the furnace convection section to recover energy from the flue gas.

The hydrogen leaving the reaction section is purified in a pressure swing adsorption (PSA) unit to 99.97mol% hydrogen purity before being sent to downstream users. The PSA consists of multiple beds which operate in cycles to allow adsorption and regeneration of different vessels in parallel. The tail gas from the PSA, containing separated nitrogen, ammonia and some residual hydrogen, is sent to the furnace burners to reduce the natural gas demand. A tail gas compressor is used to recycle a portion of the tail gas to the PSA feed, to increase the overall recovery of hydrogen from the cracked ammonia in the purification step.

The primary fuel source for the furnace in normal operation at high hydrogen recovery is natural gas, which is supplemented with tail gas from the PSA; this reduces the Carbon Intensity of the process. The furnace convection section includes an SCR (Selective Catalytic Reduction) unit to reduce NO<sub>x</sub> to an acceptable level before discharging flue gas to the atmosphere. It is also possible to operate the cracker at low hydrogen recovery by reducing the tail gas recycle or switching off the tail gas compressor altogether; this increases the amount and hydrogen content of the tail gas to the furnace, thus reducing the natural gas demand (which is no longer the main fuel in terms of furnace duty) and further reducing the Carbon Intensity of the process. All of the crackers being developed by competitors face the same compromise: either achieve a high recovery of hydrogen from ammonia (whether that ammonia is used as process feed or fuel to the burners) and rely on natural gas, or another external fuel, as the main fuel to the burners, or reduce or eliminate natural gas fuel at the expense of reduced conversion of hydrogen from ammonia. This requires balancing hydrogen recovery, and so cost of the produced hydrogen, against the Carbon Intensity associated with the use of natural gas. Air Products' ammonia cracker was designed to be flexible to operate in a high recovery mode, with higher levels



of CI and natural gas use, or low recovery mode, with lower CI and natural gas use. Which operating mode is used depends on the needs of the market and future REDIII requirements.

A complete reduction to zero of natural gas use (replaced by either more tail gas, some hydrogen product or some ammonia feed) is not deemed feasible for first implementation to ensure safe and reliable operating conditions across the range and during transients. Completely removing natural gas may affect burner flame stability (a performance and operability issue, but also a potential safety concern) and possibly affect the controllability of the plant. However, eliminating natural gas as a fuel is a concept that is being developed for future crackers.

#### 4. Technology Highlights of Air Products' Ammonia Cracker

Air Products' ammonia cracker technology is the subject of numerous patent applications covering several aspects of the innovative features of the process. While all ammonia cracker designs ultimately carry out the same reaction and aim to minimise energy usage and emissions, Air Products' design features the following technical advancements:

1. The process design of the furnace is based on decades of SMR experience informing critical design parameters such as the heat flux distribution profile, heat losses and pressure drops.
2. The furnace burner design also benefits from Air Products' extensive experience in designing and commercialising burners for various applications. The cracker burner design is novel (compared for example to SMR applications) because it needs to achieve reliable operation and flame stability throughout the process operating envelope, while minimising NO<sub>x</sub> formation from hydrogen and ammonia combustion. This enables the process to burn varying amounts of ammonia-containing tail gas from the PSA, unlocking the potential to reduce the Carbon Intensity of the process and reliance on natural gas as a fuel in the future.
3. The catalysts used to facilitate the cracking reaction have been selected to minimise the required operating temperature in the furnace tubes, which is significantly lower than in comparable SMR applications. This is done to mitigate the risk of metal nitridation of the catalyst tubes, a known corrosion mechanism in presence of ammonia at high pressure and temperature, which has only been studied and characterised at relatively mild temperatures.
4. The mild operating temperatures are achieved even though the process operates at high pressure (higher pressures reduce ammonia conversion, which can be compensated for by higher temperatures), thus avoiding the need of a hydrogen product compressor for most applications.
5. The process has been integrated to recover the maximum available heat from all sources, including hot cracked gas, furnace flue gas as well as the tail gas compressor waste heat. This results in a negligible amount of external cooling required during normal operation, and in a flue gas temperature at the stack limited only by the acid gas dew point for the stream (this is a hard limit to prevent significant corrosion in the convection section).
6. The process has no associated steam system, which significantly simplifies the design compared to an SMR (or possibly, alternative ammonia cracker designs). Steam is not required by the process, either as a reactant or as a heating or stripping medium (more on this below), since all heat recovery can be done directly from cracked gas and flue gas. In the design used by some competitor technologies, steam is generated in the process. In Air Products' design, that heat is used in the process to crack more ammonia to hydrogen.
7. The PSA is a novel design developed by Air Products, capable of withstanding and removing ammonia from the cracked stream. Air Products has an advantage over many of our ammonia cracker competitors in that we have in-house adsorption expertise that has allowed us to develop a PSA solution to purify hydrogen in the presence of ammonia, building on decades of experience with H<sub>2</sub> PSAs used in SMRs. This is a significant advantage of Air Products' design compared to some other ammonia cracker designs which rely on water scrubbing to remove ammonia before the cracked stream is purified in a traditional H<sub>2</sub> PSA since it allows both nitrogen and ammonia to be removed from the cracked gas stream in a single PSA system,

eliminating the need for a water-based ammonia scrubber and stripping column. This approach reduces capital costs, significantly improves energy efficiency and reduces waste as no large amounts of wastewater are produced. Other ammonia cracker providers purify the cracked ammonia in two steps: first a water wash column is used to remove ammonia by physical absorption, and then an adsorption system is used to remove water and nitrogen. This is less efficient for several reasons:

- a. The ammonia-containing water from the scrubbing column needs to be recycled in a stripping column, to recover the ammonia and recycle the water so that it can be returned to the adsorption column. This stripping column typically has a reboiler heated by steam, or by using heat directly from the process, heat which in the Air Products process is used to crack ammonia. The heat duty for this reboiler requires significant energy, which can either be sourced externally, directly or indirectly using steam, or recovered from the cracking process (thus reducing the amount of energy that can be recovered into the reagents) – reducing the efficiency of the process or increasing its Carbon Intensity (or possibly both). In contrast, Air Products' single separation step requires virtually no thermal energy (as it is pressure driven). As a result, essentially all the recoverable heat can be used to preheat feed and fuels, maximising the process efficiency.
- b. If steam is raised for this treatment step, requiring an assortment of additional equipment which introduces more heat losses, it may also be used as heating medium in other services, which is less efficient than exchanging heat directly against cracked gas and flue gas. Air Products' design does not include or require a steam system.
- c. The water scrubbing process may generate an ammonia-contaminated wastewater stream, which will require either disposal (which is an environmental burden) or further processing to obtain a treated wastewater stream that can be discharged. In contrast, Air Products' single separation step produces no waste streams.

The following table summarises some of the key ammonia cracker design parameters:

Capacity (H <sub>2</sub> product)	t/d	35
Product specification		
H <sub>2</sub> purity	%mol	> 99.97
NH <sub>3</sub> content	ppmv	< 0.1
N <sub>2</sub> content	ppmv	< 10
delivery pressure	barg	> 30.5
Hydrogen yield <sup>(1)</sup>	%	typically <sup>(2)</sup> 82.8 – 92.5
Turndown	%	50
Energy efficiency <sup>(3)</sup>	%	~ 95

<sup>(1)</sup> Defined as ratio of hydrogen in product stream over total hydrogen (as H<sub>2</sub>) in ammonia feed.

<sup>(2)</sup> The actual value will depend on the recovery mode selected in operation and may generally vary within the range provided.

<sup>(3)</sup> Defined as the ratio of product energy content (LHV basis) over total energy into the process (feed and fuel stream energy content on LHV basis + electric power).