JM

Johnson Matthey's world scale ammonia cracking process

John Pach, Johnson Matthey

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Johnson Matthey (JM) has developed an ammonia cracking process which is suitable for deployment for large scale hydrogen (or cracked gas) production. It has been developed using JM's core competencies of catalyst design, process design and chemical plant scale up to de-risk the technology.

The key unit operations are the ammonia cracker which decomposes ammonia to hydrogen and nitrogen, and the separation system which purifies the hydrogen product. The ammonia cracking reactor is similar in principle to a steam-methane reformer (SMR), and JM has applied significant experience from its market leading position in designing SMR's for the methanol industry. Sensible and reaction heat is supplied to the process via combustion of a fuel. Heat is recovered at the exit of the cracker and exit of the flue duct through heat integration within the process; this is a common approach within SMR based processes which has been adapted to the lower temperature conditions associated with the ammonia cracking flowsheet. Abatement technologies are installed within the flue duct to minimise emissions such as NOx and N_2O.

In a departure from established technologies, JM's ammonia cracker is fuelled by a blend of ammonia, hydrogen, and nitrogen. This removes the requirement for an external fuel or energy source, with the fuel derived from the pressure swing adsorption (PSA) tail gas and a portion of the ammonia fed to plant. JM has tested the combustion characteristics of these novel fuel blends, gaining insight into the flame characteristics and emissions associated with the departure from combusting natural gas. To purify the hydrogen stream, a combination of ammonia scrubbing, and pressure swing adsorption have been selected, with both technologies proven at scale in similar industrial applications.

JM ammonia cracker

JM offers a top-fired ammonia cracker which has been developed from JM's world leading design for large scale SMRs. Key changes include catalyst and reaction chemistry, fuel composition, environmental controls, and metallurgy. Heat recovery from the flue duct has been configured to accommodate efficiency, controllability, operability, and capital cost considerations.

Catalyst selection

The cracker uses JM's established range of **KATALCO** 27 series of ammonia cracking catalysts, which have been offered commercially for over 50 years. **KATALCO** 27-200MQ is a nickel-based, high activity, ammonia cracking catalyst. The **QUADRALOBE** shape enhances radial heat transfer across the tube, and the shape of the pellet reduces pressure drop growth with time on-line.

Within a multi-tubular reactor, such as an ammonia cracker, the burners provide radiant and convective heat to the tubes. The endothermic nature of the ammonia cracking reaction leads to a radial temperature gradient across the catalyst filled tubes. The catalyst pellets help mix the bulk gas, promote heat transfer and minimise the aforementioned radial heat gradient within the tube. Formation of a gas film at the tube wall limits heat transfer, however, this can be managed with the correct catalyst pellet shape and size. A catalyst with good packing can disrupt the gas flow by causing more turbulent flow. By having a smaller gas film more heat is transferred into the catalyst to drive the endothermic reaction which can result in lower tube wall temperatures and a more efficient process.

Concerns have been expressed by the industry that the relatively small amounts of moisture contained within merchant ammonia can deactivate certain types of ammonia cracking catalyst. JM has conducted testing to confirm that this is not the case with **KATALCO** 27 series.

JM is also investing in extensive characterisation of the ammonia cracking reaction both for product development and to better understand aspects such as reaction kinetics, product activation and chemical inhibition. The driver for this work is that whilst existing small-scale applications can tolerate a degree of under or over performance, relatively small changes in performance will be critical to the economics of world scale ammonia cracking plants and it is essential that sufficient knowhow exists to allow such plants to be optimised at the design stage.

Ammonia combustion

Ammonia has been proposed as a fuel for many years. Although having a reputation for being difficult to burn and for generating high concentrations of nitrogen oxides there are some obvious advantages for deploying it as a fuel in an ammonia cracking process.

The use of ammonia as a fuel leads to synergistic benefits in that the process is more tolerant to ammonia slip from the cracker and there is no necessity for a high efficiency PSA unit. This is because, ammonia slip from the cracker and PSA off gas can be used as fuel for the ammonia cracker. The ammonia fuel saved can then be used as feedstock. Emission levels $<0.1kg\ CO_2-e/kgH_2$ can be achieved.

JM has commissioned full scale burner tests to verify the practicality of using ammonia as a fuel and to confirm emission levels. These have been carried out under a wide range of conditions including start-up, shutdown, and normal operation.

The results have been used to validate JM's design tools for use in designing ammonia crackers.

Ammonium nitrate and ammonium nitrite

Ammonium nitrate, and ammonium nitrite, can form when both ammonia and NOx are present at relatively low temperatures. Under the right circumstances, both can be explosive and there are many publicised examples in the nitric acid industry.

Although there should be little prospect of forming such substances during normal operation JM has mapped out a safe operating window which considers failure conditions and forms the basis of its ammonia cracker design. JM has also filed patent applications on the topic.

Metallurgy

JM has selected metallurgies that have been demonstrated in relevant service and has also used computational materials engineering to further its understanding of alloy degradation under ammonia cracking service. In addition, JM is conducting materials test work to further validate and enhance its understanding of the performance of alloys in ammonia cracking service. Patent applications have also been filed relating to techniques which can be used to reduce the severity of nitriding.

Emission control

JM is a leader in emissions control technology and is ideally placed to optimise the development and placement of emission control products within an ammonia cracking flowsheet. The pollutants of concern are acid forming oxides of nitrogen, ammonia and nitrous oxide and JM has solutions to meet regulatory requirements.

- **Acid forming oxides of nitrogen (NOx):** As might be expected, the presence of ammonia in a fuel tends to promote the formation of NOx. In JM's ammonia cracking process, the resulting NOx concentration remains within JM's range of experience and abatement solutions are available to achieve any known regulatory standard.
- **Ammonia (NH_3):** JM has offered ammonia abatement products for many years and JM's abatement solution design meets known regulatory standards.
- **Nitrous oxide (N_2O):** JM has offered N_2O abatement products for many years. Test work has been carried out to extend the operating window of an existing product to allow optimised N_2O abatement within an ammonia cracking flowsheet

Cyclic operation

Cyclic operation poses a challenge in terms of both mechanical integrity and catalyst longevity. JM's ammonia cracking process has been designed to accommodate the fluctuations in plant load that will be required in a renewables powered economy.

Ammonia removal

JM chooses to remove ammonia upstream of the PSA unit. This has the advantage of allowing the PSA unit to be designed and optimised to remove less strongly adsorbed substances such as nitrogen. The ammonia that is recovered is used as fuel in the ammonia cracker, the net result being that overall performance of the plant is only weakly dependent on the performance of the ammonia cracker.

Pressure swing adsorption

Separation of hydrogen from the cracked gas stream is critical to achieve the required purity of the product stream.

PSA is a well-established separation technology that is proven at scale required for this flowsheet and can achieve hydrogen recovery rates of 90% or above. PSA units are used in existing hydrogen production plants and can achieve the required hydrogen purity level for this application.

The tail gas from the PSA unit contains nitrogen, unrecovered hydrogen and residual ammonia and is used as a fuel source for the ammonia cracker. PSA is selected over other types of gas separation processes due to the high capacity of unit required and high purity of hydrogen product (>99.96 mol-% can be achieved).

References

1. Pach J. Johnson Matthey):"World scale ammonia cracking", presented at Nitrogen+Syngas 2024, Gothenburg, Sweden, 4-6 March 2024.

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Billingham, UK
Tel +44 (0) 1642 553601
www.matthey.com

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