Fabrice Cuoq, Jérôme Vachon and Anthoni W. van Zijl, SABIC Technology & Innovation, the Netherlands, along with Theodore Arnst, Nalco Champion, an Ecolab Company, USA, investigate the relationship between fouling and phase integrity in dilution systems.

CAUSE AND EFFECT

A reliable and stable dilution steam system (DSS) within an ethylene plant is essential for efficient heat transfer and energy recovery. It is responsible for separating condensed steam from condensed hydrocarbons and for the production of dilution steam for furnaces. Any disturbances in the DSS can be highly problematic; fouling can lead to substantial energy losses, plant capacity restrictions, frequent cleaning procedures and unplanned shutdowns. These situations translate to millions of dollars in added expenses annually.

Fouling problems can manifest themselves in many forms, including the formation of radical polymers, solidification of pyrolysis tars, and deposition of corrosion byproducts, to name a few. The root cause of these issues relates to poor phase separation (hydrocarbon from water) and is influenced by many factors that are often difficult to control. Because of the uniqueness of every DSS, an industry standardised treatment method is not possible. However, there is a strong incentive to elucidate the dynamics within the system and develop improved mitigating solutions as a stable, reliable DSS performance brings a strong cost advantage and improved chances of uninterrupted production.

This article shares the findings of a collaborative research project to investigate the root cause of fouling formation in a DSS. Fouling is the 'effect' that is readily
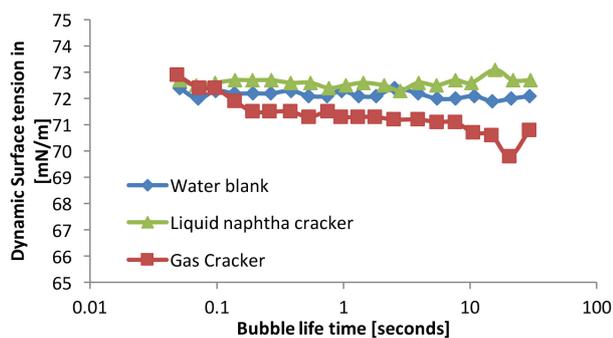
Figure 1. Dynamic surface tension measurements can determine the presence of surface active agents.

identified and observed; it is the manifestation of poor process water integrity. The cause of poor process water quality is generally oil-in-water emulsion formation that causes carry-over of heavies, such as pytars, and polymerisable monomers, such as styrene, to the DSS.

Research aimed at quantitatively answering questions such as the following:

- Which chemical species are present in process water that contribute to emulsion formation?
- What is the role of pH on emulsion stability?
- What is the primary source of ammonia in process water as the latter can affect pH?
- What are the conditions that could explain fouling in unexpected areas of the DSS?

The drive is the philosophy that an improved understanding of the 'cause' will promote the development of mitigation strategies to eliminate DSS issues or, at least, minimise its impact on plant operations.

The DSS can be considered a large loop for the process water in the plant. The dilution steam is condensed in the quench water tower (QWT), separated from pyrolysis gasoline (pygas) in the quench water settler (QWS), stripped of light hydrocarbon in the process water stripper (PWS) and turned back to steam in the dilution steam generators or the feed saturators in some designs (DSG/SAT).

The cracked gas stream coming out of the furnace section contains significant amounts of reactive monomers and pytars, which are potential fouling precursors in the DSS. It is important to emphasise that pytars are a problem specific to gas crackers as liquid crackers include a primary fractionator to remove heavy material. Sections that discuss fouling impact of pytars are referencing gas crackers only. In the QWT, which includes the quench water loop (QWL), the reactive monomers and pytars condense with the pygas and steam. Temperatures of 40 – 90°C and long residence times are enough to induce unwanted polymerisation. The polymer is unlikely to lead to direct problems because the polymer is still soluble and emulsified in the pygas. However, the colder regions of the QWL can suffer from pytar solidification if there is insufficient pygas to keep the pytar fluid.

The process water and hydrocarbon (including any polymer and pytar within) progress to the QWS. Here, the

primary issue relates to emulsions. The severity and stability of an emulsion are influenced by residence time, mixing energy, pH, emulsifiers (such as large heteroatom containing compounds), and particulates consisting of polymer, pytar and/or corrosion byproducts. Recycle streams are often responsible for emulsion formation as they are a common source of particulates, acids/bases or amphiphilic molecules. Emulsions provide a mechanism to transfer hydrocarbons, including foulants, to the downstream units.

If the water and hydrocarbon separation is effective, relatively clean process water enters the PWS. Dissolved hydrocarbons, including reactive monomers, can be present and should be stripped out in this unit. The temperature is high (110 – 130°C), and if stripping is insufficient, polymerisation can occur. In addition, emulsions can transfer high loads of hydrocarbon to the PWS. Removal of any solvating hydrocarbon will then lead to the deposition of pre-formed foulants and the high temperatures will cause ageing of the deposits.

The stripped water, emulsified hydrocarbons and any suspended solids will flow to the DSG/SAT. High temperature and/or poor pH control can lead to severe corrosion problems, typically 'under deposit' corrosion. The concentration of non-volatiles through steam production leads to precipitation and deposition of corrosion byproducts, polymer and pytar.

Fouling

Many fouling issues in the DSS relate to the polymerisation of reactive monomers. Styrene, indene and dienes readily undergo radical polymerisation. Dienes can also react through Diels-Alder cyclo-addition, especially cyclopentadienes.

Reactive monomers are ubiquitous in the pygas and reactions are certain to proceed in every plant to some extent. The extent of polymerisation and oligomerisation is directly influenced by temperature, residence time and monomer concentration. For instance, in the QWT and QWS, temperatures are moderate, while residence time and monomer concentration are relatively high. Therefore, polymerisation can occur. In contrast, the temperature is high in the PWS, but the monomer concentration is low as, in principle, only the water dissolved species are carried to this unit and get stripped out directly. Inefficient stripping or bad separation of pygas and water in the QWS increases fouling severity. Finally, polymerisation in the DSG/SAT unit is minimal, in theory, but organic fouling and deposition in this location does occur in these sections.

Solvent influences the rate of organic reactions. Depending on the location and the quality of separation in the DSS, the solvent is either water or a mixture of pygas and water. Water is known to accelerate Diels-Alder reactions and radical polymerisation. Diels-Alder cyclisations between cyclopentadiene and polar dienophiles can be 15 – 500 times faster, compared to the same reactions in other solvents, while the dimerisation of cyclopentadiene is reported to be 150 times faster than in benzene.[1-3]

Radical polymerisation is another mechanism that leads to fouling in DSS; parallels can be drawn between these

unwanted radical polymerisations and the on-purpose emulsion polymerisation technique used in various industrial applications. In emulsion polymerisation, the reactions take place in a binary phase solvent system. The monomer is usually dispersed as droplets within an aqueous phase with the help of surfactants. The radicals form in the aqueous phase and enter a dispersed droplet of monomer. The radical initiates polymerisation and the rate of termination by other radicals decreases because of the isolation of the radical within the droplet. In addition, thermal initiation of styrene polymerisation in a mini-emulsion was 3 – 15 times greater than that in bulk and was related to the oil-water interface, with radical generation in the aqueous phase playing a negligible role.[4]

In summary, this article reports conditions that may explain the high severity fouling that is occasionally observed in plants. First, Diels-Alder reactions significantly accelerate in water. Secondly, radical polymerisation of styrene is accelerated in emulsified binary solvent systems, analogous to conditions, which are observed in DSS, emulsions of pygas and process water.

The industry collectively refers to the C5 to C9 fraction as pyrolysis gasoline, 'pygas'. Another byproduct is a collection of higher molecular weight hydrocarbons, which have a high viscosity that ranges from an oil, to a tar, and even a solid, when observed in aggregate. This byproduct is known as 'pytar'.

In liquid crackers, a primary fractionator receives the furnace effluent after it leaves the transfer line exchanger (TLE). Pytar accumulates in the bottom of the primary fractionator as quench oil. This prevents the majority of the pytar from entering the QWT and downstream units.

In a gas cracker configuration, i.e. cracking ethane, propane and/or butane, there are insufficient quantities of pygas and heavy hydrocarbons to facilitate proper operation of a primary fractionator. Therefore, these hydrocarbons accumulate in the QWT and need to find an outlet, often through the DSS. Various studies on TLE fouling discuss 'tar' formation and it is inferred that high molecular weight compounds condense in the TLE and enter the QWT as a liquid phase.[5-7] Meanwhile, the pygas enters the QWT in the gaseous state, and it condenses in the upper sections of the QWT. In the absence of light hydrocarbons, pytar has a density that is greater than water, and it is for this reason that 'gas crackers' have an oil/water separator designed to handle three phases; heavy oil phase (pytar), water phase, and light hydrocarbon phase (pygas).

Pytar composition is highly variable and can, therefore, exhibit a range of viscosities. It contains a high quantity of polynuclear aromatic compounds (PNAs), which are mutually soluble with the highly aromatic compounds of pygas. When three to five-ring aromatic structures of pytar mix with one or two-ring aromatic structures of pygas, the pytar can be very fluid in nature. Conversely, if a composite of the large ring structures is devoid of the smaller structures, the pytar is a solid material. Temperature also plays a role in the physical properties of pytar. At high temperatures, the pytar has a lower viscosity and flows more readily, while it can solidify at low temperatures.

Table 1. Summary of emulsifier candidates for liquid and gas crackers

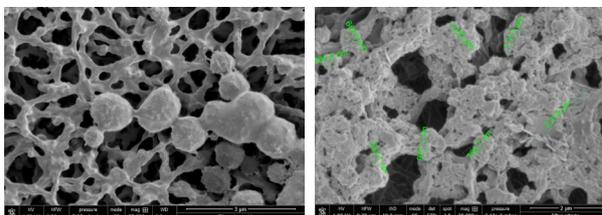|	Liquid cracker PW	Gas cracker PW
Findings	• Small aromatic compounds containing heteroatoms • Low concentration of PNAs • No dispersed solids in the water • No evidence of fatty acids	• Aliphatic species containing heteroatoms • High concentration of PNAs • Dispersed solid PNAs in the water • No evidence of fatty acids
Hypothesis concerning the emulsion	• Adsorption of small hetero-atomic aryl compounds at the interface • Nanoparticles contributing in emulsion stabilisation	• Interaction PNAs and aliphatic hetero-atomic species stabilise pygas droplets

Figure 2. Scanning electron microscopy (SEM) images of cellulose nitrate filter; unused filter (left) and filter after filtration of liquid cracker PW (right).

Pytar can contribute to fouling through various scenarios:
- Pytar entering the QW circulation can 'freeze'. When hot QW is used to heat low duty reboilers (e.g. C2 splitter or demethaniser), the fluid pytar droplets encounter the cold reboiler tube and the pytar solidifies onto the surface, impeding heat transfer.
- Pytar carried with the process water can accumulate in the PWS and DSG, where the high temperatures strip the volatile components from the pytar composite. This results in an increase in the pytar's viscosity. It may maintain fluidity at the high temperatures to 'escape' the DSG via the blowdown, but will solidify once exposed to the blowdown cooling exchanger.
- Finally, a small fraction of pygas with pytar dissolved within can circulate with the QW. As the QW passes through heat exchangers, the pygas droplets coalesce. When the QW and pygas enter the top tray or distributor of the QWT, the pygas is floating on top. Pygas has a lower surface tension than water, which facilitates entrainment in the rapid upward flow of process gas going to the process gas compressor. The low molecular weight pygas components vaporise, leaving the pytar components behind as foulant.

Process water phase integrity

Poor phase separation in the QWS leads to process water that contains a high amount of organics – the culprits for fouling in the PWS and DSG. Reactive monomers can enter the PWS as dissolved organics in the water (e.g. styrene
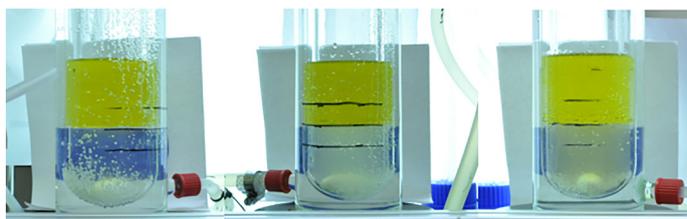
Figure 3. Gasoline/water phases of QWT samples at three pHs after demixing experiments; pH 5 (left), pH 7 (middle) and pH 9 (right). Turbidities of 3, 10 and 197 NTU, respectively.

solubility of ~600 ppm at 60°C)[8] and as hydrocarbon phase domains (droplets) dispersed within the water phase. When a plant suffers from a stable emulsion, these hydrocarbon droplets do not coalesce with time and are carried to the PWS. In other cases, the residence time is too short for full coalescence. 'Breaking' (or destabilising) the emulsion eliminates the carryover of droplets and reactive molecules, as the pygas phase would phase separate and accumulate to the surface of the water and be removed.

Prevention or elimination of emulsions is a quintessential parameter to decrease fouling in the DSS. One chemical approach to eliminating emulsions is through the use of an additive designed to expedite the phase separation and improve efficiency of separation. However, there is not a singular industry standard; the recommendation is to screen the performance of a series of chemistries using representative laboratory simulation methods, or 'bottle testing' with emulsions from the process.

An emulsion is a class of disperse systems consisting of two immiscible liquids. One liquid (the dispersed phase) is dispersed as droplets in the other liquid (the continuous phase). To distribute two immiscible liquids in a stable way, a third component, the emulsifier, needs to be present at the interface. Without an emulsifier, the emulsion is not stable and the droplets of the dispersed phase will coalesce. The rate that an individual droplet moves due to gravity is proportional to the density difference between the dispersed and the continuous phase, the square of the droplet radius, and the inverse of the viscosity of the continuous phase.

A good emulsifying agent needs to have a good surface activity. It should also be able to form a condensed interfacial film, and should have a diffusion rate that is comparable to emulsion forming time. Generally, an emulsion is either sterically stabilised (e.g. a long amphiphilic polymer or solid particles) or electrostatically stabilised (e.g. fatty acids).

The work described herein aimed to identify the emulsifiers responsible for emulsions in QWS using QW circulation water samples recovered from a liquid cracker and a gas cracker. The pH and conductivity of the process water samples evaluated were pH 8.9 and 120 µS/cm for the liquid cracker sample and pH 5.5 and 450 µS/cm for the gas cracker sample.

Dynamic surface tension measurements provided an answer to the question: are there small surfactants at the interface? (Figure 1). In both cases, the dynamic surface tension of the PW is similar to that of pure water, indicating the water contains no small surfactant molecules. Therefore, the emulsion is likely sterically stabilised by long amphiphilic polymers or by particles that are less mobile to come to the interface during time of measurement.

Interfacial PNA stacking is a potential source of steric emulsion stabilisation. PW and pygas samples were analysed for PNAs (i.e. naphthalene, anthracene, pyrene, etc.) using classic GC-MS to evaluate potential influence on emulsions in DSS. The liquid cracker samples showed low PNA concentrations in the PW (0.15 ppm) and the pygas (160 ppm). These low values contrast with those obtained for the gas cracker: the process water had up to 60 ppm PNA content and 6.5% was present in the pygas. Filtration prior to analysis was necessary to prevent plugging of instrumentation, so the results for the gas cracker samples are an underestimation of the actual values. Therefore, PNAs do not stabilise the liquid cracker PW, while partial stabilisation of the gas cracker PW by PNAs is possible.[*]

Filtration of the liquid cracker process water over a cellulose nitrate filter gave a clear filtrate, in contrast to the initial solution that was turbid. Scanning electron microscopy (SEM) images of the retained material revealed a cauliflower structure on top of the filter fibres, which could be an aggregate of nanoparticles and sticky polymers (Figure 2). The clarity of the PW filtrate indicates that the emulsifier molecules were collected on the filter. Analysis of the residue on the filter by LC-MS indicated that it contains hetero-atoms N, O and S, although the detailed composition was not identified. This experiment was not performed for a gas cracker, as particles were visually observed on the glass sampling bottles.

LC-MS analysis of the liquid cracker PW showed a high amount of small aromatic species (C10 to C20) containing nitrogen, sulfur and oxygen. Analysis of the gas cracker PW showed a high amount of aliphatic species (C20 to C50) containing nitrogen and oxygen. Unfortunately, no exact structures could be identified. For both PWs, these compounds could play a role in stabilising the emulsion as some could be quite amphiphilic.[**]

Table 1 summarises the findings concerning the nature of the emulsifiers for liquid and gas crackers. A hypothesis concerning the nature of the emulsion is also shown for both types of crackers, highlighting the differences between them.

High pH (>8.5) in the QWT/QWS stabilises emulsions and has a dramatic effect on hydrocarbon and water phase separation. It is often claimed that the optimal pH for a good water/gasoline separation is between 5.5 and 7. To verify this claim, demixing experiments were performed at three different pHs (5, 7 and 9) with plant samples from the QWT (water and gasoline) and their respective turbidities both qualitatively (visual determination with a blue background) and quantitatively determined (Figure 3).[***] The results of the study demonstrate that pH has a strong influence on two factors of emulsions. First, the time required for phase separation increased with pH and, secondly, the turbidity of the process water at equilibrium increased with pH, from 3 NTU (nephelometric turbidity unit) at pH 5, to 10 NTU at pH 7, to 197 NTU at pH 9.
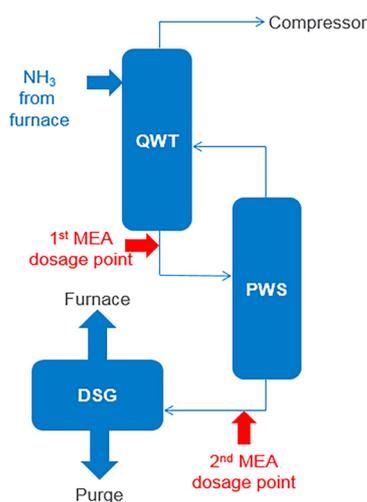
Figure 4. Representation of the process water section from a liquid cracker with MEA dosing points.

Ammonia in the cracked gas, which concentrates in the DSS system to high levels, can cause high pH. Many cracker operators dose monoethanolamine (MEA) to the PWS and DSG feed lines to maintain a high pH for corrosion control. As a pure component, MEA's volatility is rather low (~170°C). However, it forms a binary mixture with water, and at DSG conditions, typically 170°C at 8 bar, it evaporates to some extent and proceeds to the furnaces.[9] According to material balances completed by some ethylene producers, between 20 and 35% of MEA dosed leaves the DSG with the dilution steam. Under cracking conditions, MEA forms 10 – 30% ammonia, depending on the coil outlet temperature (COT).

An ammonia/MEA balance study in operating ethylene plants can help to understand the influence of MEA dosage on the concentrations of ammonia. As an example, ammonia and MEA concentrations were measured at five different locations in a liquid cracker: top QWT, bottom QWT, top PWS, top DSG and bottom DSG (Figure 4). From the QWT, most of the ammonia proceeds to the PWS and only a small portion to the top of the column towards the compressor. From the PWS, only ~10% returns to the QWT while ~90% continues to the DSG. From there, ~65% of ammonia returns to the furnace while only ~35% is purged in the blowdown. Thus, a significant amount of ammonia builds up in the system through the furnace recycle.

In this particular case, two MEA dosing points are present in the system – one at the bottom of the QWT and one at the bottom of the PWS. MEA is apparently too heavy to cycle back from the PWS to the QWT, so everything proceeds to the DSG, where ~80% of MEA exits the DSS with the blowdown and ~20% carries over to the furnace. Based on the COT in the furnace during these measurements, 20% of MEA converts to ammonia. Therefore, it was estimated that the MEA recycle to the furnace contributes only 12% of ammonia. The remaining 88% of ammonia in the plant comes from other sources not yet identified.

In summary, a high pH value, partially caused by the high ammonia concentration in the QWT, can cause emulsions that are often at the root of fouling problems in PWS and DSG of ethylene plants. Amine based neutralisers used for corrosion control in the DSS contribute to this, but it is believed that other sources of nitrogen, such as feedstock impurities, are involved in the ammonia build-up in the DSS system. Awareness of the recycle streams entering the DSS is critical for troubleshooting; these streams can be internal (such as from another section of the ethylene plant) or external or from another production unit. Recycle streams bring impurities that can have a significant impact on corrosion, emulsions and fouling in the DSS.

Conclusion

Concepts and tools help investigate the causes and effects of DSS issues – specifically, the conditions that impact process water phase integrity (emulsions and pH) and the fouling that occurs due to organic carryover (polymerisation and pytar deposition). Although aspects of fouling are considered common knowledge within the industry, incidences of unplanned plant shutdowns and production loss attributed to fouling prove that gaps remain in this area.

Future work will involve applying this knowledge into developing more effective mitigation strategies for plants and supporting troubleshooting efforts if unexpected fouling does occur. A detailed understanding of the conditions that promote fouling will afford operations to more confidently apply increasingly creative approaches to grow plant profitability and competitiveness, i.e. the consequences of operational changes on plant operations will be more predictable.

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Notes

* An important consideration here is that PNAs are not ideal candidates to stabilise an oil-in-water emulsion. Theoretically, they are better suited to stabilise a water in oil emulsion due to their high hydrophobicity.
** The liquid cracker PW was analysed as received from the plant, whereas the gas cracker PW was first filtered on a 0.45 µm syringe filter in order to remove particles that could clog the GC and LC lines.
*** Demixing experiments involve intensively mixing two immiscible phases at 80˚C and an overpressure of 0.5 bar to then visually monitor the phase separation behaviour of the system and analyse the quality of the water phase after the intense mixing step.

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