Some Problems in Handling Naphtha

It is very acceptable raw material for ammonia plants as long as precautions are observed, even though some problems do occur from time to time, experience shows.

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This article provides a brief resume of some of the operating problems encountered in the handling of naphtha in Imperial Chemical Industries' ammonia plants at Billingham. The problems largely involve the feed and fuel systems around the reformer section.

It must be stressed that these plants were designed to operate on naphtha feed and fuel in 1966 and operated thus until 1971, when all three plants were converted to natural gas usage. The experiences discussed are, therefore, somewhat historic in nature but may hopefully be of use to those still using naphtha or considering its usage.

The continuous deposition of carbon in the first pass of the naphtha feed vaporizer was a serious operating limitation. The plants were monitored for naphtha throughput and preheater coil tubeskin temperatures; and usually after processing about 40,000 tons of naphtha, the plant was taken off ammonia make to allow a steam/air decoke operation on the coil.

Eight steps in the decoking

The principal steps in the decoke procedure were as follows:

1. Reduce reformer rate to 7 cu.m./hr. naphtha, 40 metric ton/hr. steam and vent gas at inlet "Vetrocoke" plant.
2. Purge HDS free of naphtha with N_2 and drop the reformer pressure to 150 lb./sq.in.gauge.
3. Cease firing on vaporizer and isolate first-pass coil (naphtha-preheat coil) from sources of naphtha and hydrogen.
4. Depressure coil, and purge with N_2.
5. Commence decoke operation.
6. Purge coil with N_2; pressure-test first-pass section with N_2.
7. De-isolate, re-admit H_2. Start firing preheater.
8. Resume reforming operation.

Thus, the first-pass vaporizer coil was decarbonized by firing the preheater on the appropriate side and passing steam through the coil. Minor modifications were made to all three plants to allow decoking on the first pass while the reformer and high-temperature (HT) shift sections are kept at temperatures with steam and thereby almost halving downtime. The general arrangement for the decoke is shown in Figure 1. During the procedure the air is injected at a controlled rate to oxidize the carbon deposit to carbon dioxide.

Further plant changes were made to try to prolong running times between decokes. A limit of 610° C was placed on the vaporizer tube wall temperatures. This limit was held by reducing the Hydrodesulfurizer inlet temperature to 320° C and thereafter slowly reducing output rates.

Secondly, a cylindrical metal heat shield was installed at the base of the vaporizer to protect the hot tube regions of the first-pass coil from direct radiation and flame impingement. The coils were also changed from mild steel to 1¼ chrome/molybdenum.

While all these changes extended slightly the plant life between decokes, it was not until the results of experiments with anti-foulants were completed and the following procedure adopted that we achieved a significant breakthrough to the processing of 90,000 tons of naphtha between decokes.

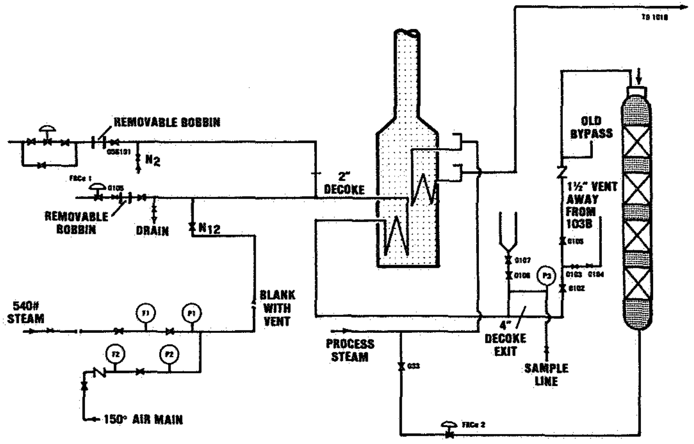

Figure 1. Modification for on-line decoke of naphtha vaporizing coil.

Use of Anti-foulants

The anti-foulant "Betz Petromeen AF103" was finally found to be the most suited to our conditions and this article describes an injection run of three months during which the overall heat transfer (HTC) was calculated periodically and the demise compared with a run on another unit operating without anti-foulant. It must be stressed that the anti-foulants are only effective if the heat transfer surface is initially cleaned so that the run started after a decoke on the plant.

During the first five weeks, corresponding to approximately 2,000 metric tons naphtha evaporated, there was no significant difference between the two sets of results. Thereafter, on No. 1 Unit (anti-foulant addition) the HTC value remained very steady at 7 K-cal./hr./sq.ft./°C but on No. 2 Unit the value dropped over the next five weeks from 7 to 5, during which time the preheater had become an operating limitation.

When the injection of Petromeen to No. 1 Unit naphtha feed was stopped after 11 weeks, the HTC dropped suddenly from 7 to 5, and re-admission of the additive after a week had no effect.

Injection procedure is detailed

The anti-foulant dosing equipment is outlined in Figure 2. It consists of a dope tank, calibration vessel, two positive displacement DCL micro pumps (one running, one spare) coupled to a 1-in. header connected with separate isolations to points A, B, and C. Because of the difficulty in predicting unit availability it was considered expedient to have injection facilities available to all three units. In this test C and B were closed and A open, putting Petromeen to the No. 1 plant feed pump suction. The pump rate is varied by altering the pump stroke and checking the calibration vessel. A concentration of anti-foulant of 20 ppm. v/v was used in this test, but for operating convenience changes in the following range were made: 7-10 cu.m./hr., 200 cc./hr.; 10-20 cu.m./hr., 400 cc./hr.; over 20 cu.m./hr., 590 cc./hr.

Petromeen was injected into the naphtha as soon as the feed was put to the vaporizer on Aug. 29, 1968, and addition continued for 78 days. During this period the unit made ammonia continuously, but because of a primary reformer limitation the feed rate was limited to 25 cu.m./hr. (84% of design). Regular measurements were taken of the vaporizer tube wall temperatures and this was used to calculate the HTC values.

Due to a suspected high pressure differential (ΔP) over the top bed of the hydrodesulfurizer, Petromeen injection was stopped after 78 days and after 45,000 cu.m. of naphtha had been processed. Attempts to check this gave values of 20± lb./sq.in. and after subtracting the effect of the static head of naphtha on one of the gauge lines it gave a ΔP value of 0-5 lb./sq.in. Because of the difficulty in measuring ΔP's by taking gauge differences, a special DP cell has been installed across the HDC top bed of No. 3 unit, and this is located at the very top of the vessel to keep the impulse lines clear of liquid, thus eliminating the static head correction.

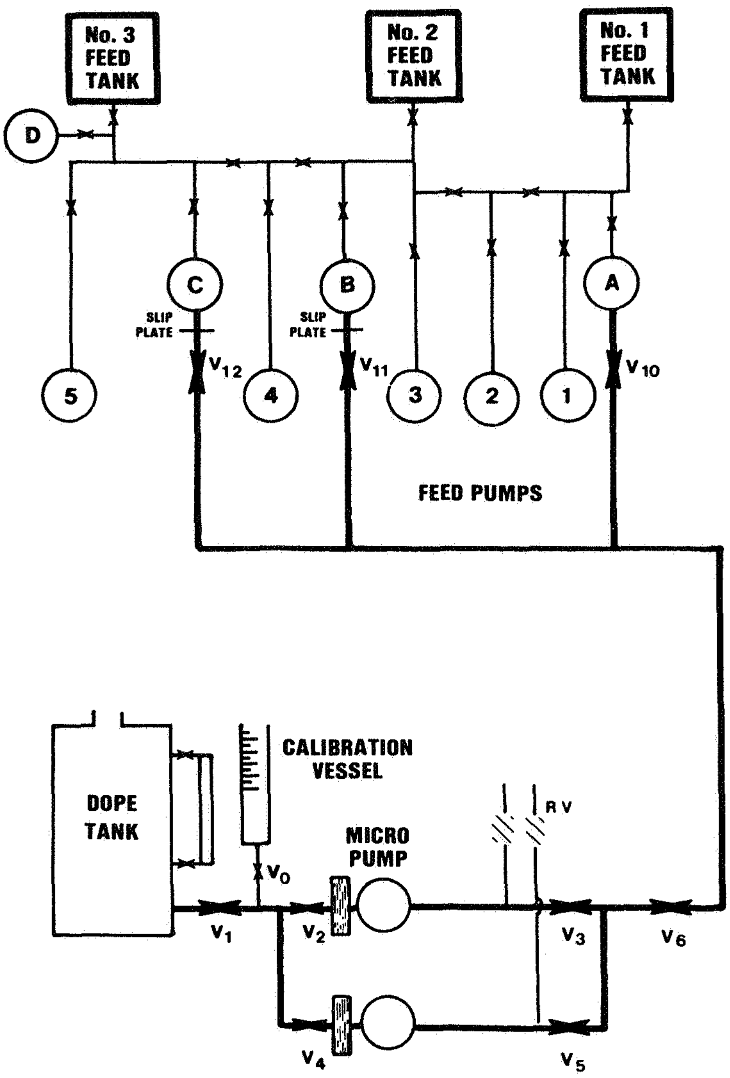

Figure 2. Addition of anti-foulant to feed naphtha on L.P. ammonia.

When it was confirmed that no high ΔP existed across the HDS, the anti-foulant was re-admitted to the naphtha and doping continued until the unit shut down 10 days later. Although the high ΔP across the top bed had been a false alarm it was proposed at the subsequent shut down to remove the HDS top cover and initially inspect the top of the catalyst for excessive carbon carry-over. This investigation showed considerable quantities of a very light fluffy carbon that had obviously blown over from the preheater onto the zinc oxide bed.

An alkalized catalyst is essential for the successful operation of a naphtha reforming process. As well as having a need for high physical strength and the required catalytic activity, one of the main requirements is the presence of about 7% K_2O to allow low steam/carbon ratios in operation without fear of carbon deposition. Unfortunately the potash tends to volatilize from the catalyst and is deposited in the cooler parts of the plant—such as the secondary waste heat boilers and the HT shift converter.

Contrary to common belief, it was noticeable on the Billingham plants and shown in Table 1 that:

1. Rates of K_2O evolution were very similar on all three plants.

2. The K_2O level evolved did not vary significantly with time and seemed independent of the K_2O content of the catalyst.

3. During plant start-up, shut-down, or change in operating conditions, the expected peak levels of K_2O measured were not noted.

Later plant operations with a mixed alkalized and non-alkalized catalyst showed that potash evolution rates were reduced five fold initially but after about 6-8 weeks of operation the rates were those shown in Table 1.

The non-alkalized catalyst filled the lower half of the tube and because it had a higher activity the furnaces were operated with lower tube temperatures.

The lower catalyst was shown by analysis, in Table 2, to be an effective potash catcher, although eventually all the pure potash would leave the furnace and be deposited downstream.

Table 1. Rates of evolution of potash after nine months' operation

	(ppm) K_2O in condensate exit primary		
% Flowsheet	No. 1 Plant	No. 2 Plant	No. 3 Plant
20	2-4	1-4	2-4
40	3-5	4-6	4-6
60	2-8	4-8	4-8
90	3-5	4-6	3-5

Table 2. Analysis of potash deposits on catalyst

Distance from top of tube	% K_2O on catalyst
4 ft., 10 in.	6.0
8 ft., 10 in.	5.9
12 ft., 10 in.	5.9
16 ft., 10 in.	5.3
20 ft., 10 in.	4.6
24 ft., 10 in.	4.4
25 ft., 10 in.	4.0
26 ft., 10 in.	1.5*
31 ft., 10 in.	1.7*

* Catalyst 46-2 Non-alkalized

The potash usually showed its presence in the increased pressure drop observed across the HT shift converter. This pressure drop was usually removed by a hot demineralized water or condensate wash of the catalyst at an appropriate shut-down.

Although not a serious problem, potash attack occurred on the weld at the base (cold gas end) of the secondary reformer trim boiler, and this problem was easily overcome by the insertion of an "Incoloy" sleeve at this point on all three plants.

Finally, although we never saw the expected peaks of K_2O during the start-up and shut-down conditions it was a golden rule that we minimized the time and temperatures at which steaming/oxidation conditions prevailed in these operations.

The need for rigorous attention to steam/carbon ratio control to avoid deposition is well-known and will not be dealt with here; however, the cracking of naphtha inadvertently at start-ups is less well known and deserves comment.

After bitter experience with slow carbon build-up and resultant problems with hot tubes and gas mal-distribution, we discovered the need for many more drains at low points in the system. Particular care must be taken at start-up to ensure that no naphtha vapor is being circulated over the reformer catalyst during this period. We always found it advantageous to start cold nitrogen circulation with all drains cracked open, and a gas analysis to check the near absence of carbon, before any burner light-off was permitted.

Fuel system problems include burner and filtration

Difficult and hazardous furnace conditions can ensue if the naphtha fuel system is not carefully designed. Our naphtha fuel experiences lead us to favor a dual spill-back system with automatic pressure control. The controller is sited close to the pump-end of the system and spill-back is to the supply tank; and the spill-back at the burner-end is back to the tank via a fixed sized orifice. This system seems to be the most practical to give minimum disturbance to the system while burners are being commissioned.

It is a wise procedure to determine a regular burner 'light off' pattern and to ensure safe operations the first 10% of burner should be fitted with flame failure trip protection devices.

Naphtha burners are prone to carbon and metal oxide deposits "build-up" at the tips, and the resulting back pressure causes upsets in firing patterns as well as in increased tendency for unburnt naphtha falling into the furnace, and leaks at joints in the burner locality.

A good practice is to clean burners on a routine program. It was our custom to change 10-12 burners per shift on a fixed plan. Individual burners were completely dismantled and cleaned by air blowing, drilling tips and scatter scaling before being judged suitable for re-use in the furnace.

During plant start-ups there was a regular difficulty caused by pipe mill scale and other small solids blocking burner tips and causing flame failures and upsets. It became standard

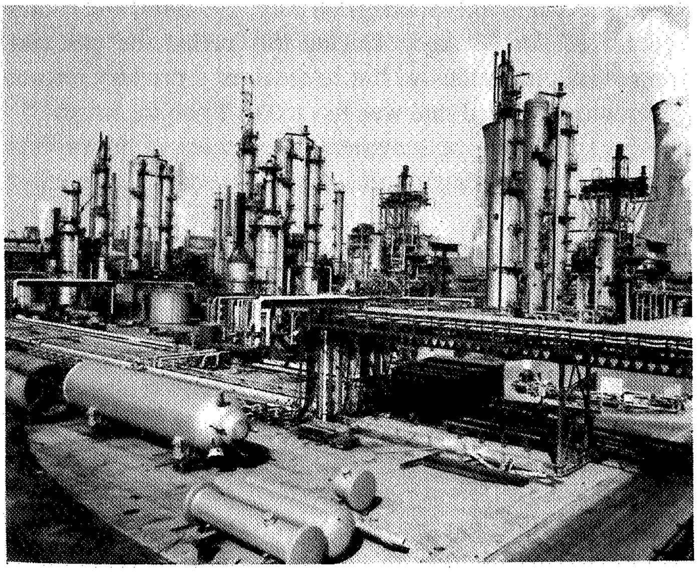

Figure 3. Operating ammonia plant.

practice to use about twelve "start-up" burners that were specifically well marked and from which the internals had been removed. These were the initial "light off" burners and were replaced when furnace conditions were stabilized, usually when about one-third of the furnace burners were in operation.

In order to work on burners and leaking burner block problems it was necessary to establish elaborate fire precautions and indeed the need for such operations with the furnace in commission was minimized by: minimum possible joints around the furnace top, e.g. two joints at isolation valve, one joint near burner block to allow removal of block, and one joint on burner block to allow removal of seats and ball. Metaflex joints were used throughout and flanged joints were preferred to threaded connections. The most successful naphtha isolations in the fuel system were achieved using stainless steel ball valves. Atomizing steam systems were fitted with traps at the end of each header and the steam condensate was regularly checked for naphtha as a means of detecting any burners fouling. The naphtha usually backed into the steam system.

The fuel system contained filters in series, but each filter was in turn duplicated in parallel. We had initial automatic filters with a 12-micron cut, followed by "Plenty" mesh filters, usually with one filter at 100-mesh and one at 300-mesh cut.

Naphtha appears to have good scavenging properties, and we suffered regular burner blockage problems due largely to pipe mill scale until we decided to change over the mesh filters on a regular shift basis regardless of the pressure drop measurements taken across the filters every hour.

Our experience on the Billingham ammonia plants was that, while these problems were encountered with naphtha and it had to be handled with care, providing the basic rules and precautions were obeyed then it was a very acceptable process raw material. #


LIVINGSTONE, J.G.

DISCUSSION

ED JOHNSON: Allied Chemical Co.: I have two questions concerning your decoking. What was the material of construction of your naphtha coil, first pass.

LIVINGSTONE: It was carbon steel initially. We did change to 1¼ chrome-molybydenum.

JOHNSON: And how did you control a runaway decoking reaction?

LIVINGSTONE: To trip out firing. The only way to do it was in fact we had temperature alarms only on the skin tubes temperatures, if they moved at all above the normal, it was 450°C, if they moved at all above the limit we set, we tripped the firing and just let the steam running in with the air out.

JOHNSON: And that was sufficient to prevent damage in the coil?

LIVINGSTONE: Yes.

JOHNSON: Interestingly, as an aside, we found that many burner manufacturers for oil would recommend a standard 40 mesh screen, but Mr. Lambert formerly at our Hopewell plant came up with a system using a filter. He found that if you used a filter in the 20-40 micron range on the oil, this extended the burner clean-out from a matter of days to a year. This might be of interest in liquid fuel systems.

E.F. NEEB, Erdolchemie: You have said nothing about an oxygen stripper—did you have an oxygen stripper at all, did you strip off the oxygen from naphtha before it is desulfurized?

LIVINGSTONE: No, we did not consider the expense justifiable. We did, however, use the process in another plant.

NEEB: We ran our plant at Dormagen, Germany, for four years with an oxygen stripper until we changed feedstock from naphtha to natural gas. We have had very good success with oxygen stripping, there was almost no coking of the coils in the naphtha vaporizer. In four years of operation we never had to decoke the coils.

LIVINGSTONE: Yes, I think that if, in fact, we'd been going on with naphtha, we almost certainly would have gone to oxygen stripping. It seemed to have been the answer at our Immingham plant where, in fact, we do or at least we did have until we converted the plant to natural gas.