

# **Pure Evil – Tall Tales of the Most Heinous Hydrocarbons in Refinery Amine Systems**

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**Nate Hatcher**

*Phillips 66  
Refining Business Improvement  
Houston, TX  
+1 832-765-1082  
nate.a.hatcher@p66.com*

**Maddie Mills**

**Marshall Heltz**

**Bob Vitt**

**Jason Kaliszeski**

**Skyla Scott**

*Phillips 66  
Lake Charles Refinery  
Lake Charles, LA*

**Leonard Nyadong**

**Jesse Contreras**

*Phillips 66  
Energy Research &  
Innovation (ERI)  
Bartlesville, OK*

## **ABSTRACT**

The characteristics and defining features of the deadliest hydrocarbons to refinery amine units are illustrated through scenarios where amine systems became nearly inoperable due to oil contamination. There is a general recognition in the industry that hydrocarbons are bad in amine systems. Far less well understood are the reasons why some hydrocarbons lead to mild discomfort while others can wreck a system in very little time, even at very low concentrations.

Through the troubleshooting efforts involved during multiple events, these systems were restored to normal operations. Prevention and mitigation techniques to survive severe oil contamination will be emphasized along with analytical techniques that were critical in identifying the bad actors. Pictures of contaminated solutions along with analytical data that were important in identifying the bad acting hydrocarbons will be shared for the general awareness of the industry. A few of the villains in these tales may include: Luby Oil, Ben Diesel, Cokey OilCan, Sir Factant, Kim Clean, Fin Ole, Mr. Ewax, and Kara Seen with a special guest appearance from Aunty Foam.

## The Villain Line-up

What would a tale be without a cast of villains? To assist with identifying the properties and characteristics of hydrocarbons that determine their consequences in amine systems, a line-up of the most evil villains in our stories has been created.

### Luby Oil

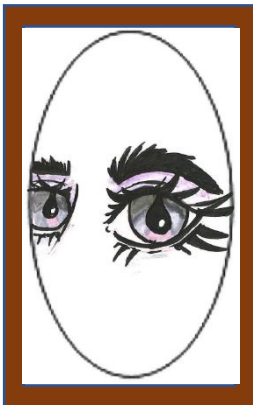


Heavy and dense, Luby is normally very jovial when she's left in the hydrocarbon producing units. With a specific gravity of 0.88-0.97, she does not float very well in the Rich Amine Flash drum. Luby will slide right along to the Regenerator. Because she does not carry much vapor pressure, Luby tends to sneak out the bottoms of the Regenerator. When she loops back around and encounters a liquid treater, she'll gladly hop back out of the amine solution into the LPG product causing oil ring test failures. For this reason, many amine systems will configure the heavier oil product amine contactors onto a separate amine loop from the liquid treaters.

In a gas treater, Luby tends to attract a lot of particles by her friendly nature at the interface to stabilize foam. Two mutant forms of Luby Oil are known to exist. Sometimes Luby keeps herself looking young and fresh with age (corrosion) inhibitors and antioxidants supplements. These chemical supplements helps Luby mingle more with the amines and explains her sometimes bubbly nature.

### Kara Seen

Sometimes difficult to be seen, Kara often sneaks her way into the amine system when the inlet gas is too hot or a separator boot upstream malfunctions. Kara is sometimes used as a sponge oil in upstream gas plants. With a specific gravity of 0.78-0.82, she can start to become a handful and slip away in the Rich Amine Flash Drum. Properly designed amine systems can resist her temptations. Kara has to be "seen" in the sight glasses though, which she regularly evades.



Kara loves to make Amine Regenerators dance. She is still light enough to be steam stripped up the column. She is too heavy though to leave the system. Hence, she hangs out in the reflux/pumparound system where the amine binges on her until it becomes nauseated and throws up foam. Kara has wrecked many a sulfur plant downstream by sizzling the reaction furnaces.



### **Ben Diesel**

When he gets into your amine system, operations become Fast & Furious. HDS cold HP separators have to have boots big enough to contain him. Ben carries a specific gravity between 0.82 and 0.85 depending upon whether he is bulking up or shredding. Thus, Ben is very problematic to settle in the Rich Amine Flash Drum.

When used as a sponge oil upstream, it is very important to have a filter/coalescer to prevent aerosols of Ben entering the amine. Otherwise the amine unit can become a “Has Ben”. Kara Seen together with Ben Diesel make a deadly combination. Like Kara, parts of Ben can become trapped in the Amine Regenerator leading to foaming when Ben tries to bust out of solution in his muscle car, a 1968 Dodge Charger.



### **Kim Clean**

A product of selective breeding by everybody’s friendly neighborhood chemical cleaning vendor to combat Luby Oil, Ben Diesel, and Kara Seen Kim has surface active properties that can morph her into a super villain when not thoroughly rinsed from equipment during turnarounds. QuikTurn®, ZymeFlow® and similar ingredients may encompass Kim Clean. Kim has been known to transport iron sulfide particles and hydrocarbons everywhere. Leaving as little as 10 ppmw of Kim Clean agent has been known to turn amine units into a bubble bath.

### **Sir Factant**

A descendent from the royal blood line of the original super villain, King Factant, Sir has been around since the late Cretaceous period. All other hydrocarbons carry characteristics passed down over the generations from him. Sir was originally less potent, but later mutated into a more virulent form at some point in history. He has wrecked enough amine units in the industry to be permanently Knighted into infamy.



The main characteristic of Sir Factant involves his ability to cause surfaces to spread (expand) with less energy through his powers of reducing surface tension. When Sir Factant arrives at the scene, froth becomes foam and even shaving cream that sits on the surface.

Sir Factant has been encountered in both cationic and anionic forms in various detergents. He carries both a nonpolar and a polar end which allows him to conveniently line up and hang out at places like gas/liquid, liquid/liquid, and solid/liquid surfaces. He can gang together in micelles

to cause amine to be moved out of the liquid treater into liquid hydrocarbon products, or alternatively let hydrocarbons ride along into the amine. This causes copper strip failures due to the  $H_2S$  that invariably rides along with the amine micelles inside the hydrocarbon. In other forms, Sir Factant has allowed copious amounts of gas to be passed in the rich amine leaving high pressure hydrotreating contactors. In one case, this led to two-phase slug flow in the rich amine piping that resulted in the level control valve pulsing up and down nearly 1 foot on a spring can.

### Cokey OilCan



Cokey has the ability to hold other lighter hydrocarbons in his heavier barrel, allowing them to be transported and gassed off in the Rich Amine Flash Drum. Cracked stock hydrocarbons are worse than straight run hydrocarbons in amine units. With a density approaching that of water and aromatics that are more soluble in aqueous solutions, Cokey's pants have been said to be quite dirty. When treating FCC or Coker gas, poly nuclear aromatic compounds (PNA's) may be present in the oil can which are pure evil. PNA's, the defining feature of Mr. OilCan, behave as solids up to 130-165°F which will allow them to hang out at some surfaces (e.g. Regenerator trays and reflux packing). When heated, the solids become liquids and are usually too heavy to escape the Regenerator. Purging the Regenerator reflux is often the most effective, and sometimes only way to remove oil boiling in this range. There may be an extremely heavy (and dark) tail of hydrocarbon in the sponge oil of some gas plants.

### Aunty Foam

When used judiciously in very small quantities, Aunty can be a sweet relief for the amine system



by taming foaming problems. However, Aunty can become a real meanie when overused. Aunty comes in both silicone and polyglycol formulations. Designed to work at surfaces, Aunty is surface active. She thus has trouble leaving the system. When used frequently and above trace concentrations, Aunty ultimately becomes part of the foam lattice over time, turning into a real menace herself. Polymeric components can concentrate enough at the surface to lock a normal hydrocarbon foam into a tighter and more deadly combination of emulsion plus foam with demonic qualities.

Aunty readily is adsorbed onto the charcoal in activated carbon, defeating the purpose of the carbon in removing other surfactants and hydrocarbons, leading to more frequent changeouts. Aunty's surface-active properties will readily emulsify and transport amine out of liquid treaters into hydrocarbon products. The encapsulated amine solution contains  $H_2S$ , which causes increased caustic consumption in washes downstream and can lead to copper strip failures along with acid soluble oil (ASO) production in alkylation units.

## Mr. Ewax



Ewax is believed to be the child of Luby Oil and Cokey OilCan. At room temperature, Mr. Ewax is a solid that tends to attract particles and float around as a 2<sup>nd</sup> phase. Ewax can be very elusive, sometimes taking the form of a liquid in the hot rich amine piping and Regenerator while at other times appearing as a solid in systems like the cooled lean amine and Regenerator pumparound/reflux. This can make Mr. Ewax very hard to detect.

Ewax does carry some vapor pressure allowing entry into the amine solution from hiding in the vapor tail of a feed. In solid form, Ewax deposits everywhere, ruining filter/coalescers, particle filters, coating trays and packing, as well as plugging and defeating oil detection instruments. In solid form, Ewax is technically classified as a “sol”, which is a colloidal suspension of solid particles in a liquid. As a liquid, Ewax moves through the system as an emulsion. He can also sublime from a solid into a gas. Ewax is by far the sneakiest of the hydrocarbons with his shape-shifting abilities.

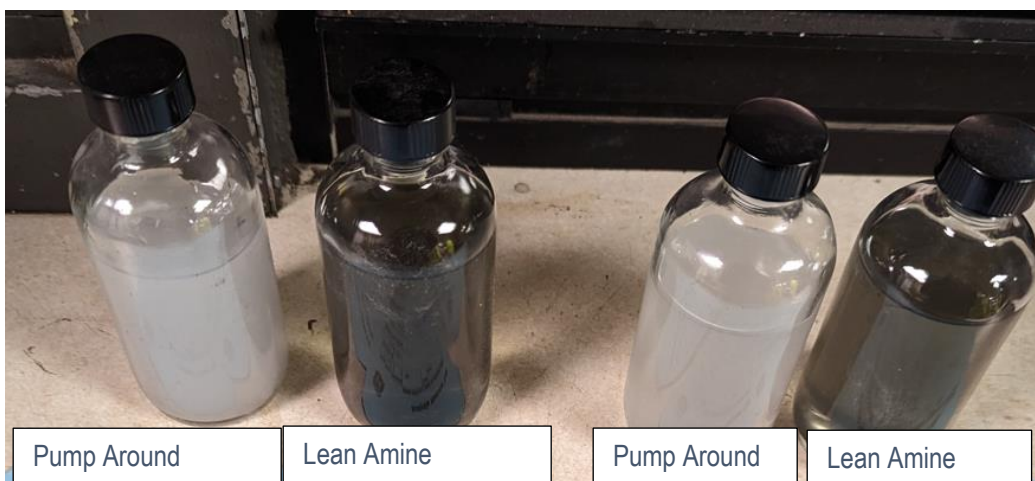
With our cast of villains appropriately introduced, we can now proceed into some tall tales.

## Crime Scene Number 1

Multiple regenerator foaming events occurred prior to and during the day of March 13, 2023. During the morning, the one ARU regenerator foamed and then another followed shortly thereafter when liquids from the sulfur plant knockout (KO) downstream were pumped back into the other regeneration system's Rich Amine Flash Drum. Regenerators were sluggish to respond to anti-foam, refinery rates were trimmed back to minimum to preserve the amine inventory and stay under environmental limits for fuel gas H<sub>2</sub>S levels.

### Evidence

A picture showing the condition of the amine on the morning of the event is shown in Figure 1.



**Figure 1** Amine Condition Morning of 3/13/2023



The grayish ARU pumparound purge samples are indicative of an emulsion of hydrocarbon, particulates and anti-foam. The lean amine from one system was dark black indicating macroscopic iron sulfide particles. Color of the second system lean amine was a little better, but the cloudiness indicated heavy hydrocarbon.

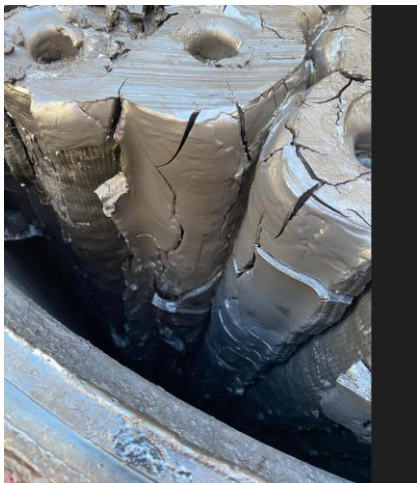
A sample of pumparound water during an actual foaming event was collected and the refinery extracted the hydrocarbon and analyzed by SimDist. Testing indicated mostly kerosene boiling range material with a long tail into the 650-700°F end point. Upon further testing in the refinery lab, a significant portion of the hydrocarbons were found to be ringed and heavy aromatics. This eliminated several contactor sources including the liquid-liquid treaters from the troubleshooting effort.

A refinery fuel gas contactor along with hydrogen HP contactors were walked down with operations. Bottoms level gauges in the contactors along with associated inlet KO drums were isolated, drained, steamed, and returned to service in succession.

One recycle hydrogen contactor that was reading 55% level in the DCS was found to have a completely full bottoms level on the local sight glass after steaming. A skimming connection previously installed had been removed from this service some time ago. Accumulation of liquid hydrocarbons here was believed to be a major contributor to the problems, although the heavy aromatics are not normally expected to be present here. Note that a slurry oil HDS contactor had been taken down several weeks prior to the events of 3/13/23.

There are two filter/coalescers servicing the recycle hydrogen circuit, an older horizontal unit, and a newer vertical unit. Operations commented that both units are drained of hydrocarbon daily. There is a low point for liquids to accumulate in the piping downstream of one coalescer. Coalescing elements in the older unit had not been changed in some time. The pressure drop indicator across the older filter/coalescer appeared to no longer be working.

Lean amine into and out of each cartridge filter was sampled and the filters were found to be ineffective despite low pressure drop 2-3 psi. One filter was found to be completely plugged with several feet of sludge in the bottom. Pictures of the elements follow in Figure 2.



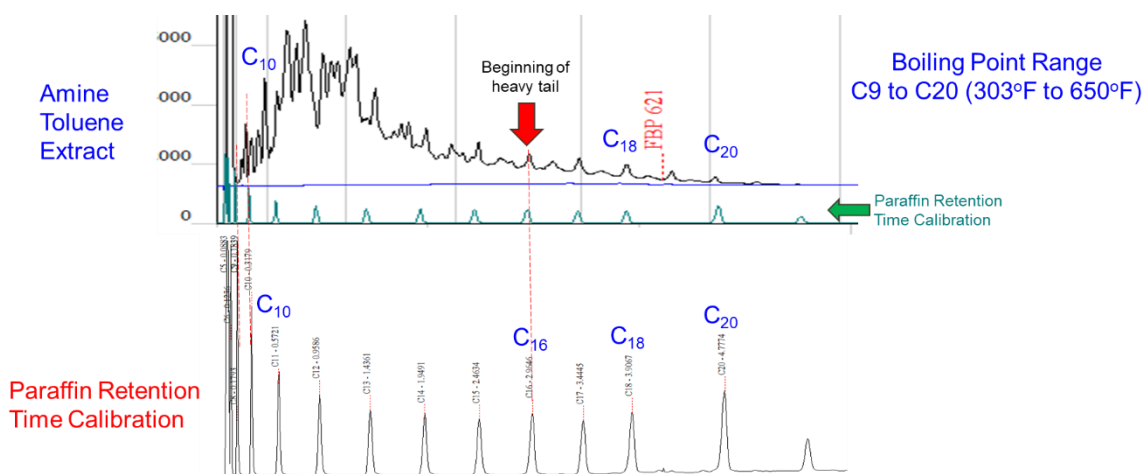
## Figure 2 Filter Elements from One Amine System

Samples of the solids were sent to Phillips 66 Energy Research and Innovations (ERI) laboratory in Bartlesville for further characterization. Note that flow indication to the filters did not exist for operations to know whether the filters were seeing flow.

Cloudiness of the circulating lean amine as well as on the direct outlets of the two carbon beds indicated that the carbon beds was exhausted.

### DNA Evidence

Figure 3 shows the GC SimDist Chromatogram of the hydrocarbon extracted from the pumparound water showing a boiling range between C<sub>9</sub> (303°F) and C<sub>20</sub> (650°F). However, the overall profile (C<sub>9</sub> to C<sub>16</sub>) is most consistent with kerosene boiling range material with a slight heavy tail of C<sub>16</sub><sup>+</sup>. It is somewhat unusual that the paraffin peaks are relatively small for a straight run distillate, indicating that this material could be a product from a cracking unit. The heavy tail may have been an indication that there is a separate diesel range material present.



**Figure 3 Chromatogram of Hydrocarbon Liquids Extracted from Pumparound Water**

SimDist results for the hydrocarbon that was extracted from the pumparound water along with several other tests run by ERI are included in Table 1 to characterize the oil.

**Table 1 Characterization Tests on Pumparound Water Toluene Extract**

Test Method	Run	Parameter List ID	Parameter ID	Result	Units	Parameter ID	Result	Units
ASTM-D7213: Sim Dist Wt%-LCR	1	ASTM-D7213: Sim Dist Wt%	0.5 % weight (IBP)	214.4	°F	60 % weight	272.8	°F
			02 % weight	224.2	°F	70 % weight	276	°F
			04 % weight	230.8	°F	80 % weight	281.8	°F
			05 % weight	232.6	°F	90 % weight	436.6	°F
			06 % weight	234.6	°F	92 % weight	449.6	°F
			08 % weight	238.2	°F	94 % weight	471.8	°F
			10 % weight	242	°F	95 % weight	485.4	°F
			20 % weight	255.6	°F	96 % weight	503.2	°F
			30 % weight	262	°F	98 % weight	551.4	°F
			40 % weight	265.8	°F	99.5 % weight (FBP)	620.6	°F
			50 % weight	269.4	°F			
ASTM-D6729-Type: PIONA-LCR	1	ASTM-D6729-Type: PIONA	Olefins	0.493	volume %			
			Aromatics	94.919	volume %			
			i-Paraffins	0.38	volume %			
			Paraffins	0.401	volume %			
			Naphthenes	0.042	volume %			
ASTM-D6729-C#: Total By C%-LCR	1	ASTM-D6729-C#: Total By C#	C4 Total	0	volume %			
			C5 Total	0.067	volume %			
			C6 Total	0.276	volume %			
			C7 Total	92.511	volume %			
			C8 Total	0.062	volume %			
			C9 Total	0.195	volume %			
			C10 Total	0.216	volume %			
			C11 Total	0.975	volume %			
			C12 Total	1.876	volume %			
			Toluene	92.349	volume %			
			Undecane	0.107	volume %			
			Dodecane	0.276	volume %			
			3-methylhexane	0.013	volume %			

### The Verdict – Case 1

Kara Seen was found guilty of breaking and entering into the amine system by the faulty level indication in the HDS hydrogen treating system. She is still awaiting sentencing.

### Mitigation Steps Undertaken

Amine strength was reduced from 45%wt to 35%wt to assist with settling oil. While this move was not expected to provide much relief, the reduction in hydrocarbon solubility with lower MDEA strength was felt directionally would help to reduce emulsified oil in the amine.

The skim connection on the HDS Recycle H<sub>2</sub> Contactor was recommissioned a couple days after the problem started.



Particle filter elements on the dirtiest system were changed out on 3/16 and the amine looked visibly better the next day. Particle filters on the other two systems were subsequently changed several days later.

Replacement carbon was ordered for each system. The first system was replaced 3/22.

Flash drums were skimmed while pumparound/reflux water purging was maximized from each Regenerator.

## **Crime Scene Number 2**

Unfortunately, before the amine system could be fully recovered on 3/21/23 a Regenerator foamed again hours before a scheduled turnaround on another ARU system was going to begin. Liquid carryover knocked down two sulfur recovery units downstream and rocked most of the refinery for several days. Light gasoline-like hydrocarbon was found in the ARU and collected for analysis.

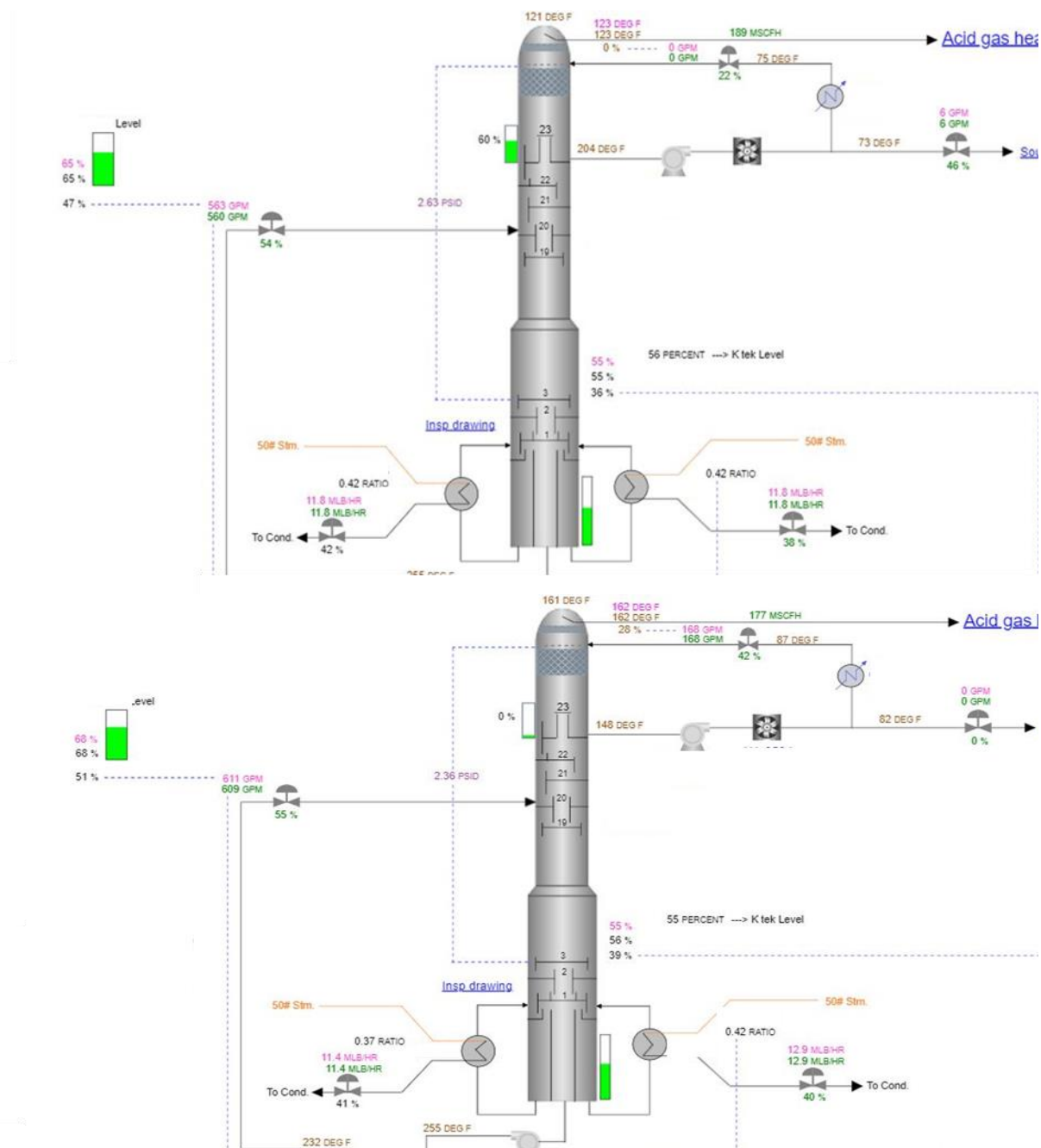
Over the day of 3/21, the condition of the regenerator overhead system deteriorated. The heat removal capability across the pumparound packing drastically reduced by about 50%. Overhead acid gas temperature increased from 123°F to 162°F. Pumparound draw temperature also decreased from 204°F to 148°F. Attempts to cut pumparound flow or increase reboiler steam would result in foaming symptoms. Figure 4 contrasts the Regenerator operating data at the beginning (top) vs. end of the day (bottom).

The refinery enlisted ChemGroup MPR Services to bring in a mobile hydrocarbon and particulate removal skid to improve the amine hygiene while the sister facility cleaning systems were being brought back up from a turnaround. The skid was commissioned over the night of 3/22. One of the SRU's was restarted on 3/22.

Activated carbon arrived and was changed out on one system on 3/23. By March 25<sup>th</sup>, hydrocarbon concentration in the lean amine had been reduced by over 50%.

TracerCo was called out to scan the pumparound packing. The gamma scan analysis indicated that the packing all appeared to be in place. During the scanning process the tower foamed twice. This turned out to be quite fortuitous as the foaming was found to initiate near and above the feed tray versus the stripping section and reboiler.

It was later determined that two of the foaming events on #3 Regenerator occurred when the pumparound draw temperature increased to about 165°F. Below 165°F, the column operations appeared to remain stable. Several foaming events were also timed around upstream flash drum level floating and during skimming. The refinery found less foaming tendency when the flash drums were operated at as low pressure as possible.



**Figure 4** Regenerator Overhead System Performance Deterioration on 3/21/23  
Top – Beginning of the day / Bottom—End of day

Samples of rich amine from all Contactors along with the contaminated ARU Regenerator pumparound water were processed in the refinery lab and at ERI in Bartlesville to be fingerprinted. Figure 5 shows a picture of the pumparound water skimmed material the day that it was pulled taken in the refinery lab while being stirred.

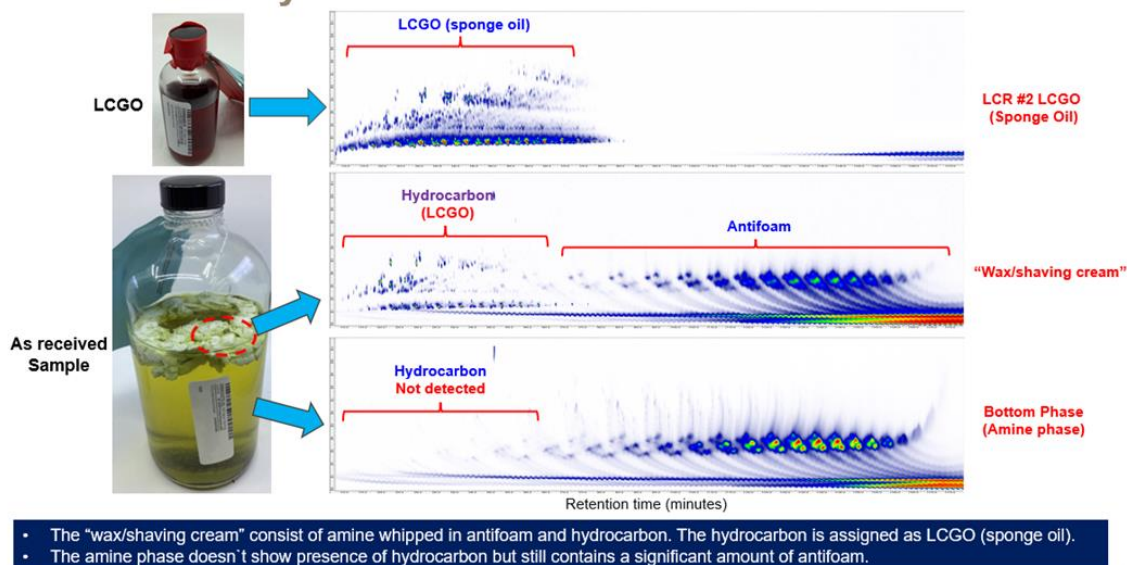


**Figure 5 Contaminated Regenerator Pumparound Water Sample**

### DNA Evidence

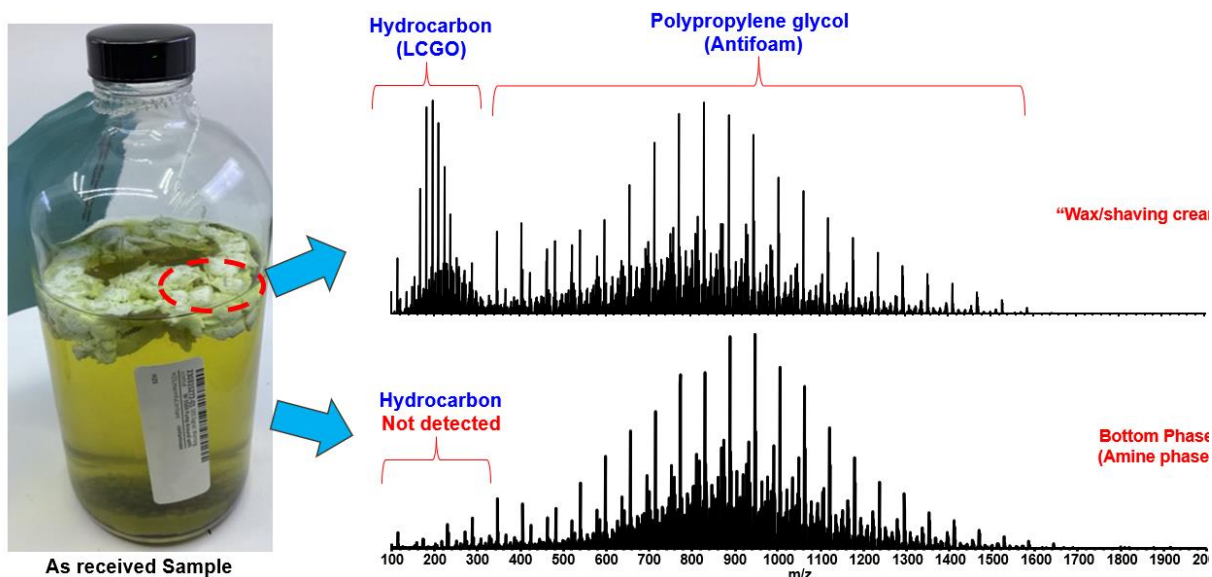
The sample shown in Figure 5 was torn apart in the ERI Bartlesville laboratory using several tests. Figure 6 shows the fingerprints from comprehensive two-dimensional gas chromatography mass spectrometry (GCxGC MS) analysis of the top and bottom layers of the sample compared to a sample of the light coker gas oil that is used as a lean oil upstream of the Coker GRP fuel gas absorber. There is a definite match of a portion of the spectrum.

### GCxGC MS Analysis



**Figure 6 GCxGC MS Analysis of Pumparound vs. LCGO Sponge Oil**

Figure 7 shows the direct analysis in real time mass spectrometry (DART MS) results of both layers. The shaving cream material was quantitated to be 89% LCGO hydrocarbon with the remaining 11% to be the polypropylene glycol-based anti-foam.



**Figure 7 DART MS Analysis of Pumparound**

The solids were found to be completely melted at 80°C (176°F) in a controlled temperature bath. It was surmised that the foaming observed in the plant at higher temperatures may have been from the waxy material melting and generating a second hydrocarbon phase with lower surface tension.

#### The Verdict – Case 2

For the second crime, Mr. Ewax and Cokey OilCan were convicted and sentenced to life in prison without parole. Aunty Foam was placed on probation and switched out in favor of a different formulation. Because recognizance was given for over-judicious use, her probation will be lifted once the inlet filter coalescer elements are returned to service. Injection connections into the regenerator pumparound loops were installed to target Aunty into the places that she was needed for more judicious use.

The refinery lived to fight another two battles with hydrocarbon following this episode and knocked out the hydrocarbon in the first and second rounds due to improved defense and mitigating measures that were undertaken.

In living through these episodes, several key lessons were learned.

- Filters and coalescers make for great guard dogs to deter villains from breaking into the premises. Taking care of preventative maintenance on these control devices helps to ensure that the plant will have a good crime fighting partner.
- Flash drum skimming as an oil removal measure serves as a bouncer for the plant. As a bulk separation device, skimming is useful to remove the bulk of the hydrocarbon. Reflux/pumparound purging, charcoal and oil removal media like MPR's HCX system are there for selective fine targeting of villains.
- A fingerprint library of some of the bad acting villains was built through these troubleshooting efforts. Future criminal identification has proven to be more timely.

- Be cautious and judicious about anti-foam addition or the villains will be able to skate through the charcoal filtration the next night.