Troubleshooting Distillation Columns
Unexpected Causes for Malfunctioning Columns

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The cause of columns performing below expectation is often intuitively attributed to issues with column internals. But there are also other reasons. Two cases are presented, the first shows how to properly deal with trapped inert gases during startup and the second case shows how reversible reactions can affect separation performance and how apparent performance loss in such situations can be overcome.

1. Unexpected Hydraulic Performance

1.1 Description of Unit

The first case is about a three effect distillation unit for a highly corrosive mixture. The column operated at the highest pressure was designed to produce a gaseous component overhead, which was further processed at a pressure of 5 bar downstream of the column. The column was operated slightly above 5 bar to overcome the pressure drop of packing, column internals, piping, partial condenser and control valve. The control valve was designed with a relatively small pressure drop with the aim to minimize the bottom pressure of the distillation column to reduce boiling temperature and corrosion risks. For startup, off-spec operation and emergency cases, a second, smaller control valve was installed to guide the corrosive gas into an absorber operated at atmospheric conditions using water as scrubbing liquid, as shown in figure 1.
The high-pressure column operating at 5 bar, comprising the highest corrosion risk, was packed with Sulzer Mellacarbon™ and consisted of a stripping section and a short rectifying section. A feed gallery to handle the flashing feed stream was made of carbon. The other two columns operated at lower pressures were packed with Sulzer Mellapak™ and packing and column internals were made of Polyethylene.

1.2 Observed Problem

During commissioning, after a relatively common startup procedure for corrosive media first done with water, the first pump down-stream of the sump of the pressure column tripped. The reason was excessive pressure drop across the strainer of the pump. Small carbon fiber particles were found in the strainer and after cleaning, only a short time later the pump tripped again due to high strainer pressure drop caused by accumulated carbon fiber particles. In addition, the pressure drop in the high-pressure column was more than a factor 3 higher than expected. In view of this unexpected high packing pressure drop and repeated strainer blockage, it was decided to shut-down the plant and to open the pressure column for visual inspection.

1.3 Observed Damage

The inspection showed a lot of damage to the bottom carbon fiber bed and some of the graphite internals. The bottom support grid from graphite was broken, but it was still able to support the Mellacarbon packing. The lowest packing layer was destroyed and the 2nd layer was severely damaged. Furthermore, the top layer of the bottom bed was destroyed and the second layer damaged. The other layers were still intact. The liquid distributor, a chimney tray with ground holes made from graphite, did not have significant damage, but it had been lifted up and fallen back in position. Some Mellacarbon packing sheets were jammed between the support grid and the distributor, as can be seen in Figure 2. The upper Mellacarbon bed did not show any mechanical damage, however, the liquid distributor at the top had damaged gas raisers and the liquid feed pipe, guiding the reflux into the liquid distributor was torn and heavily damaged.
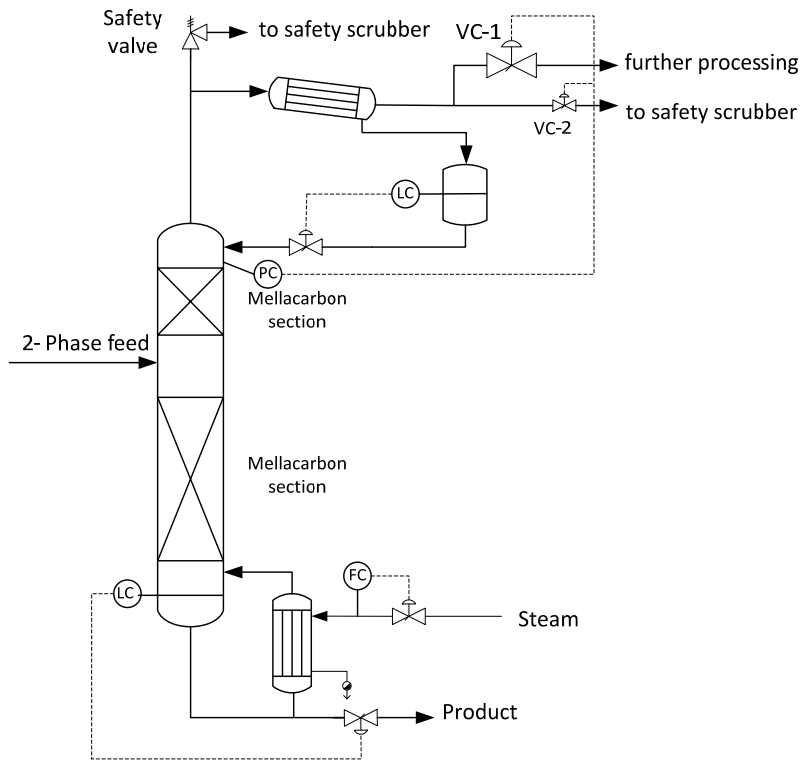
Figure 1: Simplified Process Flow Diagram of the high-pressure column

Figure 2: Left: Chimney tray made of graphite (view from below), with jammed Mellacarbon™ sheets; right: top layer of Mellacarbon™ of the upper section remained in place.

1.4 Investigation of Possible Root Causes

As the commissioning of the plant was progressing smoothly, apart from the strainer blockage, the severe damage to the packing and internals in the high pressure column came as a surprise. The more so as product specifications at startup conditions with internal loads lower than design capacity could be reached.

To find the root cause of the damage, the records of the process control system (DCS) were analyzed. An incident was reported during water tests when the safety valve of the high-pressure column opened. It was soon suspected that this could be the possible root cause. With the help of the recorded temperatures, pressures and level information from the DCS in the time slot around the incident and the assumed interventions by the operators, the sequence of events could be reconstructed.

During the water test, the high-pressure column was started up by opening the steam valve to the reboiler manually with a fixed position. The control valves VC-1 and VC-2 remained closed in manual position, so inert gases in the column were trapped. The temperature of the column sump, filled with water, started to increase due to the steam supply. When the temperature exceeded 100°C, the pressure in the column started to

increase and at 160°C, the pressure was about 6 bar. At 6.5 bar pressure increase the safety valve, which was located up-stream of the condenser, opened. At this point in time the condenser had cooling water supply and was still cold. The inert gas could now leave the column through the safety valve and the inert gas, steam mixture was released through the safety scrubber. However, the condenser down-stream of the safety valve, still filled with trapped inert gas, remained cold. The pressure in the column remained rather stable around 6.5 bar while the safety valve opened and closed intermittently. Based on the DCS records the release through the safety valve continued for a few minutes. The noise of the chattering safety valve made the operators aware of the situation and the control valve to the atmospheric safety scrubber VC-2 was partially opened. Now the inert gas from the condenser was able to escape and inert and steam were released through VC-2 and the column pressure rapidly decreased. This rapid decrease in pressure was partly due to the steam leaving through the control valve but more importantly because of the high condensation rate, as pure steam has an excellent heat transfer coefficient and the temperature difference was high. Based on the recorded liquid level, the initially empty reflux tank was filled within a few seconds. Estimates of the condensation rate indicate that, during this short period, the F-factor must have been extremely high, exceeding 25 $Pa^{0.5}$. At this F-factor, the column was flooding and the pressure drop was so high, that the Mellacarbon packing was lifted up. This uplift might have additionally increased the pressure drop because loosened packing sheets reduced the free area for the gas flowing through the liquid distributors. Consequently, the column internals were also lifted and the observed damages could occur.

1.5 Modified Startup Procedure to Prevent too High Vapor Loads in the Column

The control valve VC-2 to the safety scrubber was designed to restrict flow rates to avoid mechanical damage, even when fully opened. It was the condenser, performing much better than at design conditions, which caused the high F-factors and resulting damage to the internals. The condenser was designed to condense a relative small fraction of liquid from a gaseous phase. The design heat transfer coefficient was small and the transient situation, when pure steam entered a cold condenser, was not considered. To avoid the rapid pressure decrease at startup, the startup procedure was modified. Steam supply to the reboiler required now the pressure control valve VC-2 to be set to automatic mode and the position of the pressure control valve was limited to a minimum value allowing the inert gas to escape. Only when the overhead temperature of column exceeded 100°C, the limitation of the valve position was disabled.

2. Unexpected Separation Performance

2.1 Description of Unit

The second case describes unexpected poor performance of a column separating impurities from an ethanol/water mixture. Light and heavy boilers needed to be removed to low concentrations in the ppm range. In a first column, heavy boilers and water were removed from the bottom to achieve an ethanol/water distillate with a concentration close to the azeotrope. The top product was then fed to the second column to separate the light boilers overhead. Light boilers concentrations were very low, only approximately 100 mg/l. The plant had an automatic startup and shutdown control procedure without need for manual intervention by operating personal as the unit had to undergo frequent cleaning cycles and minimizing the startup time was important.
The first column achieved all required specifications; however, the second column had an unexpected poor performance in separating light boilers. Light boilers of interest in this context were ethyl acetate, acetaldehyde and diethyl acetal. Diethyl acetal was specified in the feed only in small quantities and its specification in the product was the least stringent. Therefore, diethyl acetal was never a concern in the design phase, though it is the light boiler with the smallest relative volatility. Based on available experimental VLE data, ethyl acetate was expected to be the most difficult component for the separation and the design was accordingly based on this requirement.

2.2 Observed Problem

As mentioned before, the first column was fulfilling all expectations, but the second column (Figure 3) did not achieve its performance as expected. The acetaldehyde content was higher than expected and the specification could not be obtained constantly. Particularly, when the column was restarted after a cleaning cycle, the acetaldehyde content was particularly high in the bottom product and exceeded the specification significantly. Only after many hours of continuous operation, the acetaldehyde concentration reached its steady state, close to the required specification.
The "bleed" stream at the top of the lights removal column was about 1% of the bottom stream and consisted of 5 to 10 wt-% light boilers. The remainder was ethanol and water.
To monitor the behavior of acetaldehyde in more detail, samples from the bottom were taken during startup in short intervals. The samples were analyzed using a gas chromatographic method (GC). Figure 4 indicates the

time dependency of the concentration of light boiling impurities analyzed in the ethanol/water product in the bottom by GC.
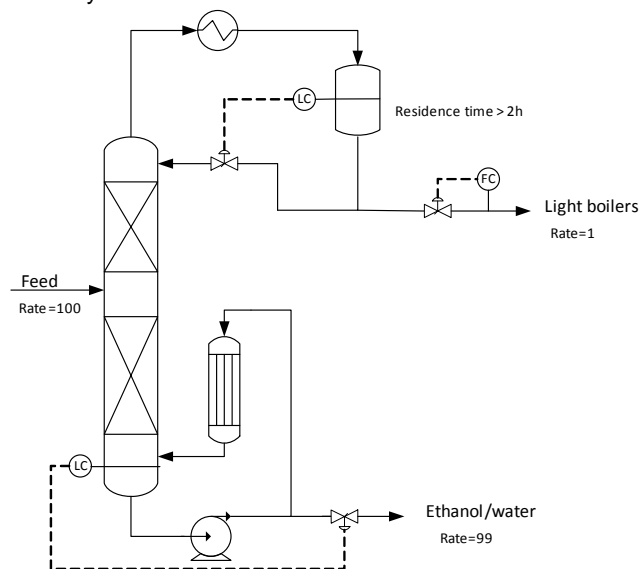

Figure 3: Simplified Process Flow Diagram of the second column, removing light boilers
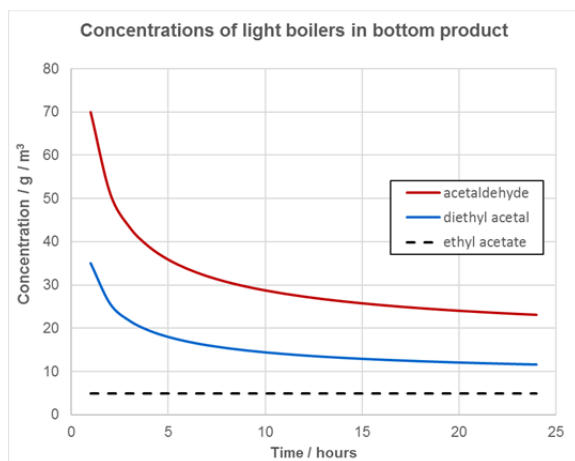

Figure 4: Time dependency of the concentration of relevant light boilers in bottom product stream as measured by the GC.

2.3 Interpretation of the Results

The results from the GC did not show any unexpected peaks beside acetaldehyde, ethyl acetate and diethyl acetal. However, the ethyl acetate concentration was stable after one hour of operation but acetaldehyde and diethyl acetal concentrations became only stable after about 24 hours. The initial high concentration of acetaldehyde and diethyl acetal in the bottom (main product) after startup was significant and exceeded the required specification by more than a factor of three. It was suspected that acetaldehyde and diethyl acetal underwent reactions during shut-down time. Question is now what reaction could cause that acetaldehyde and diethyl acetal showed such behavior? If acetaldehyde was reacting to form diethyl acetal, one would expect that the acetaldehyde content is low and vice versa, when acetaldehyde was formed from diethyl acetal, then it was expected to find a reduced acetal concentration in the bottom.

In order to further investigate possible reactions that might occur, it was decided to use NMR-technique to monitor reactions in-situ.

2.4 In-situ NMR Analyses

Solutions containing ethanol, water and acetaldehyde were prepared and analyzed using ^{1}H-NMR. The results revealed that the following reactions took place:

Hemiacetal is formed from acetaldehyde and ethanol.

$$CH_3 - CHO + CH_3CH_2 - OH \leftrightarrow CH_3 - CH(OH) - OCH_2CH_3 \qquad (1)$$

Hydrate is formed from acetaldehyde and water.

$$CH_3 - CHO + H_2O \leftrightarrow CH_3 - CH(OH)_2 \qquad (2)$$

The formation of hydrates and hemiacetals is known to occur from textbooks (Vollhardt, 1990). In the particular case of acetaldehyde, the equilibrium was established relatively fast with both ethanol and water. When the samples with ethanol, water and acetaldehyde were prepared and then measured by NMR, no change in concentration with time could be observed. Preparation of the sample, transferring it to the NMR and heating it to 75°C required less than one minute. Therefore, it can be concluded that equilibrium was closely established within less than a minute.

Though hydrates and hemiacetals have been clearly identified in the solution, these components do not exist as pure components since they "decompose" to acetaldehyde and water or ethanol, respectively, when purified. Therefore, hydrates and hemiacetals cannot be detected as individual components by GC methods. They will be detected in form of acetaldehyde and water, or ethanol, respectively.

In samples containing ethanol, water and acetaldehyde, also diethyl acetal was always found. The relevant reaction is as follows:

$$CH_3 - CHO + 2\,CH_3CH_2 - OH \leftrightarrow CH_3 - CH(OCH_2CH_3) - OCH_2CH_3 + H_2O \qquad (3)$$
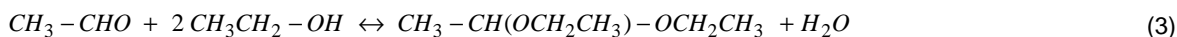
The ^{1}H NMR lines of hemiacetal and diethyl acetal were unfortunately completely overlapping and it was not possible to determine these components quantitatively.

The formation of diethyl acetal came as a surprise since it was expected that the reaction occurred only in presence of acids (Vollhardt, 1990), which act as catalysts. To ensure the reaction takes place also in the presence of water only, the following test was carried out: Pure diethyl acetal was mixed with water, forming two liquid phases. The aqueous phase containing about 5% acetal was analyzed with NMR. The formation of acetaldehyde was monitored for two hours. It was found that the reaction is slow at 75°C. The concentration in acetaldehyde continuously increased, however equilibrium was not fully achieved after 2 hours. In addition, in a separate test it was shown that acetaldehyde mixed with pure ethanol only forms the hemiacetal and no diethyl acetal.
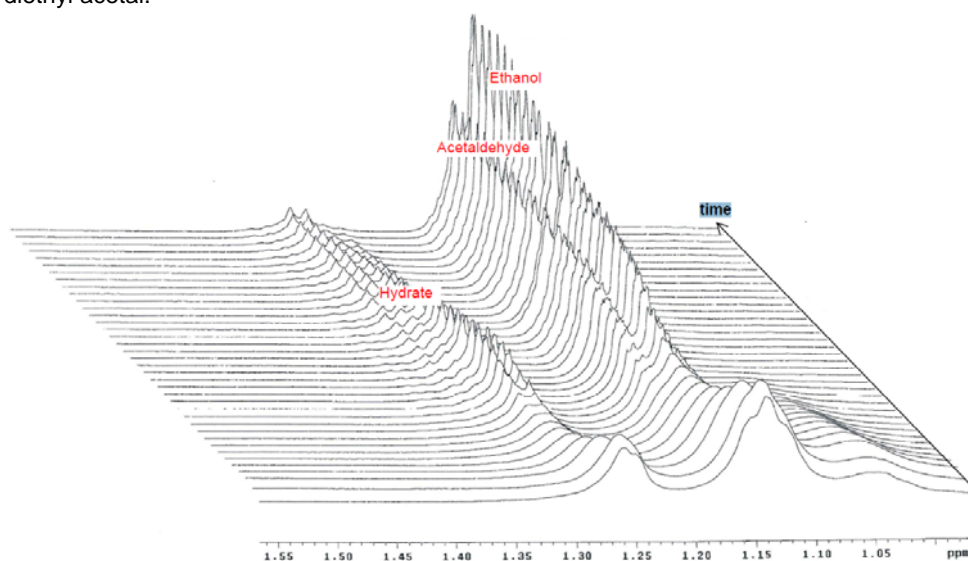

Figure 5: 1H-NMR results showing formation of acetaldehyde and ethanol for a time span of 2 hours, starting from an aqueous phase saturated with diethyl acetal, with no initial ethanol or acetaldehyde.

2.5 Explaining the Observed Column Performance with the NMR Results

As mentioned, GC analyses are not able to detect hemiacetals nor hydrates. These components are only present in solutions, forming a chemical equilibrium with water and ethanol. When these components are separated as they are in a GC, water and acetaldehyde, or ethanol and acetaldehyde, respectively are formed and these components are detected as such.

Diethyl acetal is a stable component in pure form and is detectable by GC. The reaction kinetics to form acetaldehyde from diethyl acetal is relatively small in presence of water and requires a long residence time. However, during the time between sampling at the plant and analysis in the lab the system will come closer to its equilibrium composition. During that time span, the ratio of acetaldehyde and diethyl acetal might change. An analysis will only be able to accurately determine the sum of acetaldehyde and diethyl acetal. This approach to equilibrium also explains why the measured ratio of acetaldehyde and diethyl acetal in the columns samples has been nearly constant. – Now, how does this equilibrium reaction lead to a very high acetaldehyde and diethyl acetal concentration in the bottom product at startup?

Firstly, high residence time in the overhead system: the bleed stream at the top of the column was only about 1% of the feed stream. The overhead system consisted of a condenser with a reflux tank and reflux pump. The reflux was level controlled and the bleed stream was controlled by flow rate (Figure 3). Due to this small bleed stream rate, residence time in the column overhead system was more than 2 hours.

Secondly, diethyl acetal formed during the shutdown was, when starting up, refluxed into the column making the separation significantly more difficult. As a result, the diethyl acetal bottom concentration increased. In the GC analysis of the bottom product, diethyl acetal was detected partly as acetaldehyde because the chemical equilibrium was not achieved at the time when the sample was taken (only little acetaldehyde present), but equilibrium was more closely established when analyzing the sample in the lab, showing a higher acetaldehyde content, too. This is the explanation for measuring both components with increased concentration at startup.

Thirdly, the separation of acetaldehyde became more difficult than what was expected based on VLE data, because hydrates and hemiacetals were formed. These components behave as heavy boilers compared to ethanol. Although "free" acetaldehyde has a high relative volatility and can be easily reduced in the liquid phase toward the bottom, hydrates and hemiacetals remain in the liquid phase and will reestablish chemical equilibrium by "decomposing" in aldehyde, water or ethanol. These equilibrium reactions were found to be relatively fast but not instantaneous and this leads to apparent loss of column separation performance.

2.6 Solving the Column Performance Problem

Based on the gained insight, the overall column performance could be significantly improved and the startup time after cleaning cycles reduced. Firstly, the liquid hold-up in the overhead system was reduced. Secondly, the residence time at the bottom was increased. This increased residence time was expected to have a positive effect since a low acetaldehyde concentration would shift the chemical equilibrium and diethyl acetal would decompose to form acetaldehyde, which could be removed from the bottom due to its high relative volatility. In this case, unfortunately not very elegantly, the only practical option to increase residence time was to increase the set point of the level control in the sump closer to the high level alarm.

Both measures allowed reducing startup time and achieving steady state within an hour.

Measured acetaldehyde in the bottom was reduced and bottom product specification, altered based on the findings of the NMR tests to the sum of acetaldehyde and diethyl acetal, could be achieved.

3. Conclusion, Lessons Learned

In the first case, unexpected transient conditions caused very high vapor loads for a very short period, which were able to damage the column internals. During the detailed engineering phase, it was not considered that the condensation rate could be so high due to the very good heat transfer of pure steam at transient conditions. A modified startup procedure could solve the problem. In this case additional knowledge was gained on how to deal with inert gases during commissioning.

The second case showed unexpected startup behavior and unexpected, low separation efficiency because of chemical reactions, which were not considered or were even unknown during the basic design phase. Once the chemical reactions were understood, the required actions to improve the situation could be easily implemented. The learning is: a high and inconsistent content of low boiling components in the sump may be caused by reversible chemical reactions involving high boiling intermediates.

References

Vollhardt K.P., 1990, Organische Chemie, VCH Verlagsgesellschaft mbH, D-6940 Weinheim, p.650