# The Steam Reforming of Naphtha: The Technology that Saved British Gas

# Part 2: Town Gas Steam Reformer Design and Operation

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### Abstract

This paper stems from the personal experiences of the author who worked for a short time on steam reformers at Hitchin, Herts, in Britain, and then did failure investigation on such plants as a professional metallurgist.

R&D by IC1 Billingham, supported by major efforts at ICI Heysham, to manufacture hydrogen, using light hydrocarbons and naphtha, provided the basis for the town gas reformer process that was taken up by British Gas. The principal alteration was that town gas plants ran at higher pressures and lower temperatures so as to maximise the formation of methane. The first towns gas steam reformer ran at Provan, in Scotland 1964, and was quickly followed by many others.

The paper describes the main components of the basic town gas reformer process. Its main shortcoming was the need for enrichment of the lean gas by butane, or propane, to achieve the required calorific value. Improvements, namely the Gas Recycle Hydrogenator, Catalytic Rich and ICI 500 Process were added onto the basic ICI system, enabling enrichment to be dispensed with. The Topsøe Town Gas was different, running at a lower temperature, producing 500 BTU/cu.ft gas directly.

The paper describes what it was like to operate these plants and what had to be done during start up. In contrast to the way in which modern hydrogen plants are operated, a town gas plant had to vary output, in response to reduced demand at weekends, the weather, and public holidays. Few designers seemed to build in the flexibility that was needed, causing difficulties for plant operating staff. The only company that seemed to recognise this issue was Vickers-Zimmer, who had their own unique approach to the design of reformer furnace.

The paper is dedicated to Chris Murkin and John Brightling of Johnson Matthey Ltd for their great efforts to preserve the history of catalyst developments at ICI Billingham.

## 1. Introduction of ICI Steam Reforming into British Gas

Part 1 of this series of papers, which can be found at the website <u>https://fredstarr.com</u> showed how steam reforming was absolutely critical to the salvation of British Gas, enabling it to shift away from coal, to a much more efficient lower cost process. All of these papers are written

from the personal standpoint of the author. To reiterate, he started work on steam reformers as a trainee shift engineer, at Hitchin, Herts. Shortly afterwards, he moved to one of the British Gas research stations, to do failure investigation on steam reformers.

Sadly, the way in which the Gas Industry became aware of the potential of the ICI naphtha based steam reformer, and how it was first introduced, seems to have been lost. In part, because the technology was introduced at an Area Board level, with little involvement from the R&D sector or even from the Gas Council.

Some parts of the Gas Industry must have been alive to the possibilities, however. A small onshore natural gas field had been discovered at Whitby in 1960 which supplied a "conventional" steam reformer in the town. Furthermore, a number of Area Boards had begun to use "refinery gas" for "continuous steam reforming", as it was then described. As is implied, this was mixture of gaseous hydrocarbons, piped in from an oil refinery, which in some cases could be quite distant. Obviously, the supplies of this feedstock were limited, and refiners might find other uses. In addition, a limited number of gas works in Britain had the option of switching over to the steam reforming of methane by taking gas from the pipeline carrying methane from Canvey, up the country to Leeds. However, judging from my experience at Hitchin, which was connected to the pipeline, it was an expensive option, not used very much.

The Otto steam reformer using butane, slightly predating the naphtha era, would also have given confidence to continuous steam reforming. Although intended for peak load duty, because of the cost of butane, its low manpower costs led them to being used round the clock at Hitchin. The first plants in Britain were built at Nechells in Birmingham and at Dunstable<sup>1</sup>. EO. Rose, Chief Engineer of Eastern Gas, commented that the operating staff on Otto plants had nothing to do "but sit in the sun and watch the flowers grow" <sup>2</sup>. As a trainee shift engineer, who started work on the Otto at Hitchin, the author can attest to that.

Mr George Percival, helped the author understand the history of new approaches to gas manufacture (Percival was a researcher at Midlands Research Station in the 1950s, and became a senior figure at British Gas HQ in the seventies). He has suggested that Maurice Redman at North West Gas may have been instrumental, since the first commercial naphtha steam reformer was commissioned at ICI works at Heysham, Lancashire in 1961 (although quickly followed by one at Billingham)<sup>3,4</sup>.

All of this was the culmination of R&D work on steam reforming catalysts that was started at ICI Billingham, on Teesside, in the 1930s. A series of excellent papers by Brightling, and Brightling and Murkin covering the steam reformer and ammonia catalysis work at ICI, highlight the construction of a low pressure steam reformer at Billingham in 1936 <sup>5,6,7</sup>. The unit was a greatly improved version of the furnace used by Standard Oil in California, but still using wrought, that is low carbon, stainless steel tubes. In consequence the reforming plant pressure was quite low, at 3-4 bar.

There seems to be some confusion in the papers by Brightling and Murkin about feedstocks at Billingham. Although methane is mentioned, which seems unlikely, Brightling asserts that a

mixture of butane and propane were used, as byproducts from the coal and coal hydrogenation plant. Probably methane was present in this mixture. One would guess that the resulting hydrogen would be used in the coal hydrogenation plant at Billingham, rather than for ammonia manufacture, as the former would not need a super purity feedstock.

After WWII there was a major initiative by 1CI Heysham. The first step was to build a small plant to reform the zero sulphur, synthetically made aviation fuel that was being made at Heysham. The next step was a trial of distillate fuels of the naphtha type. The big improvements were (a) a method to completely eliminate sulphur from the naphtha and (b) the lacing of the reforming plant catalyst with potassium carbonate to suppress hydrocarbon cracking and carbon laydown. In this the greatly respected catalyst expert, Denis Dowden, played a major part <sup>8</sup>.

The catalyst which emerged was given the designation of 46/1 and was utilised in the form of Raschig rings. Bridger of ICI has produced a very good short paper for the American Institute of Chemical Engineers, detailing the chemistry behind 46/1 and the methods used during the start up of reforming plants to get the best out of such catalysts, and ensure good performance in service <sup>9</sup>.

The location of North West Gas HQ, and their research facility at Stretford, and the proximity of ICI Heysham does give some support for Percival's suggestion, but the author is not completely happy with this hypothesis. My own view is that the concept was probably spread through word of mouth at a senior technical level in the Area Boards. Nevertheless, ICI, having plants running at Heysham and Billingham, must have had a considerable impact on Gas Board personal who were in the locality.

The drive for the work at Billingham and Heysham had been the awareness that the old coal based method, using gas producers for making hydrogen for ammonia manufacture was becoming uncompetitive. Capital costs and manpower requirements were excessive. Competitors, with access to natural gas, were much better placed. But Britain had yet to discover North Sea Gas. Here it is worth mentioning that ICI, in the interests of winning WWII didn't do itself much good. ICI sent its design of furnace and improved catalyst to North America, presumably on a sort of reversed Lend-Lease <sup>3</sup>. Fortunately, over here, in the 1950s naphtha was becoming a cheap feedstock.

At this point, in postulating how steam reforming came to British Gas, we need to highlight the probable contribution of Power Gas Ltd on Teesside, which had a long connection with ICI Billingham. Power Gas would have seen its market for coke-based producer gas/water gas units, which were used on old fashioned gas works, disappearing. Quite naturally, the company would have been looking at what was replacing them. It was therefore a company with unique connections to both ICI and the Gas Boards. One presumes that ICI and Power Gas would have seen it would be a small technical step to operate an ICI reformer in such a way to produce something more akin to methane-rich town gas than hydrogen. In principle, all that was needed was to run the reformer at a higher pressures and lower outlet temperatures.

Within a very short time of the hydrogen reformers at Heysham and Billingham going into commission, Power Gas had built the world's first ICI town gas reformer. The first of three streams were commissioned at Provan, near Glasgow, for Scottish Gas in 1964<sup>10.</sup>

Knowledge of the concept spread through British Gas Area Boards and Chemical Engineering companies. Orders poured in, and new plants brought into operation. By 1970, just before North Sea Gas came in, about half the gas in the UK was being made in steam reformers. New catalysts and new plant designs were being continually promoted. No two plants were alike.



Figure 1: The first ICI type steam reformer to produce town gas (with enrichment) at Provan in Scotland. There are three streams. The closest shows its reforming furnace at the far right of the photograph. Outlet pressure was 80 psi gauge.

## 2. The Steam Reformer in British Gas Days

## 2.1 Steam Reforming Reactions and Steam Reformer Design

The reaction of steam with naphtha to produce "reformed gas" is highly endothermic. The reforming furnace was designed to bring the reactants up to at least 700°C as quickly as possible to minimise any tendency towards cracking. However, overheating had to be avoided.

Although the tubes were the best available, with ductility being sacrificed to maximise strength, in truth they were quite weak, no better than pure aluminium at room temperature.

Using light paraffinic naphtha, the reforming reaction can be represented as:

$$C_7H_{16} + 8H_2O = 2CH_4 + 2CO + 3CO_2 + 12H_2$$

As will be seen from this reaction, 8 moles of steam are needed for 7 moles of carbon, a ratio of 1.14/1. In practice a 3/1 steam to carbon ratio was needed, to help supress carbon cracking, so there was a large amount of unreacted steam in the reformed gas. Accordingly, on chemical analysis, a typical **dry** gas composition, was 12.8% methane, 10.7% carbon monoxide, 15.7% carbon dioxide and 60.8% hydrogen. The level of methane could be increased by operating at a somewhat higher pressure than 7 bar. Lowering the temperature was more beneficial, but this limited to a minimum of 750°C, using the ICI catalyst.



Figure 2: Schematic of an ICI Type reforming furnace shown as an end view

SPS Andrew contributed an excellent chapter on the ICI catalyst as part of a book on ammonia manufacture, the whole book containing some very useful information on steam reforming <sup>11</sup>. Andrews was another of those who emphasised that the catalyst was doped with several percent of potassium salts, for suppression of carbon formation. This in the extreme, could lead to blockage and overheating of the catalyst tubes. As mentioned, a high excess of steam was also

needed for this reason, which would push the reaction to the right. The high level of steam wasn't too much of a drawback, as some of it was subsequently used in a shift converter, where at a temperature in the range 350-400°C, much of the carbon monoxide reacted with the steam to produce hydrogen and carbon dioxide.



### Figure 3: A reformer at Coleshill of the ICI downward firing burner type. In this case there four rows of reformer tubes which take vaporised naphtha from a common header about two thirds of the way up. The large diameter insulated pipe at the left hand side of the furnace carries superheated steam. The combustion air fans are also well shown in the middle foreground.

In the early sixties there were two main designs of steam reforming furnace. A good description of the main types is given by GR. James in his chapter in the book mentioned above <sup>12</sup>. The ICI type utilised downwards firing burners, with naphtha as a fuel. Sets of the burners were positioned between the rows of vertical tubes, the flames reaching more than half way down

the furnace. See the schematic shown in Figure 2. Although a rather simplistic burner arrangement, it put heat in the tubes in the critical section close to the tube inlets, helping to prevent cracking of the naphtha. Figure 3 shows the reformer at Coleshill which is of the classical ICI type. This plant was also designed and built by Power Gas.

The only difference to a modern reforming plant, producing hydrogen from natural gas, is that, such a plant would look quite basic and tiny. There were no pre-reforming units for converting slightly heavier hydrocarbons to methane. Neither would there be a secondary reformer, which, is used in modern streams to increase the amount of hydrogen being made. Operating pressures in today's hydrogen units are comparable to those in the later town gas reformers, but the modern steam reformer runs with outlet temperatures close to 900°C, rather than the 750°C in a town gas plant.



Fig 4: A Selas reforming furnace. Each of the square shaped blocks is the mount for the circular burner dishes on the furnace side. 12 insulated pigtails, leading from the reformer tubes, into the header are visible

At the time, the main alternative to the ICI reformer was that promoted by Selas Inc, a configuration with wall mounted burners. Fig 4. Here the burners were placed in several rows

on each of the two long walls of the furnace. Each burner sat in the middle of a large concave dish made of ceramic, whereby the jet of flame impinged on the dish causing it to radiate onto the tubes. The advantage was that the heat input onto the tubes could be modified by turning on or off different burner

Reference 4 also includes a rather crude schematic of a Selas reformer, but showing that a furnace wall could have many more burner blocks than that shown in Figure 4. But the sketch also indicates the big drawback of the wall mounted burner type. That only two rows of reformer tubes could be incorporated into the furnace box. As such the Selas design is probably best suited to modest reformer outputs, as a Hitchin, or else where excellent control of catalyst temperature is needed. Reference 12 gives a short but objective account of the different types of reforming furnaces that are on the market today <sup>13</sup>.

In an ICI furnace there were rows of tubes, comprising 10-20 in number, with each tube being about 30 cm in diameter and about 10 metres long, fed with a mixture of steam and naphtha at around 550°C from a top header. This was a long horizontal tube, above the furnace. Loops of small diameter, T22 low alloy steel, or stainless steel flexible corrugated, hose took the reactants from the header into the top of each reformer tube. At the outlet of each of the reformer tubes, where the temperature was over 750°C, small diameter tubes made of Incoloy 800, the best wrought high temperature tube alloy on the market, was used to conduct the reformed gas into the bottom header.



Figure 5: Installation of a new header on a reforming plant at Coleshill

Figure 5 shows a header being replaced at Coleshill. Because the Incoloy tubes were looped, so as to take up expansion of the header and of the catalyst tubes, which could be up to a couple of feet, they were referred to as "pigtails". In the background are the hanging loops of the pigtails, and just discernible, above them, are the flanged bottoms of the reformer tubes.

The catalyst tubes were made from lengths of spun, that is, centrifugally cast, high carbon stainless steel of the HK-40 type (Fe-25Cr-20Ni-0.4C), whose life was governed by a combination of stress and temperature <sup>14</sup>. Figure 6 shows the stress rupture values for this material at failure times of 1000 and 100000 hours. As a design criterion, after determining the probable metal temperature, plus a safety factor of about 25-50°C, the hoop stress would be set at two thirds of the 100 thousand hour estimate (at the time, all of these values would be extrapolated from short term test results). HK-40 is now obsolete, as References 13 and 14 show it has been replaced with modern spun cast alloys that allow operation at a 100° higher temperature.



Figure 6: Stress rupture values for HK-40 reformer tube spun cast stainless steel. (Replotted from Reference 14)

#### 2.2 Other features of the ICI process

Although the reformer and its catalyst were the most important features of the plant, there was a huge amount of ancillary equipment. The aim of this can be summarised as follows, with a very schematic process route being shown in Figure 7, and one of somewhat more detailed one in Figure 8.

• Evaporation of the liquid naphtha, at pressure, to a temperature of about 350°C, often using some of the heat in the flue gases exiting the reformer, in a long flue gas duct. after they had cooled to some extent through the raising of steam. All of this heating was done, out of sight in a long flue gas duct, taking the flue gas out to the chimney stack. Since the flue gas duct was packed with heat exchanger tubing of various types, there was a big pressure drop along it. Hence, a combustion air fan was needed to get air into the reforming furnace, assisted by a flue gas fan, situated just before the chimney stack.

- On some plants a small "fired heater" would be used to evaporate the naphtha. Circular ins shape a central naphtha burner was surrounded a helically wound tube or a set of up-and-down vertical tubes, through which the process naphtha was being heated. However, fire heaters were invariably used to help heat up the plant during start up.
- Desulphurisation of the naphtha down to 1ppm, within a set of pressure vessels which ran at about 350-400°C, at pressure. The first vessel contained zinc oxide to remove any "free" H<sub>2</sub>S in the evaporated naphtha. This was followed by a CoMox vessel, containing a cobalt oxide/molybdenum oxide catalyst, in which hydrogen reacted with organic sulphides to produce H<sub>2</sub>S. The final vessel also contained another batch of zinc oxide to finish off the removal of sulphur compounds



Figure 7: Schematic of naphtha, steam and gas flows in an ICI Towns Gas reforming plant

- Production of steam and superheated steam, using (a) waste heat from the hot reformed gases at 750°C (b) waste heat from the flue gases leaving the reformer furnace at 1000°C, (c) waste heat from the hot hydrogen rich gases leaving the shift converter at 400°C.
- Shift conversion, whereby, through the reaction of steam with carbon monoxide, more hydrogen was produced. This reaction was strongly exothermic, so that the gases leaving the shift convertor reactor experienced a temperature rise over the inlet conditions. The shift reaction is

#### $\mathbf{H_2O} + \mathbf{CO} = \mathbf{H_2} + \mathbf{CO_2}$

Because the reaction was so exothermic, it was impossible to carry out the reaction in one step. There were two pressure vessels each containing a shift catalyst. One for high temperature shift, the other for low temperature shift. My recollection is that there was a small shell and tube boiler in between the two reactors to reduce the inlet temperature to the second shift vessel. The alternative option was to add non-superheated steam to the flow just before the second shift reactor. As well as bringing down the temperature, the addition of more steam, drove the shift reaction in the forward direction.

There was a 50-70°C temperature rise across each vessel, with the inlet temperature for the high temperature shift being about 350°C, and that for the low temperature shift being just 200°C.



Figure 8 : Showing main routes of naphtha, steam, reformed gas and recycle hydrogen in an ICI type towns gas reformer

• Cooling the shifted gas, still further, after it had left the shift gas boilers, to around room temperature was done in fin-fan coolers to condense out surplus steam, preparatory to CO<sub>2</sub> removal. The separation of droplets of hot water from the gas was accomplished using stainless steel "knock out pots". In these, the gas was made to swirl around, throwing the droplets onto the walls, after which they drained down, to be separated off

The aqueous condensate contained a high level of carbon dioxide and was fairly acidic. Hence the need to make the pots of 18/8 stainless steel. Any mild steel pipework or valving was greatly subject to erosion-corrosion from the hot aqueous condensates. Pipe work could be eaten through in just a few months.

• Removal of most of the CO<sub>2</sub> by absorption in various solutions. On the first set of reformers 0monoethanolamine (MEA) was favoured, but there were corrosion issues and questions about its toxicity. Most plants seemed to use "activated" potassium

carbonate solutions, exemplified by the Benfield or Vetracoke processes. Here the gases were injected into base of the absorption tower, full of Raschig rings, where, as the gases rose to the top, they were "scrubbed" by a downward flowing stream of potassium carbonate solution, which reacted to form potassium bicarbonate. The potassium bicarbonate, in turn, was regenerated by trickling it down through a similar tower, through which steam was rising. The  $CO_2$  was then released to atmosphere through the stack at the top of the regeneration tower. There would be just a trace of steam accompanying the  $CO_2$ .

• After leaving the CO<sub>2</sub> plant, the gases were cooled and dried using hot glycol. They were then odorised with sulphur compounds to ensure that consumers could detect leaking gas from the smell. Finally, the requisite amount of methane, butane or propane was added to bring the gas up to the required calorific value.

### 2.3. Physical Appearance of a Reforming plant

More than one hundred separate units were designed and built, over the period 1962-69, by a variety of major UK contractors including Humphreys and Glasgow, Woodall Duckham, Wessoes, Simon Carves, Wests and Power Gas. They also employed subcontractors for design and construction of major parts of the processes. For example, furnaces, water treatment units, standby generating plant and other forms of protection from a loss of electrical supply from the local grid. The electrical equipment on the works at Portsmouth, for example, could be kept running for 30 seconds using the power from a shed that was full of lead acid batteries! Hitchin had six diesels of about 800 hp, each of which could supply to power for one stream. They were housed in an extremely modernistic diesel building , which still survives. In 1968 the Gas World magazine published a list of about 40 sites, but this is not complete, leaving out major installations such as Fulham, Breakwater (Plymouth), Seabank (Avonmouth), Watford and Canvey Island.

Given the range of contractors and sub-contractors, and because by 1966, the newer (!) plants were incorporating extra processes for enriching the reformed gas, no two plants were alike. All of them incorporated a reforming furnace, where the standard design was roughly that of a cube about 20 metres high and 15-25 metres along the sides. The alternative side wall fired design was also about 20 metres high, but as it had only two rows of tubes, the ends of the furnace were only about 10 metres in length, but the long sides, which contained the burners, were about 30 metres long. There were a number of walkways around the sides of the reforming furnace, which permitted inspection of the tubes, and on the side wall design, adjustment of the burners. On the downwards firing design it was possible to walk on the top the furnace.

On many plants, the reforming furnace was partially obscured by the three large pressure vessels used for desulphurising the naphtha, which were usually in close proximity to the reformer. The vessels containing the shift converter catalyst were also quite large, but only about half the size of those used for desulphurisation. But the most striking feature on all plants was the tall towers of the CO<sub>2</sub> removal process. However, when actually walking around the plants one became aware of the mass of ancillary equipment, such as the reformed gas and shift

converter boilers, looking like big tins of beans laid on their side; the fired heaters, which reminded one of old fashioned lanterns; and the fin-fan coolers with their rows and rows of finned tubing. Because of the noise of the cooling fans, they were a pleasure, from which, to get away. The penultimate units on any plant were the pepper pot shopped "knockout pots" to remove condensed water from the gas, and the glycol plant which eliminated all of the water vapour in the gas. The final touch, before the gas was sent off site, was the oderisation unit where about 10ppm of organic sulphur compounds was added to the gas, this being a safety requirement



Figure 8: Shows the final sections of the two CRG streams at Hitchin. The two slender towers with steam and CO<sub>2</sub> coming out of the top are part of the Benfield units. Flue gas from the "B stream" reformer and heat recovery units exit through the helical wound stack on the right. The very strange tapered chimney is for discarding waste gases during start up and shut down. Outlet pressure was 250 psi.

These units were "serviced" by masses of tubes and pipes of different sizes carrying naphtha, either in the liquid or gaseous form, reformed gas and shifted gas, boiler water and steam, ducts

containing air for the furnace and combustion products, and around the Benfield plant, with its panoply of reboilers and heat exchangers, pipes containing "rich" or "lean" liquor, and steam for liquor regeneration. Large electric motors were required for the combustion air and induced draft fans, the boiler feed and circulating pumps, and the big pumps for circulating the viscous potassium carbonate liquor in the Benfield plant.

One of the most important features on a reforming plant was the steam drum, a large pressure vessel about half full with boiling water. This took the supply of hot water for the plant, previously preheated in the feed heaters, to just below boiler water temperature. The steam exited from the top of the drum via a main steam pipe, most of the steam going into the superheaters before being mixed with vaporised naphtha. The lower part of the steam drum contained a number of pipes, which took cooler water down to the various boilers around the plant. The two most important being the reformed gas and shift boilers, which were of the tube and shell heat exchanger type. Here some boiling did take place, but the main aim was to get the cooler water back to temperature before it was returned to the steam drum. When working properly, the steam was supposed to flash off from the surface of the water in the drum.



Figure 9: The control room at East Greenwich. The site is now occupied by the O2 Arena.

All the pipework and pressure vessels on the plant was insulated with fibreglass lagging, held in place and protected from the weather by thin, shiny sheets of aluminium cladding. Since the steel encased reformer furnace was painted white, when new, these plants had a Wellsian, space age look. At night the appearance could be very striking. This futuristic look was accentuated by the control rooms, in which graphical displays and charts, some with "set points" that were used to control the flows, pressures and temperatures of the various "streams". Figure 8 showing that, at East Greenwich, is quite typical. The flows throughout the plant were governed using valves driven by pneumatic controllers. The control signals were sent electrically from the mass of cabling at the back of each control panel.

All plants contained a large high quality water treatment unit of the ion exchange type. Note that equation (1) shows that a kilogram of naphtha would require 1.24 kg of water for gasification. A simple water softening system would have quickly led to boiler tube fouling. As was mentioned the electrical demand was a few hundred kilowatts for each stream; at Hitchin the combustion air and induced draft fans each consumed about 100 kW.

# 3. Steam Reforming Plant Operation

# 3.1 Day-to-day Running

Operation of a steam reforming plant can be divided into what was going on during normal running, and the quite different set of procedures needed to start up a plant. Keeping in mind that naphtha is similar to petrol in terms of flammability, and that mixtures of gas and air are explosive. The staff, on shift, would have not been much different to that on any modern chemical plant, looking after at a least a couple of streams. The shift engineer and his deputy (no women in those days!) had overall responsibility. In addition, there was a control room operator, and a couple of people outside, just keeping an eye on the various streams. The big difference to a modern steam reformer for ammonia production was that almost every day, changes in gas demand, usually as a result of the weather would require adjustments to be made to the output. With some plants this was easier than others. Generally speaking, the more efficient a plant, the more problematic it would be, while endeavouring to maintain the calorific value of the gas within tight limits.

Nevertheless, during normal operation everything was essentially automatic, almost to the point of boredom. For example, when demand fell the first step was to cut down the flow of steam and naphtha to the reformer, at the same time cutting back the fuel to the burners. This was more complex than it seems. With the drop in output, less heat from the reformed gas and shifted gas was going into the boilers for steam raising. And there was less heat in the combustion products, so that the superheating and feed heating in the flue gas was reduced. Hence changes had to be gradual, especially as most plants had been designed for operating at near peak output.

The requirement for changes in output were sent through by the staff at Central Control who monitored the high pressure grid. They in turn responded to what the consumers wanted. It might take a few hours before a plant settled out, and one was constantly aware that too big a change, in for example, fuel flow, could put the plant into a downward spiral in which gas production was much less than desired. If one "picked up" a change in output that was part of the way through, from an earlier shift, it was never clear what they had done, and could lead to a messy situation. In one case where I felt that the demand for a reduction in output was not really needed, I did not take any action, just to see what would happen. As the pressure in the gas pipeline backed up, this fed though back to our reforming plant, the pressure of which went on rising until the relief valves were close to blowing. Only then I did cut down on the output, having learned what really determined the plant pressure!

Few of the plant designers seem to have acknowledged the need to build in operating flexibility into their designs. Doing this might have compromised thermal efficiency and would have certainly impacted on capital costs. Vickers-Zimmer Ltd was the exception, having designed a type of reformer that eliminated the need to cater for reformer tube expansion. On a typical ICI unit, the change in length would be about six inches. The reformer header would also move laterally by a similar amount. All of this requiring the set of pigtails at the bottom of the furnace to ease out the expansion strains.



Figure 10: Reformer Tube of the Vickers Zimmer type

Vickers-Zimmer eliminated the need for a bottom header, the design being roughly as that shown in their patent, US 3,713, 374. Here the reformer tube looks rather like a test tube, in

which superheated steam and naphtha vapour are conducted down to the bottom of the "test tube" through a central pipe. See Figure 10. It then flows up through the annulus which is packed with catalyst. Heating of the tube is done in the normal way.

The Vickers Zimmer arrangement was used by Belfast Gas, as owing to the political conditions in Northern Ireland, at the time, the organisation was unable to use its gas holders. In consequence, their reforming plants had to vary their output from day to night, all the time.

# 3.2 Start Up Procedure

From cold it would take about two to three days to start up a plant. There were several discrete steps. Obviously, all the air in the plant had to be swept out. All plants had a stock of liquid nitrogen which, after it was evaporated and then heated up in a fired heater, was used for the flushing out process. In the course of this a few burners would be lit in the reformer to bring temperatures up, throughout the plant, and to begin steam raising.

Once it was clear that all air had been flushed from the plant, the process of reducing the catalyst would need to begin as the nickel in the catalyst was in the form of microscopic particles of NiO. In the reduced form, as nickel, these particles were highly reactive, with the catalyst being subject to a form of spontaneous combustion if it came into contact with air. The reduction was done by circulating hydrogen. This came into the works in a trailer full of bright red hydrogen cylinders. During the reduction process, the hydrogen was recirculated round the plant, using a small set of reciprocating compressors.

After about a day, temperatures had reached the point where steam could be put on to the reformer along with the hydrogen, although the pressure in the plant was only just a fraction normal rating. Much of the steam at this time was coming from a packaged boiler of the once through type. A critical issue was whether the steam was "wet" and this could be checked by opening a valve on the superheated steam line. If the blast of steam was colourless (not "steam-white") it was taken to be dry, and the steam could then be put to the reformer. It will be apparent that various valves had to be manually opened and closed all through the start up.

Temperatures were gradually raised. Tubes were checked by noting how red hot were they. Once temperatures had reached about 800°C, it would possible to start putting in vaporised naphtha to the desulphurisers, this too being brought to temperature by the fired heater, along with the hydrogen.

As soon as the mixture of steam, naphtha and hydrogen reached the reformer, the topmost section of the tubes would darken, indicating that the endothermic reforming reaction was underway. More burners could be lit and from this point onwards, as more steam was being generated, plant pressure rose. The supply of hydrogen was discontinued, and the flow of naphtha increased.

In conjunction with all these operations, the Benfield  $CO_2$  removal plant had to be brought into use. In normal operation Benfield required a supply of wet steam (wet steam has much better heat transfer characteristics than dry steam) for operating the reboilers. These were essentially heat exchangers containing a nest of hairpin tubes heated by the steam. But during start up the main aim was to get the temperature up to a point where all the potassium carbonate was in solution. This was needed as early as possible since a two day period was then required to passivate the Benfield towers against attack by the more acidic potassium bicarbonate. This was done by circulating the solution round and round the Benfield plant. Later, once the plant was in full operation, steam was used for concentrating the lean liquor in the reboiler. This also generated stripping steam from the liquor, and was used in the regeneration tower to help strip the carbon dioxide. One part of the Benfield plant had a small side steam in which a few percent of the gas was subject to a "deeper"  $CO_2$  removal than the bulk of the gas. This stream was needed in the CoMox section of the desulphurisation process, where the hydrogen reacted with organic sulphides to form  $H_2S$ . If the carbon dioxide in this stream had not been reduced to a low level, a strong methane forming, exothermic reaction would have occurred, resulting in serious damage to the catalyst and pressure vessel.

#### 4. Improvements to the ICI Process

The shortcoming of the ICI process was that the calorific value of the gas was only 300 Btu/cu.ft and enrichment using propane or butane was required to bring the calorific value up to that of town gas. When processes dispensing with enrichment were being developed and marketed North Sea Gas was yet to be discovered. But conversion to natural gas began as early as 1968, so the opportunity for innovative town gas processes was just a few years. Apart from the British Gas CRG process, which could be integrated into quite complex plants to make SNG (Substitute Natural Gas) for which there was a sizeable market in the USA, these new "town gas only" plants disappeared from view. As such it does not seem worthwhile spending much time on these, except to highlight the rate of advance in technical development.

The motivation was to eliminate costly butane and propane enrichment, and it can be assumed that all the new town gas processes would have had comparable thermal efficiencies. Efficiency being calculated as the energy in the "substitute" town gas, as a percentage of the energy in the naphtha. Here, it is worth emphasising that the burning of naphtha in the reforming furnace was not a waste. Since the reactions in the ICI reformer are endothermic, much of the energy in the fuel appeared as chemical energy in the hydrogen that had been formed. The remaining heat in the combustion products, leaving the reforming furnace, was used for steam raising or heating the naphtha. The only real waste was in the steam being used for regeneration of the liquor in the Benfield plant. The "art" in the design of a steam reforming plant was to make sure that there was no wasted heat. A rough and ready way of assessing this, is whether there is any surplus steam. With this target in mind, all of the new processes would have had efficiencies in the 90% range. As such, the main criterion, when deciding to invest in a plant would be capital costs.

At this juncture, the figures taken from the paper by Gibson's paper are most interesting, where one of the main aims was to show the superiority of the new processes over the old coal gas retort methods. Hence Table 1, which covers capital costs, also includes Continuous Vertical Retorts. The figures are expressed in terms of  $\pounds$ / kW, would also have enabled listeners and

politicians to make a comparison with the capital costs of coal fired power stations, at the time. These were running at about £35/kW.

# Table 1

Process	Main Feedstock	Capital Cost £/kW
<b>Continuous Vertical</b>	Coking Coal	49.2
Retorts		
<b>Partial Oxidation with Refinery</b>	Heavy Oil/Refinery	21.2 - 25.8
Gas Enrichment	Gas	
Steam Reforming with GRH	Naphtha	8.3 - 20.5
Enrichment		
Steam Reforming with CRG Enrichment	Naphtha	6.6 -12.3
Steam Reforming with Methane Enrichment	Naphtha/Methane	5.0 - 8.3
Steam Reforming to Town Gas in One Step (Topsøe?)	Naphtha	5.3

# Capital Costs of Towns Gas Processes (£/kW)

It will be seen that continuous vertical retorts could be up to almost ten times the price of a steam reformer, and, one would guess, take three times as long to build, and require twenty times the manpower when operating. Partial oxidation is another capital intensive plant of some complexity, requiring the construction of a liquid oxygen plant. The process involves the "burning" of a cheap heavy oil with an insufficient supply of oxygen, which results in a gas containing  $H_2$  and CO. Downstream heat exchangers and gas separators are costly because of the presence of tars and contaminated water.

Turning to naphtha feedstock concepts which eliminated the need for butane and propane enrichment, and were used by British Gas, we have:

# • Gas Recycle Hydrogenator

The GRH or Gas Recycle Hydrogenator, developed by British Gas was also a non-catalytic process, like partial oxidation gasification, but where hydrogen was to react with naphtha, rather than oxygen. Ideally, the gas that formed would consist, in the main, of methane and ethane. In practice, more complex hydrocarbons were also produced, giving rise to a somewhat complex process train.

Since the process was non catalytic, reaction rates were relatively slow. What was needed was a design of reaction vessel in which the reactants spent some time. This was done by promoting a huge amount of recirculation of both the products and reactants in the GRH. Product to reactant ratio was more than 10/1. Since the reaction was mildly exothermic, this mixture kept the reaction going, temperature being about 750°C.

Figure 11 shows, very diagrammatically, what is going on. Fairly pure hydrogen, coming from a steam reformer train, plus vapourised naphtha, all at 450°C is squirted down the centre of a "venturi" within a relatively tall and narrow pressure vessel. In this way recirculation is promoted. On each cycle, as it were, a portion of the mixture is removed, although the process is continuous. The final calorific value being very high at 850 BTU/cu ft, the gas containing about 32% CH<sub>4</sub>, 17% C<sub>2</sub>H<sub>4</sub> and 44% H<sub>2</sub>.



Fig 11: Simplistic sketch of a GRH unit showing flow of gases



Fig 12: More realistic sketch of GRH internals showing venturi.

Another headache for designers was the requirement to heat the hydrogen / naphtha reactants to 450° using the very hot, and not very pure, mixture of methane, ethane and hydrogen coming from the reactor. The most obvious problem was that of thermal expansion, given that the temperature increase of the heat exchanger, on start up was high. Innovative designs were needed. Fouling and high temperature corrosion were problems that emerged with use. In this respect, metal dusting was a unique form of attack. Fortunately, quickly mastered using naphtha which had not been desulphurised. But carburisation was a longer term issue.



#### Fig 13 : Two GRH Streams at Breakwater, Plymouth belonging to South West Gas

Figure 1 shows the GRH plant at Breakwater, Plymouth in which the Hydrogenator vessels are located underneath the gantries. It will be apparent that these are, basically, an add-on to an ICI plant.

## • British Gas CRG

Always referred to as the "CRG", short for Catalytic Rich Gas, was another development by research teams at British Gas. The calorific value of CRG gas was about 650 Btu/cu.ft, enabling operators to dispense with the need for enrichment. At least in theory. At Hitchin the CRG plant was designed so tightly, in terms of heat use and steam generated, that most of the time a small amount of butane was needed to "make "the required calorific value

The reactions in the CRG were essentially similar, to that in the standard ICI steam reformer whereby steam reacts with vapourised naphtha. However, as the reaction temperature was around 480°C, rather than 750°C, the proportion of methane and carbon dioxide in the gas increased, and less hydrogen was made. In addition, since the reaction was slightly exothermic no external heating was needed. Accordingly, the catalyst was held within a large pressure

vessel about 10 ft in diameter and 25 ft high. Operating pressure was 250 lb/in<sup>2</sup> or higher. Figure 14 shows the process flows in the CRG at Hitchin.

The vessel was packed with catalyst with the reaction only occurring over a few inches, but as the catalyst degraded, the reaction zone moved down the bed. The main shortcomings were that inlet temperatures had to be kept within tight limits, and, with use, the catalyst gradually degraded.

All the naphtha on the plant was first vapourised, desulphurised and sent to the CRG. A proportion of the "rich gas" from the CRG was used as the feed to the primary reformer, being mixed with steam, of course. The remainder of the rich gas was mixed with the lean gas stream coming from the primary reformer, just before the Benfield plant.

The CRG outlasted town gas, becoming a vital component of more sophisticated plants built to provide "synthetic natural gas", as the Americans called it, for regions along the east coast of the USA. British Gas used the same initialism "SNG", but to us it was always Substitute Natural Gas.



Figure 14: Process flows on a CRG plant. All the naphtha goes to the CRG reactor. Note that the primary reformer takes some of the rich gas from the CRG as feedstock.

### • ICI 500 Process

ICI's approach was not to mix a high BTU gas with that from a reformer, but to boost the calorific value of all of the reformed gas by putting it through a secondary reformer Here a stream of hot lean gas, straight from the header of the ICI reformer was mixed with superheated steam and vaporised naphtha, which were then reacted over a catalyst that ran at a temperature of about 600°C. A true towns gas substitute was produced with a CV of 500 Btu/cu.ft. The process flow route is shown in Figure 15.



Figure 15: Process flow routes in the ICI 500 Process

As with the CRG, the catalyst was contained within a large carbon steel pressure vessel, <u>protected on the inside</u> with a thick layer of insulating refractory. According to Richard Dennis, who was a shift engineer on the plant, and is a personal friend of the author, the pressure vessel was of the water-cooled double skinned arrangement.

This system only makes sense if the water in the space between the two vessels runs at the same pressure as in the reactor itself and is allowed to reach boiling point. In this way, the temperature of the wall on the innermost vessel runs hot enough to prevent the steam within the reactor condensing on the innermost wall. For example, if the reactor pressure was 400 psi, the water in the space would also be at this pressure. It follows that once the water reached boiling point, the temperature in the space would be at 231°C. However, if the partial pressure of the steam in the reactor was only 220 psi, corresponding to 55% of total gas composition, condensation only happens below 202°C. In this way, the refractory is kept dry and there is also no risk of the walls of the vessel being corroded.

This arrangement was not needed on the CRG reactor as the temperatures were under 450°C, and a carbon steel vessel could tolerate this sort of temperature, if the refractory lining failed. This wasn't possible with the ICI 500 process, the reactions going on at 600°C. The double skin approach is used on the secondary reactors in modern hydrogen plants where the temperature reaches over 1000°C.

There could be problems during start up from cold, with the ICI 500 secondary reactor, when the water within the space had not heated up. Condensation would then be a risk. Another of my workmates from those times, Roger Taylor, who was also a shift engineer at |Chelmsford, seems to remember concern about this on one occasion. As such, my workmates recollect attempting to assess actual wall temperatures of the reactors at Hitchin and Chelmsford with Tempilstik temperature indicating crayons. These days infrared detectors would be used for this job.

It is curious that Eastern Gas built an ICI 500 process at Chelmsford, after the CRG at Hitchin. Perhaps there was a marginal benefit in efficiency? But as well as the need for a double skinned reactor, a lot of refractory lined pipework was needed because of the temperature between the primary and secondary reformers, which would have been at least 750°C. The outlet temperature of 575°C, from the secondary reformer, was lower, bringing it just within the nominal temperature capabilities of Type 316 stainless steel. One of the higher strength austenitics. Here, unlined pipework could be used. However, long term running, at temperature, resulted in metallurgical changes in this material. The result was heat affected zone cracking at Chelmsford of repair welds, and intergranular corrosion at Portsmouth. These issues will be discussed in Part 3 of Steam Reforming in the Gas Industry.

Including the plants at Chelmsford and Portsmouth, one was built at Croydon. Unlike the CRG, the ICI 500 process was not able to make much headway in the USA.

# • Topsøe Town Gas Process

The Norwegian company, Topsøe A/S produced a catalyst which ran at 650°C, which because of the low temperature, produced a gas which contained quite a high proportion of methane, giving a gas of comparatively high calorific value. In essence it was producing a hydrogenrich, town gas directly from naphtha. So, unlike its competitors, it did not require the combination of lean gas and rich gas reactors. Topsøe were installed at Northampton, Slough, Staines, Fulham, and Poole.

How successful they were in practice might be debatable. My research station was on the Fulham site. If there had been big problems, I am sure we would have heard something. Years later I met very briefly someone from Northampton, and he was quite contemptuous of Topsøe, without enlarging on what was wrong.

Nevertheless, the Topsøe process was about a simple as one could wish. So not surprisingly, "Steam Reforming in One Step", in Table 1, which one presumes would be Topsøe, comes out with the lowest capital costs. But since it could only produce towns gas, it had a limited future in a world increasingly dominated by natural gas.

If Substitute Natural Gas "SNG" was needed, the CRG process was a good starting point. The main market was in the USA, where, during the seventies, gas supplies in that country were temporarily on the decline. In this country, a small number of town gas reforming plants were modified to produce SNG, in case of shortage of supplies from the North Sea. For the writer, as a metallurgist, this brought a new set of failures to investigate.

# 5. Discussion and Conclusions

Hopefully, this account, much of which is based on memory, will give a reasonably clear and reliable account of the range of naphtha based steam reforming activities within British Gas. The author began work at Hitchin, in 1966, as a trainee shift engineer on the CRG plants. It was in preparation for my fellow trainees, Roger Taylor and Dick Dennis and myself, taking over the ICI 500 process streams that were being constructed at Chelmsford.

In fact, I did not go to Chelmsford. I wasn't very happy as a shift engineer, it not being intellectually stimulating, but it enabled me to step into an R&D job at British Gas, London Research Station, in Fulham. They needed a metallurgist to take over a project to investigate "reformed gas boiler corrosion". Me, being a metallurgist with some reforming plant experience, was an appropriate choice for them and a lucky one for me.

I will discuss the reformed gas boiler problem in Part 3 of this set of papers on steam reforming in British Gas. The reformed gas boiler project fizzled out, but I was picked up by Peter Beech, a man in his late forties who had become the trouble shooting expert for North Thames Gas. He got me to do the metallurgical investigations for him. and my reforming plant background obviously helped. This was late 1969.

Later on, I did my own investigations on plants at Chelmsford, Portsmouth, Seabank and Breakwater, Watford and Hitchin. When steam reforming ended, with the advance of North Sea Gas, I was made responsible for developing materials for advanced gasifiers. Here again my "training" at Hitchin was more than useful in thinking about what materials and equipment would be needed in future. In effect I was closely involved with naphtha and oil based gasification for about twenty years, which should give this account some objectivity.

There is no doubt that the ICI steam reforming of naphtha, which had grown out of their prewar work with the reforming of light hydrocarbons was a godsend to British Gas. Along with the massive reductions in capital, feedstock and running costs, a vital factor was the speed with which these plants could be built. Two years, from breaking ground, to operation, was normal.

The ICI process would have also stimulated work on gasification catalysts in general. There wasn't much point in competing with ICI's 46/1 directly, although the ingenious Dr Nicklin over at Stretford Labs of the North West Gas Board had formulated a Nickle-Uranium, lean gas, catalyst. Utilising "depleted uranium" it avoided carbon laydown, without having to dope a catalyst with potash, this alkali being responsible for reformed gas boiler corrosion. ICI

overcame the potash problem, which seems to have been worse on town gas reformers than hydrogen types.

However, the main shortcoming of the ICI reformer, the lean gas that it produced, requiring enrichment, resulted in the development of the CRG, ICI 500 and **Topsøe** processes and other catalysts needed to make SNG. The stream reformer approach, originally conceived as a more economic way to make hydrogen, also came in for development. Most of the steam reformers of today use natural gas as a feedstock, but the plants began incorporating a secondary reformer, not too dissimilar in shape to that used in the ICI 500 process, but where air is added, along with steam to the lean gas from the reformer. After treatment it gives an appropriate nitrogen / hydrogen mixture. Such a process leads us to plants suitable for the hydrogen economy, providing the economics make sense, but with oxygen, rather than air going to the secondary reformer.

When thinking about the hydrogen economy, there is a lesson which we as shift engineers learnt, that needs to be a major feature in the specification for reforming plants intended to produce "the gas of the future". Steam reformers of any type were then, and now, designed to run at 100% output, at the highest possible efficiency. But as with present day gas demand, the requirement for hydrogen will vary with the season, with the weather, and the time of day. Plants will vary rarely run at design conditions. We had this challenge back in town gas days, and although a reformer could be made to run at a reduced rate, changes in output had to be done very carefully. In the Section on Plant Operation, I briefly alluded to the fear of losing control of reactor temperatures etc. This issue is never mentioned when we are told how steam reforming will give us all the hydrogen we need. Yes, this might be so. But will we be getting it at the right time in the right quantity?

Finally, as an ex-gas industry man, who finished his career at the European Commission's Joint Research Centre at Petten, in the Netherlands, working on proposals to make hydrogen from coal and gas, while capturing  $CO_2$ , I cannot enumerate the ways in which I would like to thank ICI Ltd for their efforts with steam reforming that this great company began so long ago.

Johnson Matthey Ltd have taken over work on catalyst development from ICI, but their research facilities and offices are still on the Billingham site. Through the Johnson Matthey Technology Review, I have made contact with John Brightling and Chris Murkin, who have done so much to preserve the early history of catalyst development at ICI. So I have great pleasure in dedicating this paper to these two gentlemen.

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