Transcend IDEA™ Update – Carbon Beds in Amine System

Understanding Carbon

Carbon beds are an integral part of most amine based (MEA, DEA, MDEA, DIPA, DGA) gas treating units. In some cases, the carbon bed is on the rich amine stream, although it is often on the lean stream. In most cases, there is a small slip stream 5 – 25% (of the main flow) that contacts the carbon. The ostensible reason to use a carbon bed is for hydrocarbon removal. We analyze the utility of carbon beds in removing hydrocarbons in the context of a typical amine treating process and the typical contaminants that exist in the process. We further evaluate other technologies that can be applied to leverage the efficacy of carbon bed treatment of amine streams.

INTRODUCTION. Gas streams containing acid gases (H_2S, CO_2) are often treated with aqueous solutions of alkanolamines such as monoethanol amine (MEA), diethanol amine (DEA), methyl diethanolamine (MDEA), diisopropanol amine (DIPA), amino-ethoxy-ethanol (diglycolamine, DGA) etc. The alkanol amine absorbs the acid gases in the absorber. The “rich” amine is then sent to the stripper column, where the acid gases are released under heat and reduced pressure. The resulting “lean” amine is returned to the top of the absorber column for acid-gas absorption. A simplified schematic of the amine treating system is provided in Figure 1.

The recirculating amine system can concentrate contaminants that are removed from the inlet sour gas; or contaminants that are formed in the system through corrosion, degradation or other mechanisms. The most common contaminants that accumulate within amine systems are solids (usually corrosion products, but also solids that enter from the inlet gas), heavy hydrocarbons, amine degradation products, heat stable salts, and surfactants.

The most common systems used to remove these contaminants from the amine stream and prevent their infinite accumulation are: (a) rich flash tank; (b) particle filters; (c) packed carbon bed; and (d) reclaimers. The. rich flash tank is intended to remove heavy oils by settling. The particle filters are expected to remove solid contaminants by filtration. The reclaimers are intended to remove amine degradation products and heat stable salts, although some (such as vacuum distillation and thin film evaporation) can also remove solids and hydrocarbons. Carbon is usually claimed or believed to be capable of removing amine degradation products and hydrocarbons.

This article investigates (a) whether carbon, in the quantities that are used, offers a significant means of hydrocarbon removal; and (b) if there are other better mechanisms that can be used to leverage the carbon bed.

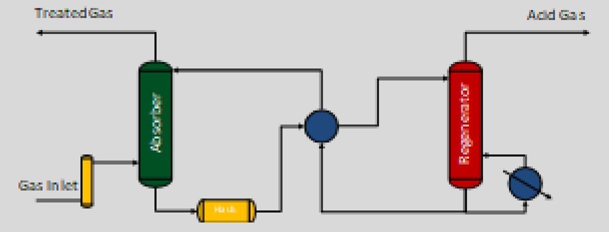

Figure 1. Amine System Loop

CARBON ADSORPTION. Adsorption is a process whereby molecules passing through a packed bed of solids are attracted to and held to the solid surface by attraction forces that are weaker and less specific than covalent or ionic chemical bonds. Energy is typically released when the molecule adsorbs on to the surface of the solid, which means that adsorption capacity increases as temperature declines. Increasing available surface area generally increases the available capacity for molecular capture. As a result, good adsorbents tend to have very high specific surface areas (surface area per unit volume).

Adsorption is often confused with absorption. Adsorption is a surface phenomenon; whereas absorption is a process by which another substance is taken up *within* the bulk of absorbing medium. Activated carbon is an adsorbent, which means that the availability of its microporous surface area is essential to its efficacy.

Activated carbon is a graphite form of carbon with an amorphous structure. It can be formed from a variety of carbonaceous materials (coal, asphalt, wood, coke, coconut shell, etc.), through a process that results in the formation of a highly porous structure. Since it can be produced from inexpensive materials, activated carbon is a very cost-effective adsorbent for a variety of contaminant removal requirements. The activated carbon structure will depend on the raw material from which it was derived, with differing physical and chemical properties. Activated carbon typically has very high surface area (800 - 3000 m^2/g). Once the owner/operator decides that the carbon is spent, the carbon is either removed from the vessel and replaced with fresh carbon or regenerated in-situ. The spent or used carbon may be regenerated during which the adsorbed molecules are generally released by reducing the pressure or increasing the temperature of the carbon. Typical regenerative mechanisms include thermal swing (using hot inert gases, or steam) and pressure swing modes.

Micropores are typically defined as pore radii less than 1 nm, meso-pores are pore sizes with radii between 1 - 25 nm, and macro-pores are pore sizes with a radius greater than 25 nm. The macro-pores and meso-pores are essential to allowing transport into the carbon, whereas the micropores are where the bulk of the adsorbed pore surface resides.

CARBON CAPACITY. The most common measure of the capacity of activated carbon are the Iodine Number and the carbon tetrachloride (CTC) number which are used for liquid and gas phase adsorption respectively. The iodine numbers are reported in terms of milligrams of adsorption per gram of carbon. An iodine number of 1000 indicates that the carbon can adsorb up to 1000 mg or 1 g of contaminant per gram of carbon. The CTC number represents the uptake of carbon tetrachloride on a percent basis, so that a CTC value of 50 indicates that the carbon adsorbed 50% of its weight in carbon tetrachloride, or 500 mg/g. The molasses number is a measure of the capacity of the mesopore capacity of the carbon to adsorb larger molecules (generally larger than 2 nm). This figure is typically in the 200 mg/g range.

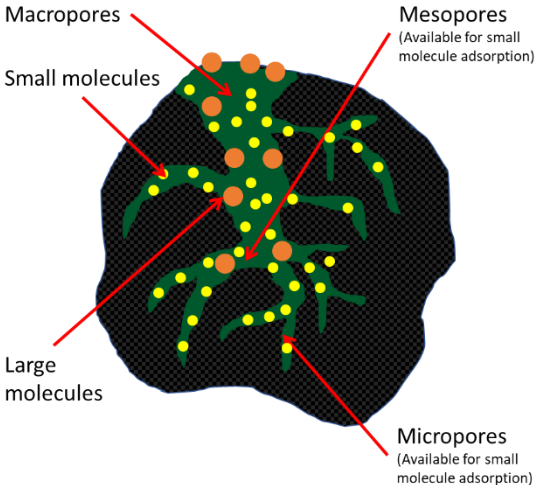

Figure 2. Activated Carbon Pores and Adsorption Site Schematic

The iodine atom has a van der Waals radius of 198 pm (0.2 nm) and is therefore expected to be able to fill up the entire microporous space in the activated carbon, for liquid phase adsorption. The molecular diameter of typical hydrocarbons is much larger, for example:

Butane	0.4 nm
Octanes	0.5 – 0.7 nm

By comparison to Iodine (0.2 nm) a heavy oil molecule (C12+) in an amine will have a much larger molecular diameter, probably exceeding 1 nm. So, the iodine number represents a potentially unachievable upper bound to the adsorption capacity of the carbon for heavy oil from amine. For that reason, the molasses number should be used for larger molecules to achieve a more accurate measure of available uptake. Note, however, that the actual uptake will always be dependent on the concentration in the external bulk phase, which further de-rates the actual adsorption capacity of the carbon

CARBON BED DESIGN FOR AMINE SYSTEMS Activated carbon is used in amine systems on either the rich or lean side. Activated carbon is used either in the form of canisters (6” OD x 36” L or 11” OD x 22” L), or fixed beds, in a kinetically suitable mesh size.

The typical residence time in a bed designed according to industry best practice will be at least 15 minutes. The residence time in a canister is generally shorter which is justified by the finer mesh material (allowing faster diffusion and adsorption kinetics) that is typically used, and the relative ease of canister replacement.
Due to the high residence time requirement, amine systems will only process a small slip stream (generally 5 – 15% of the total system flow) through their activated carbon beds.

In the early days of amine treating (1930s), activated carbon was intended to remove amine degradation products, but today, activated carbon is primarily deployed for the removal of hydrocarbons.
The activated carbon adsorbent is intended to remove dissolved components from the amine system. This is illustrated in Figure 3. Initially, the pores are filled with the amine, and then as hydrocarbons dissolve into the amine from the gas stream, the hydrocarbons diffuse through the macro and meso pores and get adsorbed on the interstices of the carbon according to the size of the molecule and the pore sizes available.

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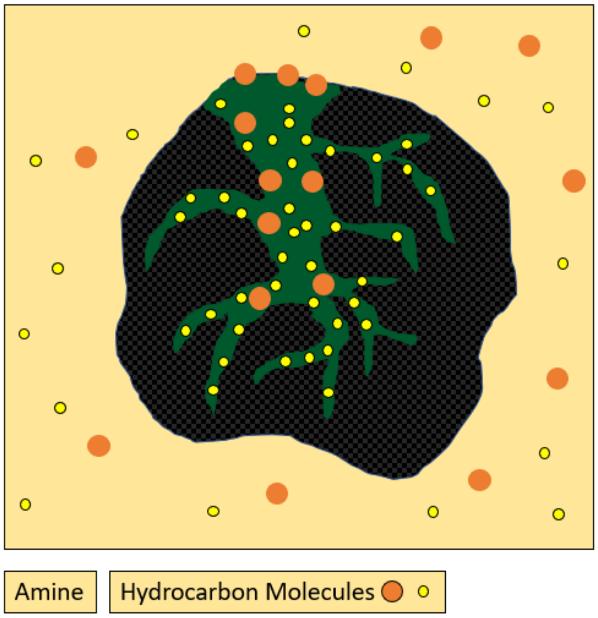

Figure 3. Schematic of adsorption

Figure 4 shows what happens when the amine contains hydrocarbons above the solubility limit. In this case, a heavy oil dispersion or emulsion recirculates within the system. The carbon particle is very likely to be coated by the dispersed hydrocarbons, resulting in significant pore blockage, thereby reducing the available adsorption surface area.

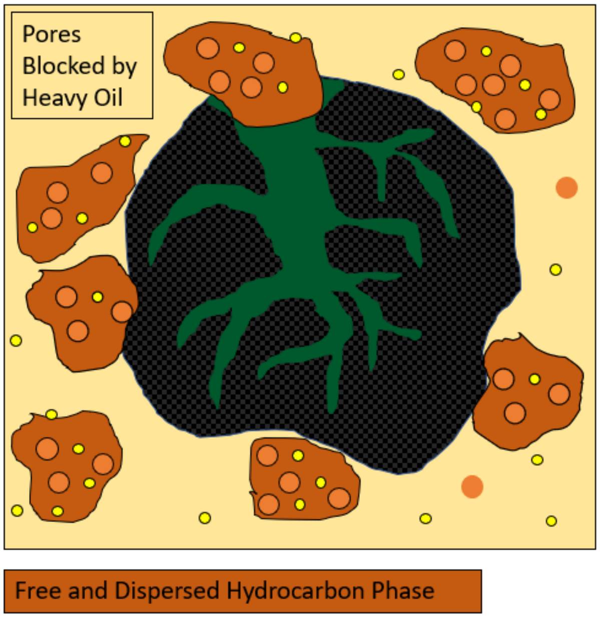

Figure 4. Schematic of adsorption, showing the impact of free hydrocarbons on pore blockage

Foaming in amine systems is attributable to solids, hydrocarbons and surface-active agents. The presence of solids and emulsified hydrocarbons are commonly correlated with foaming incidents in the amine system. Foaming incidents also tend to agitate settled hydrocarbons and solids from the tower internals, exacerbating the original incident.

AMINE SYSTEM EXAMPLE. For the purpose of understanding the efficacy of carbon adsorption in an amine system, we will consider a case of an amine system used to treat a sour gas stream. The process parameters are listed below:

Gas Flow Rate: 400 MMSCFD
Gas Operating Pressure: 900 psig
Average Molecular Weight of Treated Gas: 22
Gas Molecular Flow Rate: 1,060,000 lb-mol/day
CO_2 content: 5%
H_2S content: 5%
Amine System Flow Rate: 1,000 gal/min
Amine System Volume: 180,000 gal

Given these parameters, and a typical molasses number, we can estimate the total adsorption capacity of activated carbon in an amine system.

Amine Slip-Stream Flow Rate (15%) to Carbon Bed: 150 gal/min
Carbon Bed Volume: 300 cubic feet
Carbon Bed Weight (typical density of 30 lb/cf): 9,000 lb
Available Uptake of Large Molecules: 1,800 lb
Available Uptake of Small Molecules: 9,000 lb

It is reasonable to assume that the incoming gas contains 2-10 ppmv of hydrocarbon aerosol that can get picked up by the amine. This translates into a hydrocarbon ingression of approximately 2-10 lb-mol per day. If the hydrocarbon has an average molecular weight of 100, the lower limit is equivalent to 200 lb/day. In addition, some vaporized hydrocarbon is also picked up by the amine. An especially significant amount of vaporized hydrocarbons will be picked up if there are aromatic species in the inlet gas, or if the gas treating solvents have an affinity for the aromatics.

A typical amine may be expected to have a solubility limit of approximately 100 ppm_w which results in the recirculating amine in our example carrying up to 150 lb of hydrocarbon (180,000 gal x 8.3 lb/gal x 100/1,000,000). The hydrocarbon solubility capacity of the amine (150 lb, in our example) is generally lower than the ingression of aerosolized (200+ lb/day) and vapor hydrocarbons (variable). If the incoming hydrocarbon is not removed (by the carbon bed, in the regenerator), then the hydrocarbon will start condensing into a separate phase that will recirculate around the system. Some of this hydrocarbon will gravitationally separate in the flash tank, but much of it will recirculate as a stable emulsion.

The condensed hydrocarbon may not necessarily be visible as a separate phase in an amine sample bottle. The human eye is only able to resolve droplets larger than 20-micron, and due to pump action and heating and cooling in an amine system which break droplets into smaller ones, the hydrocarbon droplets are generally not detectable by the naked eye. In addition, droplets of a very small size, i.e., below approximately 20-micron, settle very slowly and will remain suspended for a long time. A sample in a glass bottle may appear hazy, but due to the limited depth of the bottle, the human eye may not even be able to detect the presence of a haze.

Rich Side Carbon: If the carbon bed is on the rich amine, all the dissolved hydrocarbon in the amine will be immediately available for adsorption onto the carbon. This means that the 200+ lb/day of hydrocarbon entering the system will be available for adsorption by the carbon bed. Since the carbon bed operates on only 15% of the amine flow, the balance of the hydrocarbon will recirculate, free to be stripped in the stripper, to affiliate with solids and form a shoe-polish-like substance which may settle in dead zones, on heat exchange surfaces or in mass transfer equipment. The heavy hydrocarbons that do not boil off in the regenerator, will recirculate and the amine will reach the solubility level in a matter of days after startup.

If we assume that the amine is saturated in hydrocarbons at a solubility level of 100 ppm_w, the upper limit of the total hydrocarbon adsorbed by the carbon is approximately 180 lb/day (150 gal/min x 1440 min/day x 8.3 lb/gal x 100 ppmw (HC)). Given the carbon capacity of between 1,800 lb – 9,000 lb of hydrocarbon adsorption, the carbon will be spent in 10 – 50 days.

This assumes that there is no free hydrocarbon fouling the carbon. The 10-day estimate (based on the Molasses Number) is a likely applicable because much of the soluble hydrocarbons (C6+, 0.5 nm+) will be larger in size than the Iodine atom (0.2 nm).

If the amine has emulsified hydrocarbon, it is very likely that the carbon particles will be coated by the hydrocarbon, thereby introducing a significant mass-transfer resistance to hydrocarbon adsorption, i.e., the carbon is essentially spent at that condition. The use of carbon adsorbents on the rich amine section is particularly subject to fouling by free hydrocarbons because the ingress hydrocarbons will not have had an opportunity to be stripped from the amine in the regenerator prior to contacting the carbon. If we assume that the available carbon capacity is reduced to 30%, that means that the carbon capacity is now 600 – 3,000 lb. ***This suggests that the carbon is spent in 3 – 15 days.*** Most primary gas treating amine systems (i.e., not including tail gas amine systems) are contaminated with recirculating emulsified heavy hydrocarbon, so it is most likely that the carbon in these systems is spent in approximately 3 days!

Obviously increasing the slipstream, and the carbon bed size can help extend the available run life of the carbon; but the root cause solutions must involve (a) reducing the quantity of hydrocarbons challenging the carbon bed; and (b) reducing the likelihood of emulsified hydrocarbons that can foul the carbon.

Lean Side Carbon: If the carbon is located on the lean amine all the light hydrocarbons (C7 and lower) will be stripped out in the regenerator. This reduces the level of hydrocarbons in the amine system. The remaining hydrocarbon in the lean amine will be heavier (C8+), with a higher viscosity, and a lower solubility level. Therefore, carbon beds on lean amine streams can expect to be faced with emulsified and dispersed hydrocarbon to a greater extent. In addition, the higher boiling hydrocarbons can expect to have lower adsorption capacity in the carbon. As a result, the likely run life will be in the 3 – 10 day period defined by the lower limits of the carbon capacity depending on whether hydrocarbon emulsions are present.

Activity Indication: Many owner/operators decide to replace their activated carbon on pressure drop. Pressure drop is a measure of solid contaminants building up on the carbon bed and is not a measure of available adsorption capacity of the carbon. A practical test for residual carbon activity is to conduct an amine foam test at the outlet of the carbon bed. If the carbon bed is not spent, and the amine is free of recirculating solids, there should be a significant difference between the inlet and effluent in foam heights and foam stability.

Utility of Carbon in Amine Systems: Carbon beds still serve a very useful purpose in amine systems. When designed and operated well, they can effectively remove surfactants, certain degradation products and even low levels of soluble hydrocarbons. However, to be effective, the carbon needs to be replaced when spent, not on a preventive maintenance schedule. In addition, their efficacy can be greatly extended if they are protected from free, dispersed or emulsified hydrocarbons and if the incoming heavy hydrocarbon load is reduced.

ADVANCED ALTERNATIVES - LIQUID-LIQUID SEPARATION – REMOVING EMULSIFIED HYDROCARBONS. The presence of emulsified hydrocarbons has a significant impact on carbon capacity due to the pore blockage challenge. This paper assumes that 30% of the carbon capacity is still available, but it is very likely that this is a very optimistic estimate, given how common it is to have carbon beds contaminated with a layer of free oil. A good approach to improve carbon bed performance involves the deployment of a high efficiency emulsion separator prior to the carbon bed. Transcend Solutions provides its ***Envision™ EHR*** technology specifically designed for emulsified hydrocarbon removal from amine systems.

The emulsion separator is preferably used to treat the entire amine flow to remove emulsified hydrocarbons, thereby protecting downstream mass transfer columns, and reducing the burden on the carbon bed. The emulsion separator may be located on the rich or the lean side of the amine loop. The advantages of locating it on the rich side include removing hydrocarbons immediately after the flash tank, preventing fouling of the exchangers or the regenerator, reducing hydrocarbon load in the amine acid gas stream, and ensuring that the lean amine will not have emulsified hydrocarbons. Locating the carbon bed downstream of the emulsion separator on the rich or lean section of the amine system is enough to ensure that the carbon will not encounter emulsified hydrocarbons that will shorten its adsorption capacity.

However, if owner/operators are concerned about rich side installation of a liquid-liquid separator, the system can be installed on the lean side before the carbon bed. It is preferred that 100% of the amine stream is treated which will also protect the downstream columns and other equipment in addition to protecting the carbon bed. However, if capital economics dictate that only slip stream treatment is affordable, an emulsion separator immediately upstream of the carbon bed will allow the carbon to have a longer run life.

Using a liquid-liquid separator is ultimately a solution to a symptom (of hydrocarbons in the amine system), rather than a root cause solution. The root cause solution would be the prevention of hydrocarbon emulsification in the amine system in the first place. However, the side solutions installed in amine systems can be economically justified if the gas phase treatment is more expensive due to pressure and metallurgy, or if, as in a refinery, there are dozens of absorbers feeding a single amine regeneration unit.

ADVANCED ALTERNATIVES - AEROSOL-GAS SEPARATION – REMOVING HYDROCARBONS BEFORE THE AMINE UNIT. The root cause of the problem that carbon beds are expected to solve is the ingression of hydrocarbons into the amine system. These hydrocarbons are most commonly aerosolized sub-micron contaminants. Some vapor phase hydrocarbons can end up in the amine depending on the treating solvent, but for the most part the offending contaminants that cause foaming and fouling in the amine loop are present in the inlet gas as an aerosol. These aerosols may be compressor lube oils, heavy aromatic naphtha from corrosion inhibition programs, hydrocarbons from hydroprocessing unit separators, etc. In any case, the sub-micron contaminants are often not stopped by conventional separators that are applied.

It is essential to have a high efficiency aerosol separator. The gas treating industry conventionally uses horizontal-filter separators to keep liquids out of the amine system. These systems have inherent flaws that limit their efficiency at removing liquids from gas streams. More importantly, they are unable to remove the low-surface tension, sub-micron aerosols that afflict amine treating systems. Transcend Solutions provides its ***Ensur™*** technology specifically designed to remove these sub-micron aerosols. If the liquid aerosols are stopped before the amine absorber column, the only hydrocarbons that can be picked up by the amine are those that exist in the vapor phase of the gas to be treated. For example, the vapor pressure of heavy hydrocarbons is very low (for example, dodecane has a vapor pressure of <20 Pa), so they are present only in ppm levels in the inlet gas.

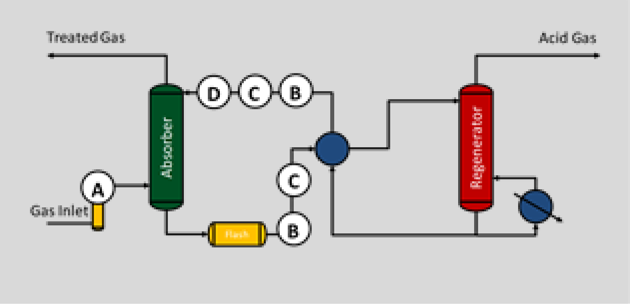

Figure 5. Schematic of amine system showing preferred location of hydrocarbon and solids removal

Carbon beds are used in amine systems ostensibly to remove hydrocarbons for the purposes of foaming and fouling prevention. Foaming is caused both by the presence of emulsified hydrocarbons and solid particles. The root cause and industry best practices include (as shown in Figure 5):

- High efficiency aerosol separation on inlet gas (A)
- High efficiency, solids removal from rich full-flow or lean slip-stream (B),
- High efficiency, emulsion separation rich full-flow or lean slip-stream (C)
- Carbon bed located downstream of emulsion separator (D)

SUMMARY. This article evaluated the capacity of a conventionally designed carbon bed to remove the kinds of hydrocarbons that challenge it. We were able to show that even under ideal conditions, carbon beds most likely only have 10 – 50 days of available capacity for hydrocarbon removal. Also, if there are emulsified hydrocarbons present in the amine stream (which is the most common situation) then most likely the available capacity will decline to last about 3 days. This limited available capacity is oftentimes not recognized by owner/operators, so the carbon beds may be scheduled for replacement every 6 – 12 months, even though their useful lifetime had long since passed. We propose technology to extend the run life of the carbon bed, by protecting it from free, dispersed or emulsified heavy oils; thereby allowing carbon adsorption to operate to its maximum extent. In addition, we propose the use of high efficiency sub-micron aerosol removal to protect amine systems from heavy oils in the first place.

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