

Hydrocarbon contamination in amine acid gas

B. Spooner and **D. Engel** of Sulphur Experts discuss several strategies that can be implemented by refiners and gas processing operations to mitigate hydrocarbon contamination of rich amine streams and thereby protect and enhance the efficiency of the amine units and downstream sulphur plants. The problems immediately resulting from hydrocarbon contamination of the amine acid gas being routed to the sulphur recovery unit and their effect on the plant operation and efficiency are also identified and discussed.

Amine units are used by refiners and gas processing operations around the world to remove acid gases such as H_2S and CO_2 from gas and liquid streams. The H_2S and CO_2 are then sent to a sulphur recovery plant for further processing.

Sulphur plants are designed to process acid gases, and are susceptible to damage by other hydrocarbon contamination. Excess hydrocarbons will be present in the acid gas stream from the amine unit if the amine unit is not designed or operated properly.

Undesirable hydrocarbons exist in the inlet gas of most amine absorbers, in either gas or liquid phase. Either way, the amine solution can and will absorb these hydrocarbons to a certain degree. Various types of amines are somewhat soluble in hydrocarbons depending on the conditions, which explains the absorption in part. Entrainment of free hydrocarbons and emulsification of hydrocarbons in the amine solution are also possible.

Hydrocarbons can create numerous operational and performance problems in both the amine unit and downstream

sulphur recovery units (SRUs) and must be minimised. Furthermore, there is a global trend of increasingly stringent environmental air quality legislation. For instance, the United States Clean Air Act limits the emissions of volatile organic compounds (VOCs) to 250 t/a and the total amount of benzene, toluene, ethylbenzene and xylene (BTEX) emissions to 25 t/a for a facility.

The aromatic BTEX hydrocarbon species are especially difficult to combust and they burn with a sooty flame that fouls downstream catalyst beds. Destruction of BTEX requires high SRU reaction furnace temperatures ($>1050^\circ C/1925^\circ F$). Many facilities have difficulty operating their SRU reaction furnaces at these elevated temperatures. Thus, there is strong operational and legislative motivation to minimise the amount of hydrocarbons in the acid gas and in the amine system.

Reducing hydrocarbons in amine systems is advantageous to not only the sulphur plant, but also within the amine system. Hydrocarbons in amine can result in foaming, fouling and destruction of gaskets in plate and frame lean/rich exchangers.

Hydrocarbons in amine also represent lost production for the plant. Amines are not meant or designed to remove hydrocarbons, which are the components of natural gas (or liquefied petroleum gas (LPG)), which are used as fuel or sold.

Fig 1: Generic amine plant

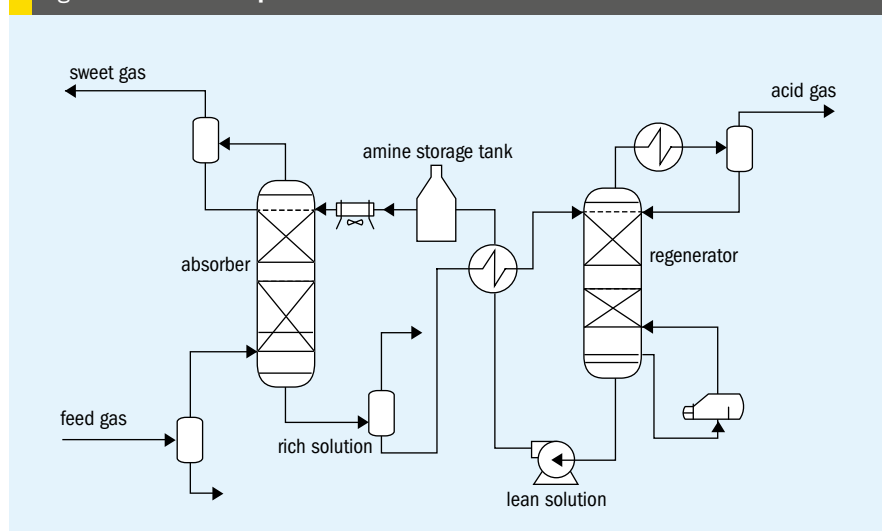


Fig 2: Amines contaminated with varying degrees of hydrocarbon



Amine sweetening process

Using alkanolamines for acid gas removal is a process that has been in use since 1931. Today, amine treating is used worldwide in gas plants, refineries, steel plants and power plants.

Simplistically, an amine system absorbs CO_2 and H_2S contaminants out of a gas or LPG stream in a contactor unit (absorber) at high pressure and low temperature, and binds the contaminants to an amine molecule through a set of chemical reactions. The binding reaction is then reversed in a stripper unit (regenerator) at low pressure and high temperature. The CO_2 and H_2S loaded amine (referred to as 'rich' amine) is thus regenerated for reuse, and the CO_2 and H_2S exit the system via the acid gas stream and may be further processed (see Fig. 1).

Other than some specialty applications, the inlet gas to most amine absorbers will contain a variety of hydrocarbons. When this occurs, most gas-phase hydrocarbons will remain as gas and flow harmlessly up through the amine and exit out of the top of the tower. Liquid hydrocarbons in LPG treaters will mix with the amine and will separate if enough residence time is given to the amine in the bottom of the treater. In a gas-liquid contactor, very little separation time is included in most designs and therefore, all liquid hydrocarbons will travel with the rich amine. If the rich amine entering the regenerator contains hydrocarbons, the rich amine will then vaporise and travel with the acid gas. If the acid gas is routed to a sulphur plant, the hydrocarbons can create problems, both operationally and mechanically. In the experience of Sulphur Experts, amine acid gas (AAG) containing more than 2% hydrocarbon is an indication of problems upstream of the stripper.

This article discusses how to mitigate hydrocarbons in the rich amine feeding the regenerator, thus reducing fouling, foaming, corrosion and many associated operating problems both in the amine regeneration unit (ARU) and the SRU.

Hydrocarbons in amine

Hydrocarbons will first enter the amine system in the contactor. Any hydrocarbons that end up in the rich amine will arrive there either by absorption (solubility), entrainment, condensation or emulsification. Amines are organised into three categories: primary, secondary and tertiary. A paper published by Critchfield et al⁴, explained how hydrocarbon solubility in amines relates to the molecular weight of the amine. The order of hydrocarbon solubility, in order of lowest to highest is as follows:

- monoethanolamine;
- diglycolamine;
- diethanolamine;
- methyldiethanolamine;
- diisopropanolamine.

There are two main types of hydrocarbons that can enter an amine plant: polar and non-polar. Non-polar hydrocarbons are generally free hydrocarbons, which do not blend well with amines and can be relatively easily separated and removed. Polar hydrocarbons have a unique chemical characteristic, whereby part of the molecule is hydrophobic and the other part is hydrophilic. This basically results in an emulsion of amine and hydrocarbon. If the level of contamination is high enough in the amine, significant amounts of hydrocarbons (being pulled along by the surfactant) are carried with the solution to the flash tank.

Although slightly different in chemistry, aromatics (i.e., BTEX) exhibit characteris-

tics similar to polar hydrocarbons, and are even more harmful to the SRU. The thesis of Borda¹ provides a good review of the available data on BTEX and VOC solubility in amine solutions. Bullin & Brown² proposed theoretical conditions for minimising the pick-up of hydrocarbons and BTEX. This was based on simulation. The accuracy of these simulations has been called into question by Borda. Borda presents new BTEX data fitted to a different correlation and compares the results from this, and results from the same simulator used by Bullins and Brown, to plant data. The simulator significantly over predicted the actual hydrocarbon solubility.

Over-prediction of hydrocarbons in rich amine by a simulator is hard to rationalise. It is expected that real plant results would always have more hydrocarbons than predicted by a simulator. It is important to note that most data for hydrocarbon solubility in amine solutions is based on lean amine solutions that are not loaded with aqueous CO_2 and H_2S . Hatcher et al⁵ explain the over prediction of hydrocarbon solubility in rich amine through a 'salting-out' phenomenon, as described further in the operational parameters section of this report.

Hatcher et al use an alternative simulator to Borda and it is based on mass transfer rather than equilibrium models.

Figure 2 is an example of different levels of hydrocarbon contamination that can occur within the same system. These samples were all taken from individual contactor rich amine outlets at the same refinery.

Hydrocarbons in rich amine streams can be present essentially in the following three forms, as previously detailed by Spooner and Engel⁶:

- **Free hydrocarbons.** These non-polar hydrocarbons will float on top of the amine solution within a few minutes if given the chance (see Fig. 3). This typically occurs in the flash tank.
- **Soluble hydrocarbons.** All hydrocarbons will have certain solubility in amine solutions (see Fig. 4). The extent of the solubility will depend on the following:
 - type and concentration of amine (common hydrocarbons such as $\text{C}_1/\text{C}_2/\text{C}_3$ are two to three times more soluble in amine compared to pure water³);
 - pH of the amine;
 - amine contactor pressure and temperature, and
 - type of hydrocarbon and polar functional groups such as carboxylic

acids and alcohols (aromatics are included in this group).

- **Emulsified Hydrocarbons.** When surfactants are present, hydrocarbon contaminants can form very small droplets in the amine solutions (see Fig. 5). These droplets are stabilised by molecular surfactants (similar to soaps or detergents) and also by small size suspended solids. Emulsion droplet sizes can range from a few microns to about 500 microns. Micro-emulsions, which are the most stable emulsions available (and can take weeks to separate) are typically found when droplet sizes are <10 microns.

Effect of hydrocarbons on the sulphur plant

A detailed description regarding the negative effects of hydrocarbons on the SRU was presented at Sulphur 2012 in the paper, entitled “Reducing hydrocarbons in sour water stripper acid gas”. As a brief summary, hydrocarbons entering the sulphur plant will result in the following:

- difficulties maintaining stable operation;
- decreased capacity;
- lower efficiencies, and
- potential issues with catalyst deactivation and sulphur quality as a result of soot.

It is in the overall best interest of the sulphur plant to minimise the level of hydrocarbon ingress. Because sulphur plants receive feeds from two different sources (i.e., the amine and sour water stripper systems), it is necessary to focus attention on both streams.

Effect of hydrocarbons on the amine plant

Hydrocarbons do not chemically bond to the amine, so there is no direct harmful effect on the actual amine solution. Given the right amount of time, or use of technology, any hydrocarbons mixed into the amine can be removed and the amine can then be reused. In the meantime, however, while a mixture of hydrocarbon and amine is circulation through the plant, many negative consequences can result, the most common being as follows:

- **Foaming.** Probably the first and foremost concern when amines are

Fig 3: Free hydrocarbons in amine



Fig 4: Soluble hydro carbons concentrated in reflux water



Fig 5: Emulsified hydrocarbons in amine



Fig 6: Foaming tendency of hydrocarbon contaminated amine



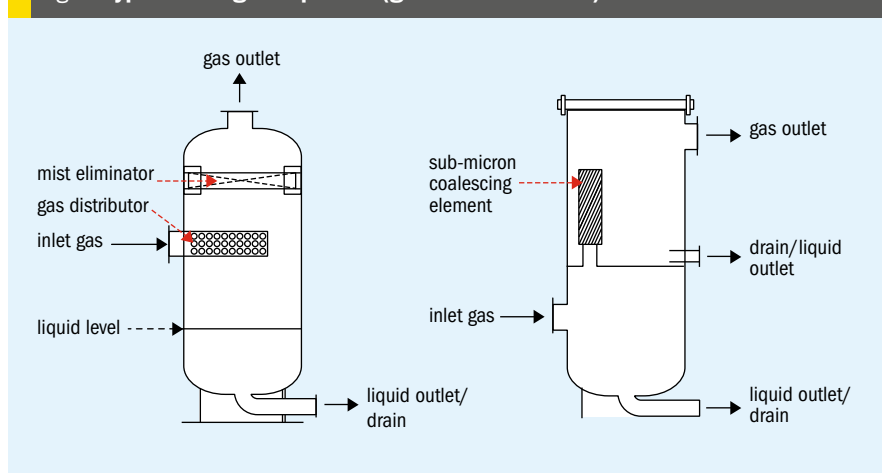
Fig 7: Black shoe polish on rich amine filters



Fig 8: Leaking exchanger gaskets



Fig 9: Typical inlet gas separator (general schematics)



contaminated with hydrocarbons is foaming. Hydrocarbons have a lower surface tension than amine, which allows the surface of the liquid to expand quite easily. When gas or steam is bubbled through the amine, the bubble reaches the surface of the liquid, but does not 'pop'. The bubble remains, and more and more bubbles build up on top of it until the entire vapour space is filled with this foam as illustrated in Fig. 6. Foaming can be a concern in both the contactor and the regenerator. When amines are in a foam state, they do not remove H_2S in the contactor and can be regenerated in the regenerator.

- **Fouling.** Hydrocarbons contribute to the black shoe polish that commonly fouls amine filters, lean/rich exchangers and packed towers (see Fig. 7). A carbon bed is used to remove hydrocarbons, but because the carbon is generally on the lean side, the amine has to flow through many pieces of equipment beforehand, where hydrocarbons can form a matrix along with iron sulphides, degraded amine, and antifoam. This is what fouls amine systems.
- **Gasket destruction of plate and frame exchangers.** There are several different types of gaskets available for separating the plates in plate and frame exchangers. None of these gaskets are immune to the harmful effects of hydrocarbons flashing across the exchanger. Liquid hydrocarbons can cause polymerisation of the gasket material and flashing hydrocarbons can erode the gaskets. Operators must rely on the flash tank to minimise the content of the rich amine entering the exchanger.

Otherwise the risk of gasket failure and leaking substantially increases, as shown in Fig. 8.

- **Loss of treated product.** Hydrocarbons in amine represent a loss of hydrocarbons in the treated gas (i.e., result in lower volumes of sales gas or LPG). These losses directly impact the profitability of the gas plant or refinery, and are obviously undesirable.

Minimising hydrocarbon content in amine acid gas

The best way to minimise hydrocarbons in amine acid gas is to ensure that excess hydrocarbon does not enter in contact with the amine solution in the first place. This requires a comprehensive and thorough evaluation of the inlet gas stream to each amine contactor in the system. Typical amine plant designs will include at least an inlet separator before the contactor to knock out free liquids. However, many of these inlet separators are inadequate for complete hydrocarbon liquid removal.

Other options for minimising the hydrocarbon content of the amine acid gas include the following:

- optimising the operation of the actual amine plant;
- optimising the amine flash tank operation. Sometimes design changes to the tank interior may be necessary to ensure minimal hydrocarbon breakthrough;
- using filtration and/or coalescing technology on the rich amine to remove hydrocarbons;
- using potential skimming capabilities on contactor, flash tank and reflux water;
- technological solutions.

Optimisation of the amine plant operation

Once the plant is designed, built and operating, there are two strategies operators can employ to minimise the level of hydrocarbon pick up by the amine: (i) preventing hydrocarbon entering the contactor with the sour gas in the first place, and (ii) operating the plant at conditions that minimise hydrocarbon solubility in amine, noting that examples include choice of amine type and strength, circulation rate, rich loading, differential temperature between lean amine and inlet gas, and reflux operations.

Preventing hydrocarbon ingress

Assessing the amount of hydrocarbon entrainment in gas can be directly analysed. Several companies perform entrainment testing at moderate costs. When done correctly, the associated optimisations that are possible as a result of the new data rapidly pays back the cost of the testing. The resulting changes that are made to process conditions can ensure reliability, integrity, capacity and energy/chemical utilisation, thereby resulting in valuable cost savings to the plant.

'Bulk' liquid hydrocarbons are meant to be removed from inlet gas streams by the inlet separator generally equipped with a mesh-pad or vane pack. More precision removal of hydrocarbons can be done using submicron gas coalescer (both shown in Fig. 9). The inlet separation devices are the most important pieces of equipment as far as minimisation of hydrocarbons in amine acid gas are concerned. Furthermore, approximately 50 wt-% of the liquids contaminants in a gas stream are one micron or smaller in size (aerosol range)¹¹. These aerosols can carry

components such as surfactants from compressor lubrication oils that cause foam stabilisation. Hence, sub-micron gas coalesce systems play a multiple role in inlet separation: hydrocarbon (and water) removal, solids removal as well as surfactant removal. Other technologies such as centrifuges and liquid coalescers can also be utilised to prevent amine foaming, which is of course important. These will also (to some extent) reduce the level of hydrocarbons in amine acid gas.

Inlet separators rely on four basic parameters which determine the effectiveness of liquid separation from gas:

- **Density difference between the liquid and gas.** Higher density liquids will be removed easier from gas than lighter ones because of the lack of gas solubility in the hydrocarbon. The two phases want to separate. Inlet sub-micron gas coalescers are far more sophisticated, with many additional parameters to consider. However, at a minimum each system must have the correct vessel design and effective internals along with accurate instrumentation and seal mechanism for proper operation.
- **Flow directional change.** Flow direction changes are possible for the gas, but not so much for the droplets of liquid. Forcing the gas around an impingement plate followed by a demister pad in the top of the vessel creates something similar to an obstacle course. The gas can go through it, but large liquid droplets (20-30 micron and up) impinge on the surface of the obstruction and eventually build in size until the droplets fall to the bottom of the separator. Figure 9 is a typical inlet gas separator, with a diverter plate and demister pad for flow directional change.
- **Velocity.** Velocity has a large effect on the volume of liquid hydrocarbon in a gas stream. The velocity of the gas stream imparts drag force on each liquid droplet, pulling the droplet along the pipe. The only opposing force to counter this is gravity. It is important that gas velocities not be so high that they overcome gravity. Gas flow, as well as gas pressure, determines the velocity through the piping. This is why a separator has to be carefully designed to minimise pressure drop across the vessel, since a drop in pressure results in the gas expanding and a corresponding increase in velocity and drag force.
- **Time.** Time is the final separation

parameter. It takes time for gravity to pull droplets out of a gas stream. Therefore, a larger separator tends to remove more liquids than a smaller vessel, assuming proper design of each.

Proper operation of an inlet separator involves ensuring the liquid level is kept low at all times. The frequency of the level control valve opening should be noted, since frequent dumping of the vessel could mean an excessive amount of liquids having to be removed from the gas stream. This could indicate that there is a possible problem upstream that requires investigation.

Separators should always operate with a low and consistent pressure drop. Low pressure is required to prevent excessive drag forces on liquid droplets and consistent pressure is to ensure that there is no fouling or plugging of the demister pad within the vessel.

Plant operating conditions

There are several operational parameters that directly affect the amount of hydrocarbon in amine acid gas:

- **Amine circulation rate.** Because of the inevitable solubility of hydrocarbons in amine (described earlier in this paper), a higher amine circulation rate of amine will carry more hydrocarbons into the circulating rich solution. Furthermore, higher amine circulation rates decrease the flash tank residence time, lowering the hydrocarbon removal efficiency.
- **Amine rich loading.** By increasing the loading (aqueous CO₂ and H₂S amine salt concentration) of the amine solution, less amine and water is available for interaction with the charged part of the hydrocarbon. This renders the hydrocarbon-hydrocarbon interactions stronger than the amine-hydrocarbon interactions, causing the hydrocarbon molecules to coagulate through hydrophobic interactions with one another. The fact that higher rich loadings reduce the amine-hydrocarbon solubility levels is even further reason to lower the amine circulation rate if possible.
- **Differential temperature between lean amine and inlet gas.** Before gas streams enter the amine contactor, the gas streams pass through an inlet gas separator, which allows for liquid hydrocarbons to be separated. Therefore, the gas leaving the separator should be at the hydrocarbon dewpoint, meaning if

the gas pressure were to increase or the temperature to decrease, hydrocarbons would condense out and form droplets in the gas line. It is important to not allow this to occur as it will result in liquid hydrocarbons in the rich amine.

For this reason, it is recommended the inlet gas separator be located within 10 m of the amine contactor, which will minimise the risk of condensation of hydrocarbons along the pipeline. It is also recommended that this line be insulated.

It is also possible for hydrocarbons to condense inside the actual amine absorber, which can happen if the gas is cooled while travelling up the contactor. This will happen if the lean amine being injected into the contactor is cooler than the inlet gas stream. In fact, because the hydrocarbon dewpoint of the gas changes as acid gases are removed (because the removal of acid gases, the hydrocarbon dewpoint temperature will be higher at the top of contactor as compared to the bottom), it is recommended that operators maintain a minimum 5°C or 5°F temperature differential between the lean amine and the inlet gas.

- **Reflux operation.** Despite optimising amine circulation rates, rich loadings and flash tank operations, there will still likely be hydrocarbons entering the regenerator. The last area where hydrocarbons can be removed before leaving with the acid gas is in the reflux system. Proper condensing of the regenerator overhead stream will minimise the level of hydrocarbon vapour and the hydrocarbons will instead circulate with the reflux. The recommended reflux temperature is between 35 and 45°C, or 95 to 115°F. Refiners tend to run on the higher end of this range to minimise the risk of ammonia salt precipitation. Gas plants, or systems with no ammonia ingress, should target lower reflux temperatures.

Since hydrocarbons are condensed in the reflux, the concentration will increase if there is no reflux purge. An increase in hydrocarbon content in the reflux is undesirable, as this increases the risk of hydrocarbon carryover with the acid gas, and can also cause foaming and other operational problems in the regenerator. Hydrocarbon contaminated reflux streams should be either continuously purged to a sour water stripper or dis-

posal tank. If purging is not available, completely emptying the reflux tank to disposal is acceptable. This should be done based on visual or laboratory analysis of reflux water (or better yet reflux skimming) for hydrocarbons.

It is important to recognise the implications of operating outside the recommended reflux temperature range.

Specifically operating at less than 35°C/95°F will not only have limited effect on the amount of water and hydrocarbon in the acid gas, but also increases the necessary reboiler duty since the cold reflux will be condensing an inordinate amount of steam traffic in the upper section of the regenerator. Operating at higher than the recommended reflux temperature will allow excessive water and hydrocarbon to escape with the acid gas, negatively affecting SRU operations as well as increasing the make-up water demand on the amine plant.

Amine flash tanks

Separation technologies based on pressure drop, velocity changes and residence time are among the most common separation systems used in oil and gas operations. All these technologies have the common theme of using simple concepts to attempt to solve a separation problem. One such example is the amine flash tank. This device removes off-gases by reducing the rich amine pressure downstream of an amine contactor.

If designed correctly, these systems also provide limited liquid-liquid separation capabilities for free hydrocarbon removal since these hydrocarbon liquids will float to the top of the amine solution within 30 minutes and can then be skimmed. No emulsified or dissolved contaminant is affected.

For a flash tank to effectively separate hydrocarbons from amine, there must be sufficient residence time as well as sufficient pressure reduction. Entrained hydrocarbon gases will flash off within three to five minutes, noting that the lower the flash tank pressure, the faster and more efficient hydrocarbon gases will flash.

Flash tank pressure is determined by the necessary flash gas and rich amine pressures. Common flash gas destinations include the following:

- low pressure fuel gas absorber inlets;
- flare;
- incineration;
- acid gas.

The rich amine must leave the flash tank and flow through the following:

- rich amine filters (if they exist)
- lean/rich exchanger
- the vertical piping up to almost the top of the regenerator.

Generally, 70 psig/475 kPag is enough pressure to push both the gas and amine to their respective destinations. It is important to not pressure the flash tank any higher than necessary since this will reduce the amount of hydrocarbon flashing. If the flash gas is routed to an extremely low pressure flare or incinerator, some plants will operate the flash tank at virtually atmospheric pressure and will install rich amine pumps immediately after the flash tank in order to push the amine through the exchanger and into the regenerator.

Flash tank residence time is a function of the size of the vessel, the level at which the amine is maintained inside the vessel, and the circulation rate of the amine. If the tank is designed only for two-phase separation, the tank will simply be an open tank with a gas outlet in the top and liquid drain at the bottom. Operators should set the level at 50 to 60% full. This maximises residence time, while still allowing for vapour disengaging space, noting that when hydrocarbons flash from liquid to gas, the hydrocarbons expand in size by up to 300% and can therefore carry gas upwards as a result of high velocities. Having at least 40% of the tank as vapour space will allow for gravity to pull the droplets of that amine back out of the flash gas and into solution.

For designers, sizing a 30 minute residence time is often achieved by assuming some variables in the Stokes Law calculations, such as hydrocarbon density and hydrocarbon droplet size. The typical values for these tend to be a specific gravity of 0.6 to 0.7 and droplet sizes of 150 microns and larger. It is important to note that these values do not account for the possibility of heavier hydrocarbons and micro-emulsions that exist in rich amine streams.

The Stokes Law calculations also do not account for any possible surfactant contaminants, which aid in stabilising micro-emulsions. Granted, designers must balance the size and cost of the flash tank with expected performance. Designing a flash tank for 10 micron droplet removal would make the flash tank so large that it would not be economical to build or fit

within the battery limits of the unit.

Assuming the residence time is adequate, any free hydrocarbons floating on the amine surface can and should be skimmed. Depending on the flash tank design, these hydrocarbons may flow over a weir or into an internal bucket that is attached to the inside of the vessel walls. When skimming, it is preferential to be able to sample the skimmed liquid to ensure it is indeed hydrocarbon and not amine. Some skimming sections have site glasses where the interface between amine and hydrocarbon can be seen. These make it very simple for operators to prevent the skimming of amine to disposal.

A number of different flash tank designs are available, some certainly more effective than others. A growing trend is to incorporate metal mesh internals to promote coalescence, which can compensate for low residence times. These promising systems so far have provided marginal results because of poor understanding of highly fouling rich amine streams. Most flash tanks, whether two or three-phase separators, are often sized based on correct parameters, but can lack the understanding of liquid and solid contaminant loading.

To use coalescing mesh-pads correctly, these have to be designed not only according to the gas velocity across the pad (using the modified Souders-Brown equation), but should also consider liquid and solid properties in addition to internal flow geometry. Any disregard of these aspects will invariably lead to element flooding and liquid carry-over or fouling with an increase in differential pressure.

Case study

In one case study used to verify the strategies presented in this paper, several operational changes were made to a gas plant in Wyoming. The effects of the hydrocarbon content of the acid gas were measured. This plant had an inlet gas composition involving:

- 61.4 kmol/h hydrocarbons;
- 11.8 kmol/h BTEX;
- 5% H₂S;
- 8% CO₂;
- system pressure of 5740 kPa(g).

As is shown in [Table 1](#), as the amine circulation rate, flash tank pressure and reflux temperature were dropped, a significant decrease in hydrocarbon and BTEX content of acid gas was seen.

Table 1: Hydrocarbon reduction case study

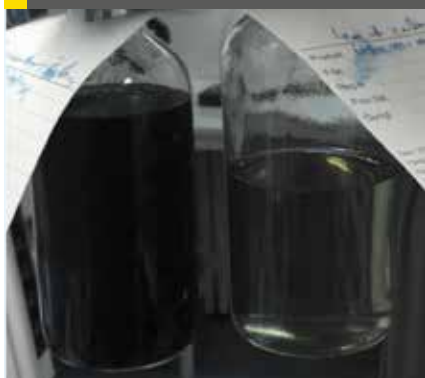
Optimisation strategies (in order of implementation)	Acid gas hydrocarbon content	BTEX content	Treated gas
Original operational conditions*	1.36 kmol/h	12.24 kmol/h	2.4 ppm H ₂ S 0.174% CO ₂
Decrease amine to 70 m ³ /h (0.314 mol/mol rich loading)	0.44 kmol/h	5.19 kmol/h	<1 ppm H ₂ S 0.479% CO ₂
Flash tank pressure dropped to 480 kPag	0.275 kmol/h	5.10 kmol/h	<1 ppm H ₂ S 0.48% CO ₂
Flash tank pressure dropped to 35 kPag, rich pump installed,	0.017 kmol/h	3.16 kmol/h	<1 ppm H ₂ S 0.48% CO ₂
Decrease reflux to 35°C	0.017 kmol/h	3.15 kmol/h	<1 ppm H ₂ S 0.48% CO ₂

*Original operational conditions: 50% MDEA; 160 m³/h; lean amine temperature 50°C; inlet gas temperature 40°C; rich loading 0.14 mol/mol; flash tank pressure 758 kPa; reflux temperature 60°C.

Rich amine liquid coalescers

Presently, many amine units only separate hydrocarbons in the flash tank. It is commonly believed that flash tanks will be able to separate any hydrocarbon in the rich amine streams. This is correct to some extent. However, the reality is that emulsions in rich amine streams are very stable, with droplet sizes near or less than the micro emulsion range (10 microns and smaller). If Stokes law is used to calculate the required residence time for the separation of a 15 micron emulsion, the result will indicate approximately two days. If the particle size is slightly smaller, then the separation time can be in the order of weeks or even months. Based on the low efficacy of residence tanks to properly separate these emulsified contaminants to the level required for feed into the regenerator, it is necessary to use secondary systems, such as coalescers.

Fig 10: Regen skimmings (left), regen bottoms (right)



Coalescence is the recombination of two or more small liquid droplets to produce a single droplet that is larger in size. This phenomenon also takes advantage of Stokes Law, which relates the velocity of separation of a particle or droplet in a medium to the diameter of the contaminant, densities, viscosity and gravitational pull. As coalescence takes place, small micron size contaminant droplets coalesce into fairly large droplets, resulting in an almost immediate separation from the continuous phase.

Mechanical coalescing systems are basically comprised of the following three technologies:

- inclined plates;
- metal mesh;
- microfibre based.

Because of the particle size and the high fouling properties of the solids and emulsified hydrocarbons in rich amine streams,

Fig 11: Reflux water with skimmable hydrocarbon



only disposable filters and microfiber-based coalescers are able to provide the proper particle removal and emulsion separation. Other systems, such as back-flushable metal-based filters, do not work because the adhesion of solids to the surface is too strong, and prevents a back-wash from being effective.

Suspended solids removal upstream of the coalescer is mandatory. Particulate removal will protect the coalescer elements and will also help destabilise the emulsion. If solids are introduced into a coalescing filter, it will plug off almost immediately and become ineffective.

Liquid-liquid coalescers are devices designed to separate small emulsified liquid contaminants in a liquid stream. These devices are segregated into the following two general categories:

- low efficiency systems with metal-based internals;
- coalescers with microfiber internals.

The two types of coalescers perform rather differently and should be used for different objectives and specific cases. While metal-based internal coalescers are effective for separating free liquids and macro emulsions (~100 microns and larger), coalescers with microfibers are more suited for separating micro emulsions (100 microns and smaller).

Microfibre-based liquid coalescers are the technology of choice for separating hydrocarbon from amine systems with multiple contactors. Metal-mesh based coalescers are not recommended in rich amine due to the rapid risk of fouling and difficult maintenance procedures.

Fig 12 : Amine plant with hydrocarbon stripping column

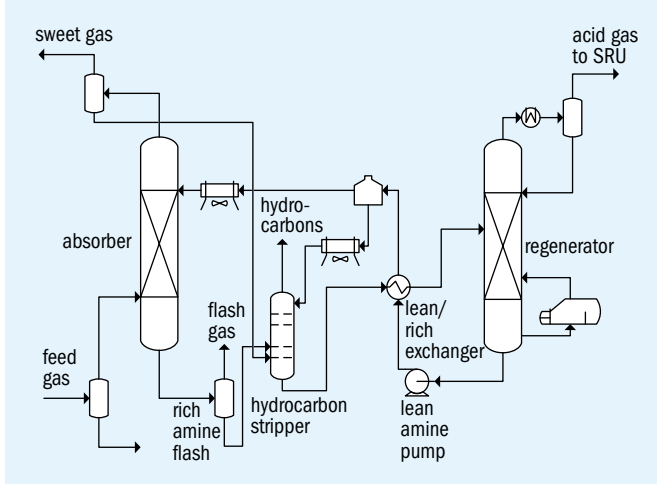
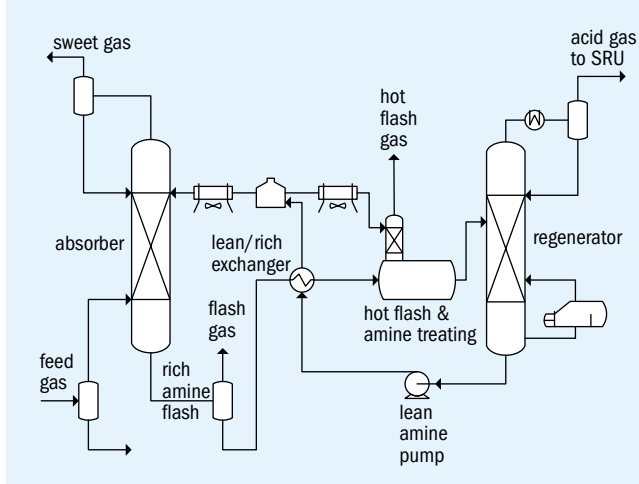


Fig 13: Amine system with hot flash vessel



Use of skimming devices

Hydrocarbons which float to the surface of amine or reflux water may be skimmed, assuming the design of the vessel allows for skimming. Most flash tanks have skim connections or hydrocarbon carryover weirs included in the design. Some contactors, reflux accumulators and regenerators also have skim connections. Whenever possible, hydrocarbons should be skimmed out of the system in order to prevent any chance of evaporation. Areas with higher residence times, such as flash tanks and regenerator bottoms have the potential for particularly high hydrocarbon volumes, as shown in Fig. 10, which presents a side-by-side comparison of regenerator skimmings and regenerator bottoms, taken less than one minute apart from the same regenerator.

Although not commonly thought of being a 'filter', the regenerator absolutely will drive hydrocarbons out of the amine, in effect filtering the solution. The vaporised hydrocarbons enter the reflux system where the hydrocarbons are possibly condensed in the reflux and where if not removed, will eventually be recycled back to the regenerator with the reflux water.

Reflux water that is contaminated should therefore be partially purged, or better yet skimmed. Figure 11 shows hydrocarbons floating on reflux water, a common sight in hydrocarbon-contaminated amine systems.

Technological solutions

More stringent legislation has led to additional treatments being proposed in order to meet current and future environmental specifications. Morrow⁷ proposed the addi-

tion of a stripping column for hydrocarbons on the rich amine line (see Fig. 12). This design uses a portion of the sweet gas to strip VOC and BTEX from the amine. The design has been patented and is described by Morrow⁷, Morrow & Wallender¹⁰, Morrow & Lunsford⁶ and McIntyre et al⁸. A VOC and BTEX removal of greater than 75% is apparently possible¹⁰. Bullin & Brown modelled the performance of a hypothetical hydrocarbon stripping column on a methyldiethanolamine (MDEA) plant and found it to remove 70% of the benzene (although 10% of the CO₂ in the stream was also liberated, which could certainly be a problem).

Bullin & Brown also model a hot flash vessel (see Fig. 13) that is located downstream of the lean-rich heat exchanger on the rich amine stream. Essentially, a higher temperature flash leads to more hydrocarbons being removed. The simulations show that this is more effective at removing VOCs and does not have a significant impact on BTEX. Unfortunately, substantial amounts of CO₂ and H₂S are liberated at these temperatures with the VOCs requiring an additional amine contactor for these gases. ■

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