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Eighty Years of Steam Reforming

The technological milestones of catalysts, reformer design and operation in Billingham since 1936

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Steam reforming of methane is a vital unit operation in the manufacture of synthesis gas (or syngas). Johnson Matthey Process Technologies is a leader in reforming technology for the industrial production of hydrogen, methanol and ammonia to the chemicals and oil and gas sectors. Many of the key innovations in the development of the early reformers and catalysts have taken place in Billingham, UK (**Figure 1**) by ICI Agricultural Division and later Johnson Matthey Process Technologies. This paper explores the history of the site at which industrial reforming technology was established in 1936 and recounts the technological milestones of the engineers' work on catalysts, reformer design and operation since that time.

Fig. 1. Map showing location of Billingham UK

The Early Years of Reforming in Billingham

The Billingham site originally produced syngas from steaming coke, but this process is only 40% efficient. From 1928, research work on methane reforming started at Billingham. Early research on steam reforming had begun as early as 1913 when BASF patented a nickel catalyst for the purpose of reforming, with a later patent by IG Farben in 1927 (1) proposing a reforming catalyst in an externally heated steel tube. To catch up, in 1930 ICI, Standard Oil and IG Farben entered an agreement to share developments (1). This coincided with the start-up of the first three steam methane reformers installed in Bayway, USA, by Standard Oil. The following year another three reformers in Baton Rouge, Louisiana, USA, entered service (1).

First ICI Steam Reformer in Billingham

It was not until 1936 that the first methane reformer was commissioned in Billingham (**Figure 2**). Whilst the design of the reformer was quite similar to those

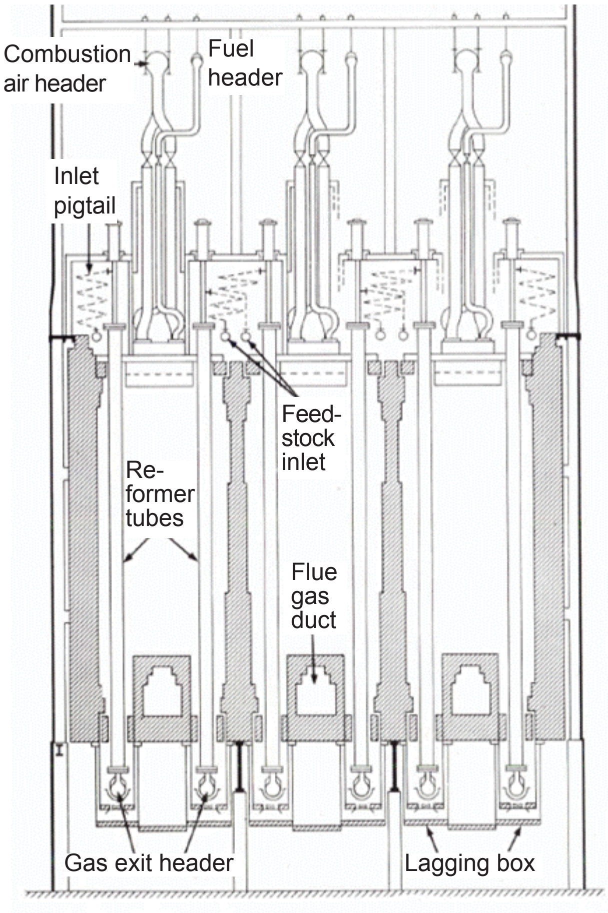


Fig. 2. Drawing of the first steam reformer in Billingham 1936 (Reproduced with permission from (2))

built by Standard Oil, the ICI engineers added a number of modifications which dramatically improved the efficiency of the reformer. It operated at 1–4 bar absolute pressure and 730–800ºC exit temperatures; the operating pressure was limited by the strength of the wrought 25/20 Cr-Ni steel tubes.

The early IG Farben formulation catalyst shape was a ¾″ (1.9 cm) cube, but ICI in Billingham developed the Raschig ring shape (ICI catalyst 22-1) which had a 1.5 cm outside diameter, 0.75 cm inside diameter and was 1.5 cm tall. This new shape both greatly increased the activity and reduced the pressure drop as it had an increased voidage. It allowed a space velocity two to three times higher than had been previously achieved (2). ICI engineers also realised that organic sulfur had been poisoning the catalysts in Bayway and Baton Rouge which had led to carbon deposition; therefore they developed the desulfurisation bed. This used zinc oxide to absorb the sulfur from a preheated feed gas, a step which is still in use 80 years later. The energy efficiency of the reformer was improved by heat integration, for example preheating the feed gas and air to the burners, as well as raising steam with any excess heat (**Figure 3**) (1).

At the advent of the Second World War there was renewed demand for nitrates for the manufacturing of explosives and eight ammonia plants were built using the Billingham designs by the US Government in 1941 (2).

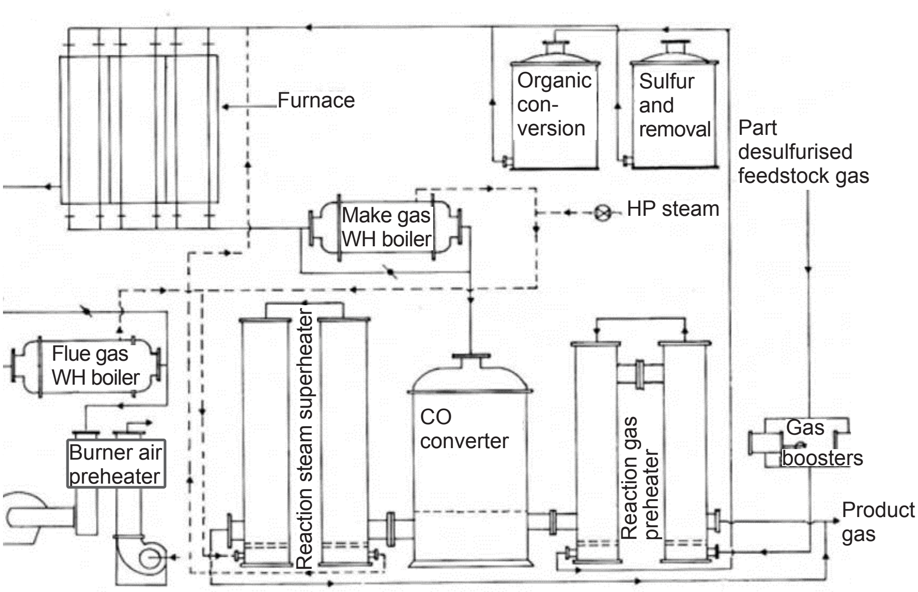


Fig. 3. The methane-steam plant flowsheet from Billingham 1936 (Reproduced with permission from (2))

Rapid Technical Developments

With reformer temperatures and pressures rising with advancing tube metallurgy, silica migration was becoming increasingly problematic. So in the mid-1950s a low silica product was produced. ICI catalyst 57-1 contained less than 0.2% Si, but was still made using the precipitated catalyst route.

As naphtha feeds were shown to be more economic than methane sourced from coke gasification, ICI started an extensive research programme to develop a catalyst which could efficiently reform naphtha (1). They discovered alkalis as a useful promoter for the catalyst, with potash being the most effective. Alkali addition benefits the catalyst by neutralising the support acidity – retarding carbon forming reactions and increasing the rate of carbon removal (1). Commercially this was launched as ICI catalyst 46-1 and enabled ICI in 1959 to design the first naphtha reforming plant. This was built in Heysham, UK, and was commissioned in 1962. This was deemed a success and was soon followed by four new plants in Billingham. These plants were operating at moderate pressures of 14 bar at the inlet, a sign of metallurgical progress.

In the late 1960s the $KATALCO_{JM}^{TM}$ brand was launched as ICI began to sell catalysts externally and became significantly more active in attending external conferences and marketing the catalyst (3).

Towards the end of the decade, ICI developed a catalyst made by impregnating a fired refractory support using a metal salt solution to produce a well distributed surface layer of nickel. This was launched as $KATALCO_{JM}^{TM}$ 57-3 and had the main advantage of being much stronger mechanically than previous catalysts. Early low silica precipitated catalysts lost 50% of their strength after reduction, whereas $KATALCO_{JM}^{TM}$ 57-3 retained over 80% strength even after four years in service (4). Pellets could also be made smaller, something not possible with precipitated catalyst, which gave process engineers the option to choose between high activity or lower pressure drop options.

Cheap North Sea Gas

In the 1970s, Billingham ammonia plants changed from naphtha feeds to run on the newly commercialised natural gas from the North Sea, however the favourable gas contract was on an interruptible supply basis – meaning that with short notice the feedstock could be cut when demand for natural gas was high. If natural gas supply was interrupted the plants were configured to switch feedstock online to a liquefied petroleum gas (LPG) stream (which was stored locally in underground salt caverns), bringing a demand for catalysts that could cope with feedstock flexibility. This brought new requirements for a catalyst with lower potash and higher activity in order to optimise the reformer for this feedstock. By the end of the decade there were two light potash catalysts – $KATALCO_{JM}^{TM}$ 25-3 (1.6% potassium oxide (K_2O)) for natural gas feeds and $KATALCO_{JM}^{TM}$ 46-9 (2.2% K_2O) for LPG feeds (5). By the end of the 1970s, $KATALCO_{JM}^{TM}$ had a product range very similar to the present: $KATALCO_{JM}^{TM}$ 57-series non potash, $KATALCO_{JM}^{TM}$ 25-series light potash and $KATALCO_{JM}^{TM}$ 46-series naphtha catalyst. By this point the catalyst beds were operating at temperatures up to 1000ºC and 35 bar pressure, primarily due to improvements in metallurgy (4).

Steam Reformer Design

A paper by Davy Powergas Ltd in the early 1970s (6) suggested that LPG transportation would not be cost effective and instead huge methanol plants (25,000 (metric) tonnes per day (TPD)) would produce fuel grade methanol to be shipped around the world. They predicted a 5000 TPD plant would require a 2000 tube reformer, a huge increase over the largest at the time (600 tube reformer for Celenese Chemicals Co, USA). Whilst the benefits of hindsight show that these predictions were somewhat optimistic especially about methanol as a fuel, they correctly predicted 5000 TPD methanol plants which we have now. Modern plants require fewer than half the tubes suggested at the time – an indicator of progress in tube materials and catalysts. Prognosticating accurately, they suggested the construction of modular top fired reformers, which enabled high tube count reformers without being prohibitively long (**Figure 4**). They suggested features such as combustion air preheating and an induced draft convection section in order to improve efficiency, which are all commonly found on today's plants.

In 2006 Johnson Matthey acquired Davy Process Technology, who by then had seen the commissioning of M-5000 in Trinidad, the world's largest steam reformer-based methanol plant operating at 5400 TPD.

The development of reformer tube metallurgy has been shown to be a key enabler in the development of steam reforming. All steam reformer tube alloys are centrifugally cast from steels with high carbon content, plus around 25% chrome, 20–35% nickel and some

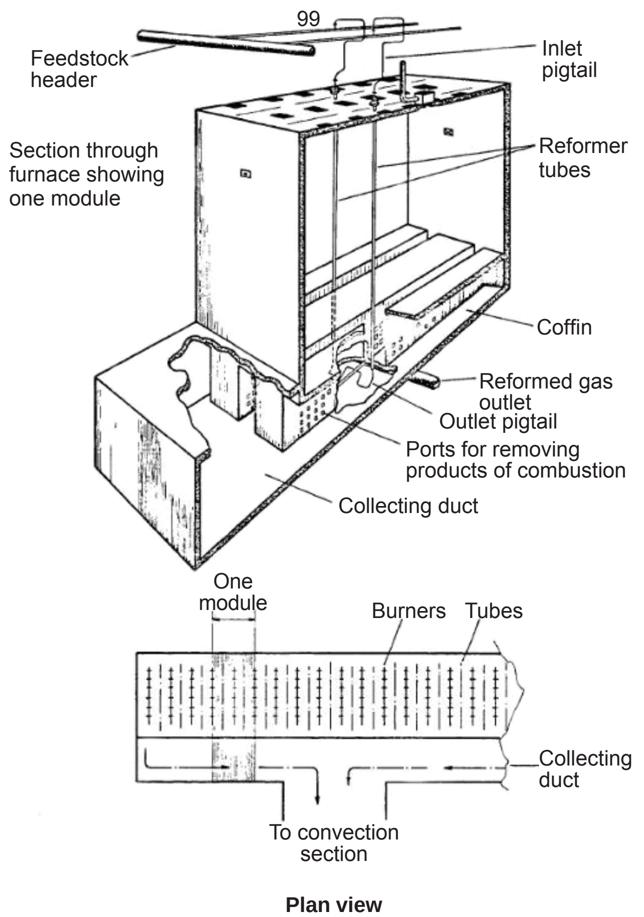


Fig. 4. Modular top fired reformer design by Davy Powergas Ltd in 1973 (6)

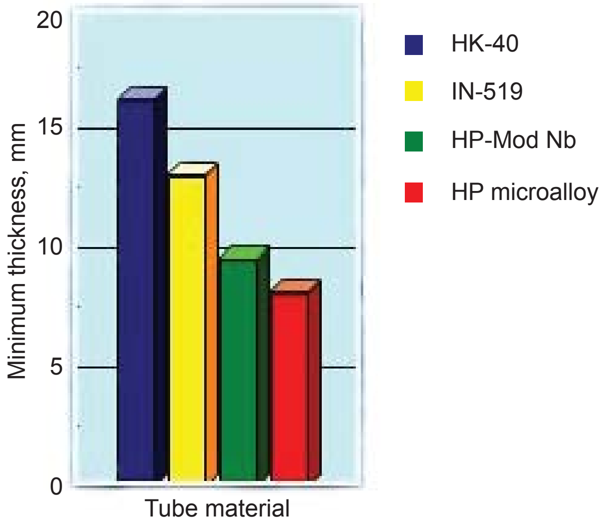


Fig. 5. Comparison of HK-40 15.5 mm, HP-modified Nb 10 mm and HP microalloy 8 mm tube wall thickness (7)

trace elements to improve strength. The microstructure has a direct impact on the creep resistance of the tube, where fine carbide particles act as a barrier to creep through the material's structure. Earlier tubes were made with HK-40 steel alloy, but in the 1980s 'HP-modified' or 'HP-Mod Nb' was introduced which contained 1% niobium to produce fine secondary carbides, yielding a significant improvement over the older alloys. In the 1990s microalloy tube materials were introduced, in which elements such as titanium were added to further improve the creep strength. The impact of this on tube wall thickness can be seen in **Figure 5** (7), allowing cheaper reformers, improved heat transfer and larger diameter tubes.

Computer-Aided-Design and Development of Shapes

The introduction of computers also had a big impact. At the start of 1980 ICI Agricultural Division had a single computer, and just five years later most managers and engineers had access to a desktop terminal (8). As computers became increasingly available computer models were developed enabling prediction of process conditions inside a reformer tube. By the late 1980s the SRATIO programme was developed by ICI Billingham, allowing the prediction of minimum S:C ratios required for a given feed composition to avoid carbon formation. In 1991 a paper at the International Methanol Technology Operators Forum (IMTOF) was written to demonstrate the ICI reformer modelling capability (9). They were able to predict carbon formation and heat profiles and to model different reformer tube materials and hence calculate tube wall temperatures. This was the forerunner to the Johnson Matthey PERFORM and PRIMARY reformer modelling tools.

The Raschig ring had been a constant feature of ICI's reforming catalyst for nearly 50 years. Temperatures and pressures of steam reformers have increased over the last few decades and the reactions are increasingly taking place on the outside of the catalyst pellet. This means the shape of the pellet is increasingly important, in particular its geometric surface area (area of the catalyst pellet per volume of bed) and this was the focus of significant development effort. ICI Billingham explored different numbers of holes and different aspect ratios to improve activity and heat transfer, minimise pressure drop, and to maintain a strong pellet (**Figure 6**) (10). This culminated in the launch of the four-hole catalyst shape (11). It was a commercial success as it was installed in over 60 plants in its first four years on the market.

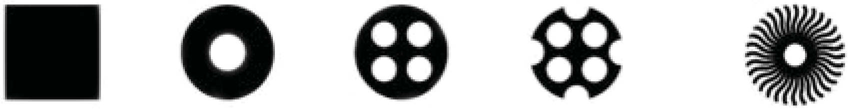
Era:	1930s	1940s	1980s	2000s	2014
Cross section	Square	Ring	4-hole	QUADRALOBE™	$CATACEL_{JM}$ SSR™
					
Form	Cube	Cylindrical pellets	Cylindrical pellets	Cylindrical pellets	Cylindrical foil supported structure
Relative activity	1.00	1.32	1.64	2.00	3.00
Relative pressure drop	1.00	0.47	0.62	0.43	0.34

Fig. 6. Evolution of catalyst shapes with time and comparison of their properties (10) (Adapted with permission from International Fertiliser Society Proceedings)

Considerable capital expenditure (CAPEX) savings are possible when designing a new reformer to use the four-hole shape. A paper at the time suggested a 20% cost reduction was possible with a 1500 TPD ammonia plant reformer by reducing the number of tubes, and thus footprint, required to achieve the same duty (12).

In 2001 the QUADRALOBE™ shape was launched. Four flutes were added to the four-hole catalyst and the ends of the catalyst were slightly domed. It offered significant improvements over the previous shape with 20% greater activity, improved heat transfer properties and a lower pressure drop. It was also a 20% stronger pellet. Marketing material at its launch claimed US$3.03 million a year savings for a 2500 TPD methanol plant (13). This shape is still in use by Johnson Matthey and remains a market leading catalyst for steam reforming. Over time a family of different sizes has been launched ranging from the highest activity shape mini-QUADRALOBE™ (MQ) to the low pressure drop extra-large-QUADRALOBE™ (XQ) catalyst. The formulations and recipes are in continuous development to meet ever changing customer requirements.

Johnson Matthey bought the ICI catalyst business, then known as Synetix, in 2002. The business fitted well with Johnson Matthey's existing catalysis expertise in automotive catalysts and metals processing. This allowed the process industries catalyst business take advantage of some of the research and development (R&D) facilities already existing within the Johnson Matthey group such as those at Sonning Common, UK.

Modern Developments

The QUADRALOBE™ shape is highly optimised and is approaching a development plateau for pellet-based reforming catalysts; it was realised that novel technologies would be required to provide a step change in performance. In 2014, Johnson Matthey acquired the Catacel Corporation, USA, which manufactures a range of stackable structured reactors now known as $CATACEL_{JM}$ SSR™ (**Figure 7**).

Fig. 7. A $CATACEL_{JM}$ SSR™ module

CATACEL$_{JM}$ SSR^{TM} is a stack of nickel catalyst coated fins which fill the reformer tube. This technology provides significantly enhanced activity and heat transfer when compared to pellets, as well as a reduced pressure drop (**Figure 8**) (14). The higher activity along with the lower pressure drop allows CAPEX savings on new plant builds compared to pellet-based catalysts, as well as offering uprate opportunities to existing plants.

The newest development for pellet catalysts is a nickel 'eggshell' reforming catalyst (15). This patented manufacturing technique, developed in Billingham using Johnson Matthey's long experience of creating platinum group metal (pgm) catalysts with a thin eggshell layer of platinum (16), allows the nickel oxide to be concentrated on the outer layer of the support. This means there is more nickel at the surface of the pellet where the reaction takes place and reduces the metal content in the centre of the catalyst (**Figure 9**). This region does not see any reaction at the high operating temperatures of the steam reformer as the diffusion rate is slow compared to the reaction rate. This is available as KATALCO$_{JM}$^{TM} 57-6Q.

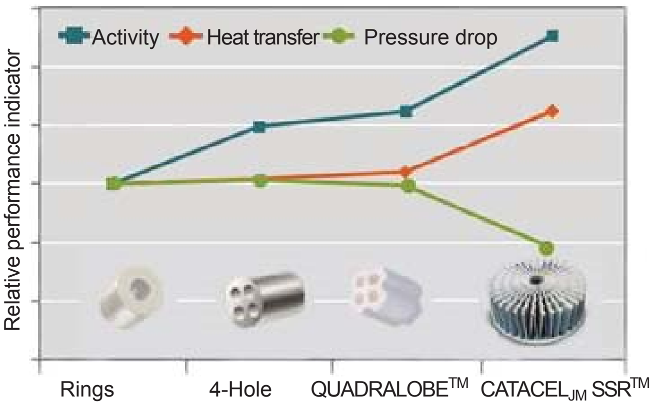


Fig. 8. Plot of CATACEL$_{JM}$ SSR^{TM} relative performance of different catalyst types (14)

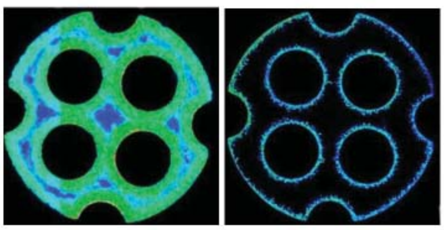


Fig. 9. Relative concentration of nickel on cross sections of QUADRALOBE^{TM} shaped pellets, comparing KATALCO$_{JM}$^{TM} 57-4Q against KATALCO$_{JM}$^{TM} 57-6Q. The brighter spots represent a higher concentration of nickel

Conclusion

Billingham has been instrumental in the development of steam reforming in the past 80 years by adapting catalysts and reformers to feedstock changes, and by having a continued desire for improvement. Its scientists and engineers have provided key developments in the shapes and composition of nickel catalysts, introduced new manufacturing methods, optimised the initial reformer flowsheet and started the development of the modelling tools we use today. The site continues to pioneer exciting new innovations such as CATACEL$_{JM}$ SSR^{TM} and eggshell catalysts in order to maintain Johnson Matthey's position as a market leader in steam reforming catalytic services.

KATALCO^{TM}, QUADRALOBE^{TM}, CATACEL and CATACEL SSR^{TM} are trademarks of the Johnson Matthey group of companies.

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