Increased steam methane reformer throughput

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Switching to a foil based catalyst technology raised throughput substantially for a hydrogen producer

Air Liquide delivers hydrogen and carbon monoxide to a wide range of companies in the refining and chemicals industry by operating more than 50 steam methane reformer (SMR) units worldwide. Each unit is designed to respond to demand which can vary over time. Amongst its fleet, Air Liquide has a 12-tube SMR in Roussillon, France. The plant's nominal hydrogen capacity was reached with conventional reforming catalyst and could not be increased any further due to the limitation of the reformer flue gas temperature. However, in 2015 the customer foresaw an increase in its hydrogen consumption. Accordingly, Air Liquide was required to investigate solutions to debottleneck the plant.

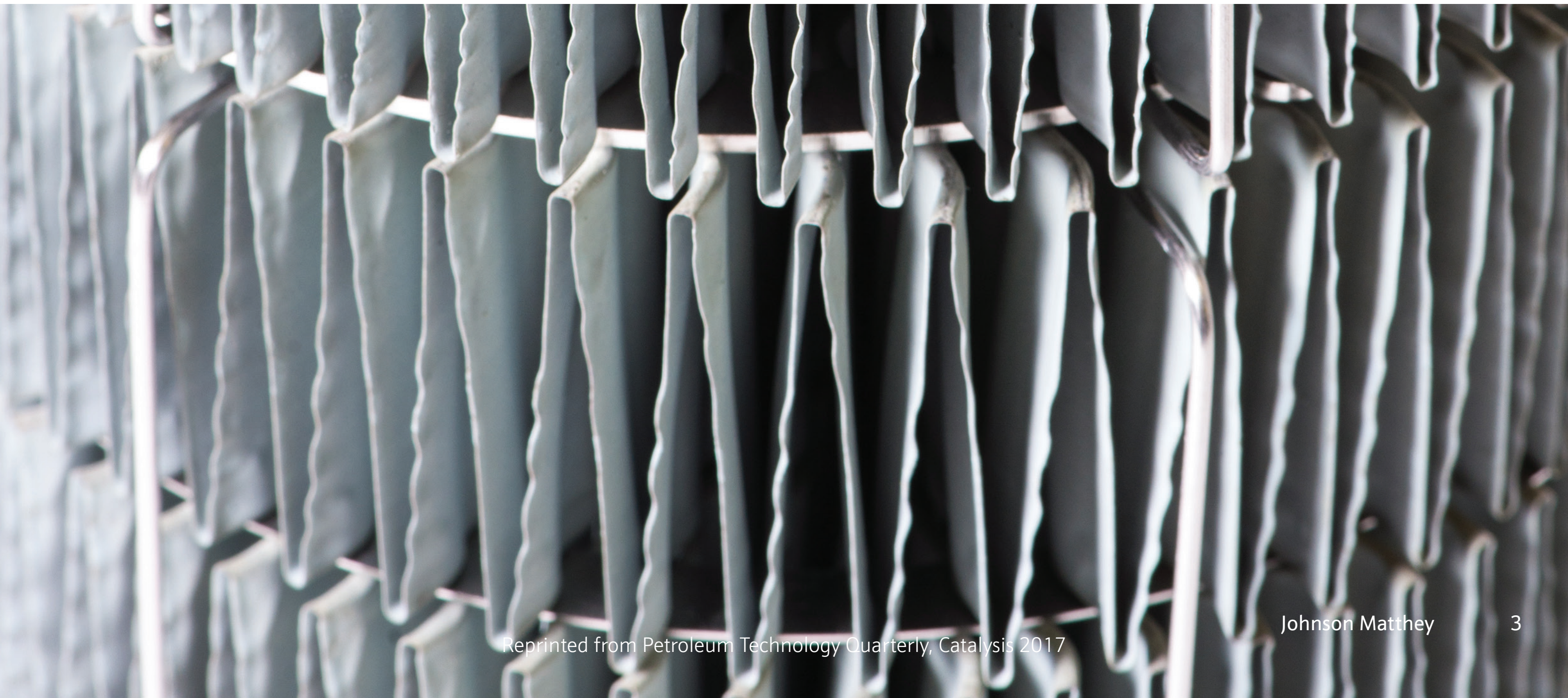
Air Liquide approached Johnson Matthey which has been involved in the development of steam reforming catalysts for many decades. Johnson Matthey identified its recently commercialised **CATACEL**™ **SSR**™ as a possible solution. This next generation reforming catalyst is a coated, foil based alternative to metal impregnated ceramic pellets. Simulations suggested the enhanced heat transfer, activity and pressure drop properties would allow the reformer throughput to be increased by the desired rate. In August 2015, the conventional pelleted catalyst was entirely replaced by **CATACEL SSR**, with the objective of increasing the production rate by 5%.

Roussillon SMR unit

The Air Liquide SMR plant in Roussillon was started up in 2010 (see Figure 1). It includes the following units: a hydrodesulphurisation unit, a reformer that comprises 12 reformer tubes with a diameter of 5in and one burner, a CO shift reactor, and a PSA unit for final product purification. The plant operates with a natural gas feed and has a nominal capacity of 2450 Nm^3/h of hydrogen with conventional catalyst.

The production rate was constrained by a high flue gas exit temperature which was close to its maximum value of 1000°C. This high flue gas temperature prevented increasing the process gas exit temperature.

Figure 1. Air Liquide steam methane reformer unit in Roussillon, France



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CATACEL SSR

For many years, catalyst impregnated ceramic pellet media has driven steam methane reforming reactions in hydrogen, methanol, and ammonia plants. Steam reforming catalyst design is a balance between many competing requirements and catalyst features such as strength, heat transfer, activity, pressure drop and avoidance of unwanted side reactions such as carbon formation. By adopting a foil based structure, **CATACEL SSR** breaks away from many of the limitations imposed by the use of ceramic pellets. It is a catalyst system that exhibits a higher activity, improved heat transfer, lower pressure drop and improved resistance to carbon formation all at the same time. Performance of this technology has been proven in the hydrogen market since May 2012.[1]

CATACEL SSR uses a special high temperature alloy as a substrate material. Alloy strip is formed into engineered foil structures called fans (see Figure 2). The fans are coated with a nickel based steam reforming catalyst using a proprietary process that ensures the catalyst remains attached to the surface of the foil during the catalyst lifetime. The fans are stacked one upon another in the reforming tube, separated by thin metal washers. The outer edges of the fans are located close to, but not touching, the internal surface of the tube.

The stacked fans deliver superior heat transfer by impinging gas on the internal surface of the reforming tube rather than relying on convective heat transfer mechanisms. During operation, gas flows down the tube and encounters the first fan structure. It cannot move through the fan and therefore it is forced out of the triangular ducts. The process gas thus jets directly onto the internal surface of the reformer tube, where it gathers heat. Having nowhere else to go, the gas flows around the edges of the fan and back into the triangular duct on the underside of the fan (see Figure 3). The washers that separate the fans from one another facilitate this flow back into the fan. Once inside the fan, the gas is free to move to the next fan in the stack and repeat the process.

The features of **CATACEL SSR** result in approximately 20-30% more heat transfer for the same (or lower) pressure drop when compared to traditional catalyst pellets. In addition, the fans offer 1.5 to 2.0 times more geometric surface area than conventional pellets. Thus it provides a step change in the achievable performance from conventional pelleted steam reforming catalyst. Figure 4 shows a comparison of the different generations of pelleted ceramic catalyst against **CATACEL SSR**.

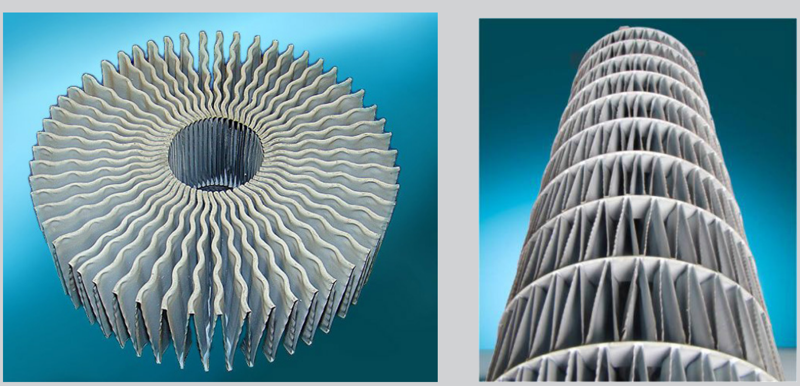

Figure 2. CATACEL SSR fan (left) and stack (right)

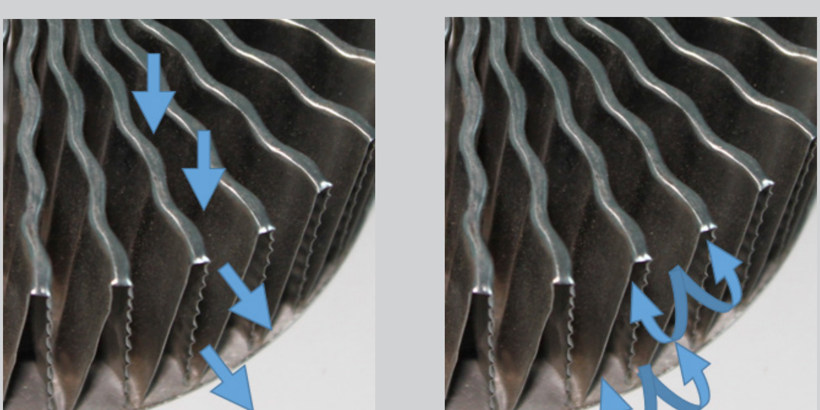

Figure 3. Gas forced out of duct and back into the underside vents

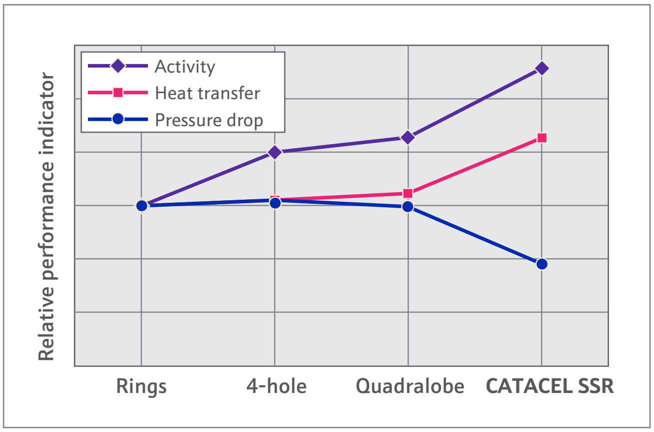

Figure 4. Relative performances of various steam reforming catalysts

Increasing hydrogen throughput by increasing reforming temperature		
	Conventional catalyst	CATACEL SSR
Flue gas temperature, °C	1000.1	997.5
Reformer exit temperature, °C	816	828.5
S/C	3.24	3.1
Pressure drop, bar	0.68	0.51
Dry syngas flow rate, Nm^3/h	4043	4178
Methane slip, mol%	6.7	6.2
Hydrogen production before PSA, Nm^3/h	2965	3078
Hydrogen throughput, Nm^3/h	2450	2490
Performances in capacity increase		
Increase in syngas flow rate, %	-	**3.3**
Increase in hydrogen before PSA, %	-	**3.8**
$T_{flue\ gas} - T_{syngas}$, °C	**184**	**169**

Table 1.

Installation at Roussillon

CATACEL SSR is supplied as preassebled stacks up to a metre long. The fans are mounted on a support structure that sits within the central space of the fans. This aids in the speed and accuracy of the catalyst installation.

As previously described, the outer edges of each fan must be located close to but not touching the inside tube surface and each stack must rest directly over the stack below without any gaps that could create hot spots. However, the internal surfaces of reformer tubes can be quite irregular, especially on plants that have been in service for some time. Hence the installation of **CATACEL SSR** is managed using patent protected deployment technology that forms part of the support structure along with patent protected installation tools and methodologies.

During the installation at Roussillon, each stack of fans was inserted in a compressed configuration and engaged with the stack (or support) below. Using compressed air, it was then expanded to bring the fan edges into the correct position versus the tube wall. Deposition was observed on the wall of some tubes but it was scraped off and did not inhibit the loading. The installation was completed according to schedule. Outage and pressure drop measurements during and on completion of the loading confirmed each stack had successfully interlocked with the stack below.

Increasing hydrogen throughput by increasing reforming temperature

The enhanced heat transfer provided by **CATACEL SSR** allows additional burner firing to take place before the maximum flue gas exit temperature is reached. Thus it is possible to achieve a higher reformer exit temperature for the same flue gas temperature. Consequently, following the installation at Roussillon the methane conversion is higher and the hydrogen production from the reformer is improved. Table 1 compares the conventional catalyst performances with that of **CATACEL SSR** for the maximum flue gas temperature allowed.

The increased capacities in syngas and hydrogen production before purification (by pressure swing adsorption, PSA) are 3.3% and 3.8%, respectively, compared to former operation. The increase in dry syngas flow rate is in line with predictions. Besides, this capacity enhancement is achieved at a lower reformer pressure drop than with conventional catalyst: 0.51 bar instead of 0.68 bar.

The heat transfer enhancement by **CATACEL SSR** is also highlighted by the lower difference between syngas and flue gas temperatures compared to conventional catalyst: initially 184°C, reduced to 169°C.

Increasing hydrogen throughput by increasing plant load

The previous case clearly indicates that additional burner firing is possible thanks to **CATACEL SSR**. The increased hydrogen production is achieved through a higher reformer exit temperature and thus a higher methane conversion. However, the hydrogen production of the unit can be increased more substantially by also increasing the plant load in addition to increasing burner firing. Table 2 summarises the performances of **CATACEL SSR** in this operating mode and compares it to operation with previous conventional catalyst under the limitation of the maximum flue gas temperature.

In this operating mode, the syngas flow rate is increased by 6.3%. The hydrogen throughput from the reformer is 5.7% higher. This capacity increase is achieved at a lower reformer pressure drop than with pellets: 0.57 bar instead of 0.68 bar.

Increasing hydrogen throughput by increasing plant load		
	Conventional catalyst	CATACEL SSR
Flue gas temperature, °C	1000	1000
Reformer exit temperature, °C	816	819
S/C	3.2	3.1
Pressure drop, bar	0.68	0.57
Dry syngas flow rate, Nm³/h	4043	4299
Methane slip, mol%	6.7	7.0
Hydrogen production before PSA, Nm³/h	2965	3135
Hydrogen throughput, Nm³/h	2450	2553
Performances in capacity increase		
Increase in syngas flow rate, %		**6.3**
Increase in hydrogen before PSA, %		**5.7**
$T_{flue\ gas} - T_{syngas}$, °C	**184**	**181**

Table 2.

Plant load		
Plant load range (dry syngas production)	Pellets (% of operating time)	CATACEL SSR (% of operating time)
Below 50%	4.2	2.0
51-70%	6.3	2.3
71-80%	13.4	38.2
81-90%	19.0	18.1
91-100%	57.1	14.9
101-105%	0.0	19.8
>105%	0.0	4.7

Table 3.

Performance over a year in operation

A year of operation with **CATACEL SSR** was achieved without any incident. Data was collected from September 2015 until September 2016 to compare with the performance of pellets over the year 2014. Plant loads for both time periods are shown in Table 3. As can be seen, the plant was operated at more than 100% load (with respect to dry syngas production) with the catalyst for an extended period of time. Obviously, the plant load is dependent on the operator's demand but the results clearly show that a maximum increase of hydrogen throughput by over 5% was successfully sustained.

Such an increase in production was possible because the flue gas temperature at the reformer exit remained below the threshold of 1000°C, even at 106% load. Figure 5 shows the decrease of flue gas temperature when the plant is operated with **CATACEL SSR** compared to operation with conventional pellets. For a load range between 91% and 100%, the flue gas temperature is decreased by up to 7°C, giving a margin to increase the plant hydrogen throughput.

The overall efficiency of the reformer and water gas shift section can be assessed by considering the total natural gas flow rate required to produce syngas. Figure 6 presents this data for different plant loads. The savings on natural gas with **CATACEL SSR** are high thanks to better conversion in the reformer due to higher reforming temperatures, and lower fuel consumption due to increased heat transfer in the reformer. Savings are in the range of 3-4% for loads between 80% and 105%, even reaching 5% at a load of 106%.

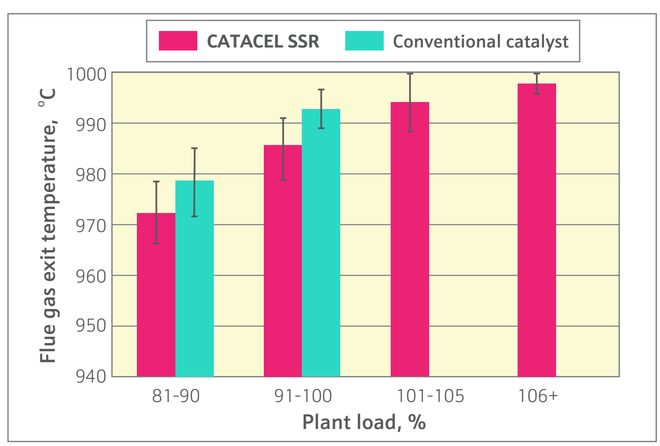

Figure 5. Comparison of flue gas exit temperature for various plant loads

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Conclusions

Hydrogen is used in oil refineries, chemical plants and in clean transportation solutions. Due to changing market conditions there is a greater need to be able to operate flexibly, robustly and efficiently to meet the user's needs. As a world leader in gases, technology and services for industry and health, Air Liquide is always striving to explore process improvements and thereby exceed customer expectations.

Steam reforming remains the dominant process for the production of hydrogen. Despite being a mature process there is still an opportunity to employ innovative technologies to drive improvement. Structured **CATACEL SSR** technology represents the next generation of steam reforming catalysts offered by Johnson Matthey, delivering a significant improvement in performance compared to traditional pelleted catalysts. Adoption of the catalyst has shown the benefits of cooler tubes with lower methane slip and lower pressure drop. Whilst greater benefits may be achieved with a reformer designed around the catalyst,[2] even for existing plants it can improve performance that can then allow the unit limits to be overcome.

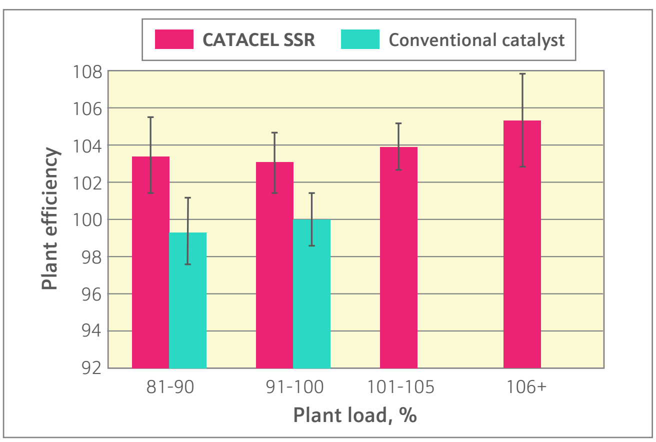

Figure 6. Plant efficiency (syngas flow/total natural gas flow) at various loads

Collaboration between Air Liquide and Johnson Matthey facilitated an understanding of the end user requirements, identifying the existing bottlenecks and possible solutions. Although the SMR at Air Liquide's Roussillon plant is tailored for conventional pelleted reforming catalyst, the benefits of the coated foil based structure to overcome the previously observed limit on flue gas exit temperature were demonstrated. **CATACEL SSR** catalyst has and continues to demonstrate that it is mechanically and chemically robust over a range of operating conditions. Assessing the reduction in total natural gas usage at different plant rates, Air Liquide has been also able to validate the increased plant efficiency and highlight the long term value. By employing the novel catalyst, the required 5% increase in throughput was achieved successfully and without incurring any capital cost to modify the plant equipment as otherwise may have been necessary.

References

1. Farnell P, Whittenberger W, Foil supported catalysts deliver high performance in steam reformers, Nitrogen + Syngas 2015 International Conference, Istanbul, Feb 2015.

2. Whittenberger W, **CATACEL SSR** novel structured catalysts for high performance in steam reformers, PTQ Catalysis, 31-33, 2015.

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