

Now We're Cooking: The Effect of Biodiesel Feeds on LPG Treater Operations

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Abstract

As governments around the world have altered the composition of feedstocks for petroleum refiners by regulating the inclusion of biomass, new problems have arisen in the area of LPG amine treating as a result.

Amine losses in LPG treaters taking feed from cracking units feeding used cooking oil (UCO), animal fats, or vegetable oils began to affect the ability to make a variety of LPG specifications including moisture and sulfur content. Additionally, units downstream of these LPG treaters such as LPG dryers, caustic treaters, and even selective hydrogenation units in front of HF alkylation units began to suffer from the poor LPG amine treater operation.

This paper discusses the nature of the biomass feeds, the breakdown of biomass in cracking, and transport of the biomass and cracking by-products to the LPG treater. Tell-tale signs of biomass contamination and reduction in treater performance are discussed. Emerging measures are discussed to deal with the amine contamination and prevent downstream effects.

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Government Mandates

Performing a cursory internet search¹, the following table shows the countries which are requiring the addition of biomass to regular crude oil-based transportation fuels. Ethanol, derived primarily from fermentation of corn is a relatively high-octane blending component for gasoline. Bio-diesel, derived mainly from plant and animal fats, can be added to middle distillates (kerosene and diesel) after some processing. Two summaries of these fat processing schemes in refining are covered in references 2 and 3.

Table 1: Biomass Inclusion Requirements by Country

Country	Ethanol Volume %	Biodiesel Volume %
Angola	10	
Argentina	5	10
Australia	4	2
Brazil	25	5
Canada	5	2
Chile	5 (V)	
China	10	
Colombia	8	
Costa Rica	7	20
Ethiopia	5	
European Union	10	10
Fiji	5-10 (V)	
India	5	
Indonesia	3	10
Jamaica	10	
Kenya	10	
Malawi	10	
Malaysia	5	5
Mexico	2	
Mozambique	10	
Nigeria	10(V)	
Panama	2	
Paraguay	24	1
Peru	7.8	2
Philippines	10	5
South Africa	10	
South Korea		2.5
Sudan	5	
Taiwan		1
Thailand		5
USA	Varies, increasing by year	Varies, increasing by year
Uruguay	5(V)	2
Vietnam	5	

Zambia		
Zimbabwe	10	
Note (V)=voluntary		

Essentially ethanol is a manufactured molecule resulting from the fermentation process. After formation, the ethanol is distilled from the liquid remaining after fermentation/and filtration of the original biomass. The ethanol must be dry for blending into gasoline, so distillation must include breaking the ethanol-water azeotrope, usually by employing benzene. Once separated, ethanol is blended into gasoline at terminals prior to shipment. Refineries play little if any role in the manufacture or inclusion of ethanol in their finished gasolines.

Biodiesel Operations

Biodiesel is a different matter altogether. Biodiesel molecules, although being 'manufactured', are not blending ready as is ethanol. This is due to the biological consequence of these molecules being built and stored by the plant or animal 'manufacturer'.

For plants, the primary use of oils that become biodiesel precursors is for the preparation of food for human consumption. Palm, soy, corn, olive, peanut, safflower, sunflower, and a variety of other seed oils are used in the recipes for food products or used to fry foods. Oils incorporated in foods are not available for use as biofuel whereas used cooking oils are becoming a common biodiesel feedstock source.

Animal fats can become biodiesel precursors by two methods. One method is recovery of cooking wastes, the fats that come out of the cooked meats that are discarded from the cooking equipment. Usually, these wastes contain water and caramelized deposits from griddle or grill. Of more importance is the fat coming from rendering processes. Tallow (beef) and lard (pork) are the traditional animal fat precursors for biodiesel.

Plant and animal fats and oils are far from pure substances like ethanol; rather, they are complex mixtures of fatty acids, fatty esters, and triglycerides of varying molecular weights. Cooking processes can degrade these oils if they are overheated or become contaminated.

It is possible to 'homebrew' biodiesel. Generally, this done where the precursor material contains simple fatty acids and triglycerides. Methanol and an alkaline catalyst will convert the triglycerides into glycerol and the free fatty acids. As long as the free fatty acids are in the correct boiling range and do not solidify at storage temperatures, they can be readily burned in the diesel engine.

For refiners, the 'homebrew' method is not really practical being a small batch production method. Another problem with fatty acids comes from the formation of peroxides at the acid function end of the molecule which can induce gum deposits which makes them unsuited for longer term storage or for fuel injector cleanliness. Because of these processing, storage, and quality issues, refiners have chosen to incorporate the processing of these precursors as part of the traditional refining processes.

According to references 2 and 3, there are two routes which refiners can take to process biodiesel precursors into biodiesel blends. The first is hydrotreating the fats and oils to eliminate the oxygenated carbons in the fat/oil chain. Oxygen in the fat/oil molecules are converted to water while saturating the

acidic carbon with hydrogen as would be found in petroleum distillates. As some cracking may take place under hydrotreating conditions, some of the acid groups may end up being cleaved forming CO₂ as a byproduct. Because no fatty acids are left after the hydrogenation, the water and any CO₂ formed can easily be separated from the reactor effluent and removed from the hydrotreater system.

The second route is to blend the precursors into the Fluid Catalytic Cracking Unit. This is where things get interesting for the amine system in the wet gas recovery plant following the FCC main fractionator. As both references point out, the mechanisms for cracking the fat/oil components are very complicated and result in a variety of oxygenated compounds the products going to the fractionator from the reactor. Some of the carboxylic acid groups are converted to CO and CO₂ which is normal for an FCC operating on petroleum-based stock. This is the result of oxygen carried from the catalyst regenerator via adsorption to the reactor section of the FCCU. The references cite experiments on biodiesel precursors showing an increase in CO level in the off-gas versus operation with petroleum-based stocks.

In one UK refinery, ion chromatography data taken on a selective hydrogenation unit upstream of an HF alkylation unit showed the presence of several small MW organic acids (formic, acetic, propionic, butyric, and valeric) poisoning the oxygenate compound sensitive catalyst. The poisoning came after the refinery began adding used cooking oil to the FCC feed. It would appear these acids were simply cracked off the larger fatty acid carbon chain at varying small chain lengths. This would not be expected if the acid components entered the MEA solution as they would be expected to react with the MEA to form heat stable salt anions and bound MEA.

Furthermore, many other oxygenated components were found in the LPG from the wet gas plants. A variety of ketones, aldehydes, furans, phenols, and mid-range MW fatty acids were identified by using a water wash skid on a slipstream of the LPG amine treater feed to remove these contaminants for analysis.

The conundrum we face here is not one of why these components are made in the FCC when feeding fats/oils to the FCC. Rather, the conundrum is why these components seem to selectively target the LPG amine treater downstream of the FCC gas plant and gasoline stabilization.

Table 2 compares properties of a couple of distillate boiling range alkanes and their corresponding fatty acids of similar carbon chain length.

Table 2: Boiling points of alkanes and fatty acids of similar carbon chain length

Carbon chain length	12	16
Alkane boiling point, °F	355	549
Fatty acid boiling point, °F	489	601

Dodecane (C₁₂) would be found in the last portion of the naphtha from and the first portion of a kerosene or diesel fraction a typical oil distillation. Almost all the hexadecane should go with the distillate fraction with a cutpoint of 650 °F. If either of the fatty materials above survived intact from the FCC reaction zone, our expectation, from a boiling point separation perspective, would be that these

components would leave with the light cycle oil (middle distillate) product and certainly not in the LPG product.

Figure 1 shows a typical FCC main fractionator; Figure 2 shows a wet gas recovery plant and gasoline stabilization system.

Figure 1

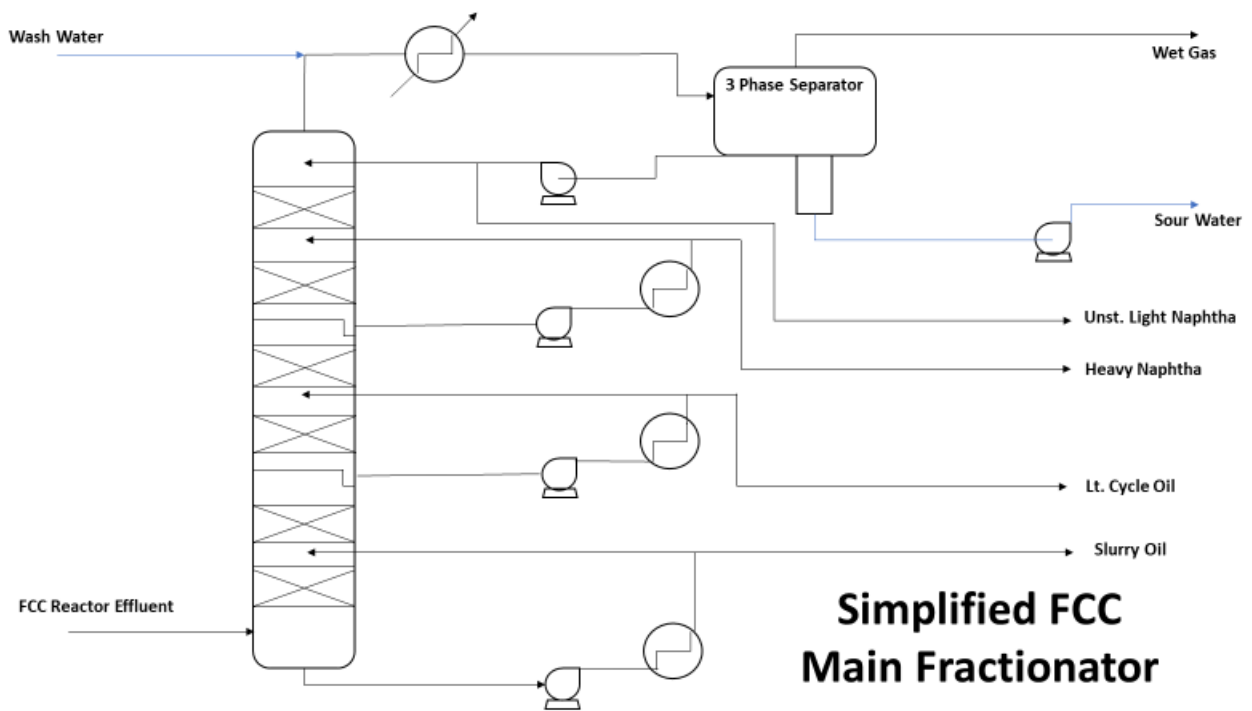
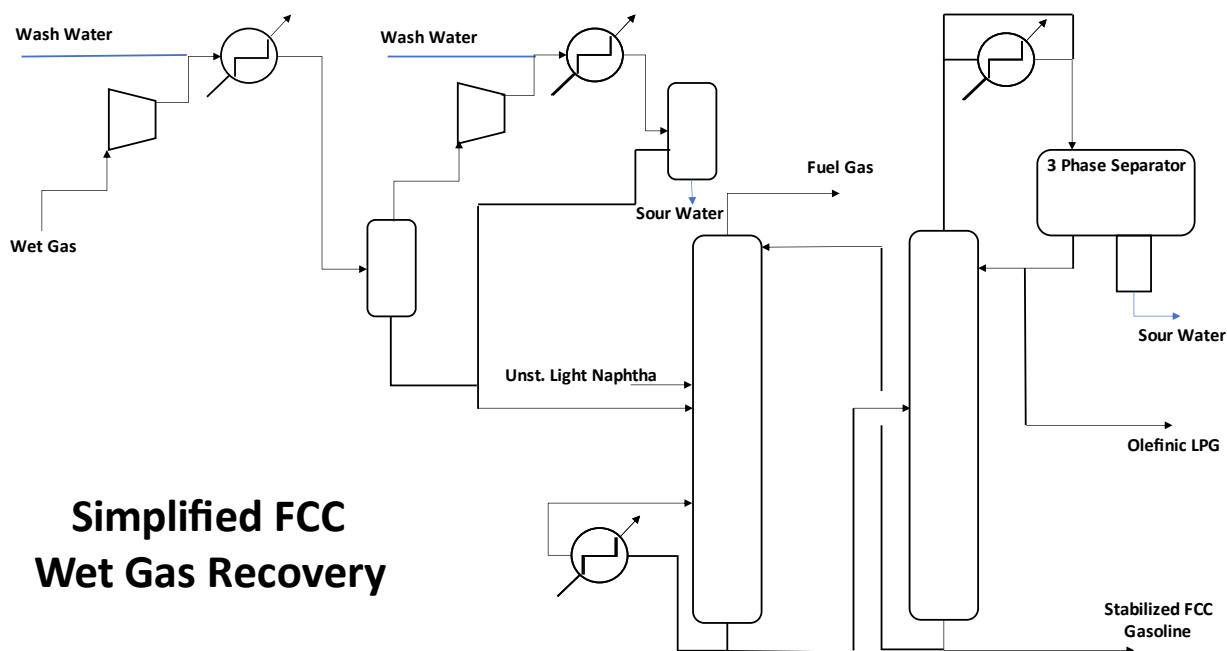


Figure 2



Similar to a TGU quench tower, an FCC fractionator operates as a desuperheater/condenser. Gaseous FCC reactor products leaving the catalyst/product separation zone at about 1000 +/- 50 °F enter the bottom zone of the tower where the first pump around section desuperheats the vapor and condenses oils that boil above middle distillate range. Slurry oil condensed in this circuit is removed and the slurry oil pump around stream is used for preheating other streams.

Vapor from the first section of the fractionator is contacted with liquid coming from the second pump around at the top of the second section. The second pump around is middle distillate boiling range material. Liquid going down through the tower vaporizes and saturates the vapor going up from the bottom section (desuperheating) so that the colder pump around fluid can condense the middle distillate product.

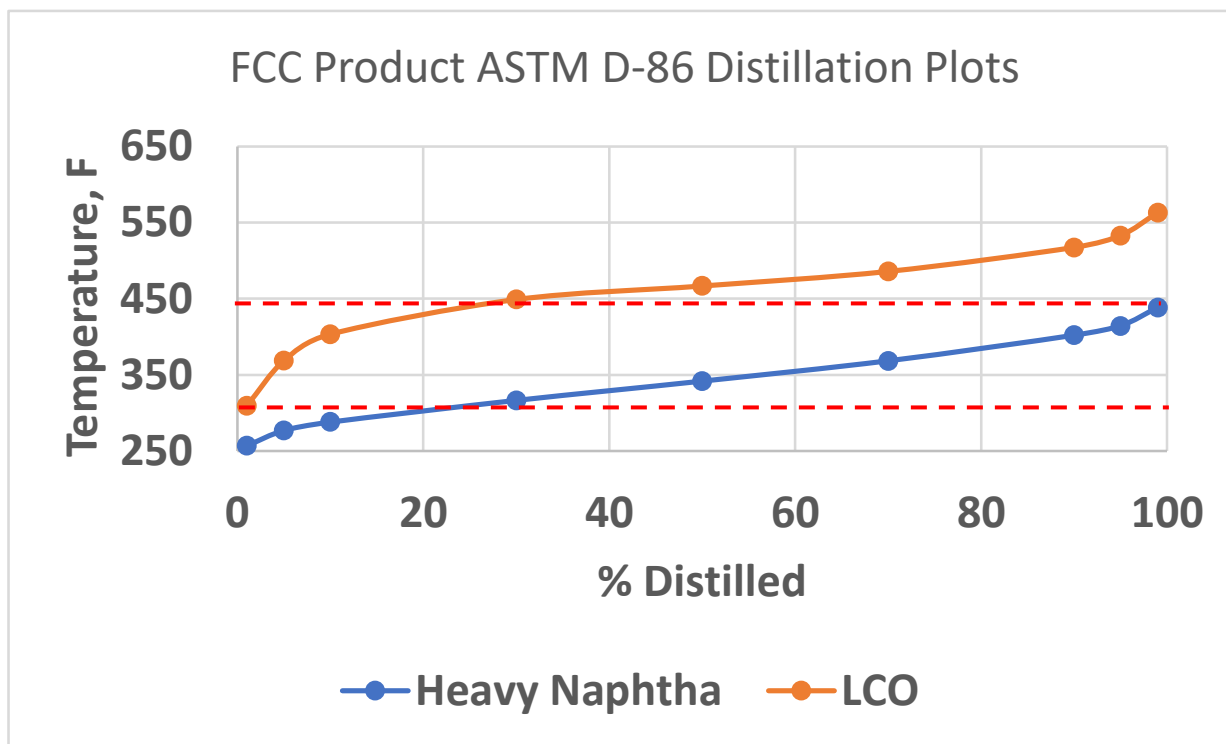
The same process is repeated for condensing heavy naphtha from the FCC reaction products. The final stage consists of condensing as much of the remaining hydrocarbon and steam as practical with air or water-cooled overhead exchangers. Three phase separation of the overhead condenser product yields 'wet gas', light gasoline, and water from steam or wash water used for corrosion control.

Our nominal expectation is that the fatty materials will be condensed alongside of their alkane counterparts since they have a higher boiling point, thus our conundrum. This is the result of looking at transport of material from a macro (bulk) point of view. To discover the potential pathway of middle distillate materials to the LPG stream, we need to adopt a non-traditional micro-transport view.

We start at a point that we are familiar with. The best that we can do in separating any mixture by boiling point is defined by the vapor-liquid equilibrium at any point in the system. The result of this can

be seen in the distillation curves of liquid products leaving the fractionator. Plotting the various distillation data as a function of temperature in Figure 3, we see that there can be considerable overlap between the end of one distillation and the beginning of another (red dashed lines). The greater the overlap, the less efficient the fractionation. Reducing overlap becomes a matter of economics. The towers must become wider and taller, and heat exchange surface area (reboilers, pump around circuits, condensers) must increase. Economic constraints will likely set the amount of acceptable overlap. The distillation curves for the bulk products are the measure for macro transport efficiency of the fractionation system.

Figure 3



So, while the plant may be within the bulk distillation specifications for each product, it is within the accepted overlap where our micro-transport phenomena begin to affect the LPG treating.

In Reference 4, the authors examined the contaminating hydrocarbon materials that were found in amines that had foaming problems. The plots above go to 99 volume % distilled; plotting the last 1 volume % for the heavy naphtha may extend the graph into the same boiling range as the C16 fatty acid. In each of these examples, they found that heavier components in vapors were carried in small equilibrium quantities acting as the source of the contamination. The heavier hydrocarbons locked in the lighter vapor by equilibrium in small quantities (the overlap) accumulated in each of the absorbers or regenerators in the examples until a foaming event occurred. As pointed out in this reference, ppmv concentrations multiplied by MMSCFD gas flows can lead to significant quantities of low-level contaminants.

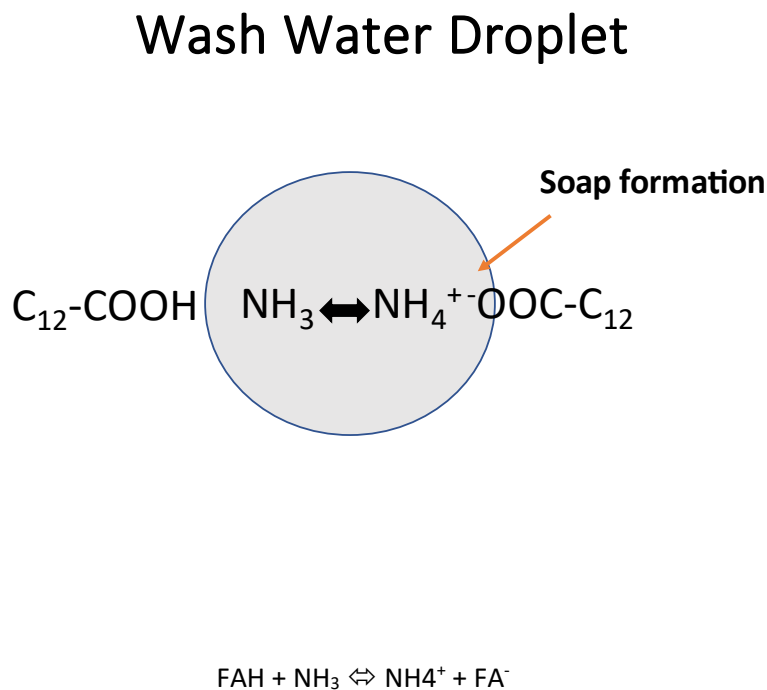
At this point, the 'strawman' intervenes and asks: "Why aren't the heavy components in small quantities causing problems in the LPG treater when running only petroleum-based stocks?" To answer the strawman, we turn our attention to the top end of the FCC main fractionator and the accompanying gas plant.

Micro Transport in Biodiesel Operations

Turning our attention back to Figure 1, the vapor leaving the top of the main fractionator goes through overhead condensers. Wash water is injected into the stream prior to the condensers. The condensed vapor, uncondensed gases, and liquid water go from the condenser to a three-phase separator. If the unit operates solely on petroleum stocks, the solubility of the petroleum-based oils in the condensed water is miniscule-oil and water don't mix.

In the case of the fatty acids there are two things that change this thinking somewhat. First, the polar, acid part of the fatty acid allows some solubility, although small, but greater than that of the petroleum counterpart. For C₁₂ fatty acid, the solubility is 4.81 mg/L and .04 mg/L for the C₁₆ fatty acid. Second, the wash water and condensed steam leaving the condensers contains ammonia byproduct from cracking nitrogen containing molecules. As shown in Figure 4, ammonia will react with the acid end of the molecule to form an ammonium salt of the fatty acid. (FAH=free fatty acid, FA⁻=fatty acid anion)

Figure 4



Neutralized fatty acids are commonly referred to as soap. Because the pKa of these fatty acids is similar to lower molecular weight carboxylic acid as shown in the table below, the solubility will increase at normal pH for these sour water streams of 8.5-9.

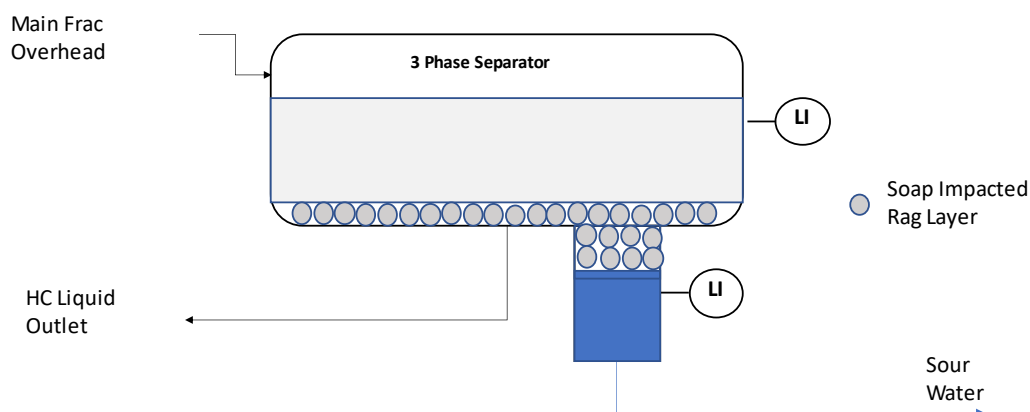
Table 3: Carboxylic acid pKa Comparison

Acid	pKa
Formic	3.75
Acetic	4.74
Propionic	4.90
Lauric (C12)	5.3
Palmitic (C16)	4.75-4.95

The soap action comes from the ability to form micellar structures at the phase boundary between aqueous solutions and oils. The polar COO⁻ group likes the polar water and the non-polar hydrocarbon part of the fatty acid likes the non-polar hydrocarbon. This surface phenomenon allows the incorporation of one phase by the other by the micelles surrounding one phase inside the other phase. As ppmv quantities of these surface-active materials accumulate at oil-water interface in the overhead separator drum, a rag layer of inseparable oil-water mix can form as illustrated in Figure 5. Depending on the geometry of the outlet nozzles on the drum, it is likely that some of this rag material, containing the surface-active agents, will leave with the hydrocarbon liquid.

Figure 5

Soap Affect in 3 Phase Separator



It should be noted the illustration exaggerates the size of a layer. It should be noted that near the outlet nozzle for the HC liquid, the layer may be only a few millimeters thick.

This phenomenon could then occur in the wet gas compression interstage and final compression stage cooling. Wash water used for corrosion control absorbs ammonia and attracts low concentration surface active molecules to the water droplet surfaces. Again, rag layers may form where hydrocarbon liquid and water share an interface causing contamination of the hydrocarbon liquid products with surface-active agents.

Any remaining surface-active materials in the gases contact a circulating naphtha stream, in this case debutanized gasoline, in an absorber-stripper tower. The naphtha likely removes them from the final gas product as the fuel gas treaters associated with the biodiesel/FCC operation don't appear to have foaming issues. However, if the naphtha stream traps these components, they simply get recycled back to the problem areas via recycle.

In the gas plant, all the condensed liquid from the main fractionator overhead drum and compressor stage knock-out drums goes through a series of fractionators to make the final products, usually an off gas for use as refinery fuel, propane-propylene and butane butylene (or a mix of the two) which can be used as alkylation or polymerization process feeds, and stabilized gasoline. Nominally the olefinic LPG and stabilized gasoline come from the debutanizer in the gas plant.

If any rag layer gets into this series of gas plant towers, we again have the problem of equilibrium, liquid water, ammonia, and intimate contact which may trap these surface-active agents in the condensing/separation part of the debutanizer. If this is the case, the recipient of the rag layer with contaminants is the LPG stream going to the amine treater.

Figure 6 illustrates operations effects on the LPG treater for petroleum-based operation only. Figure 7 illustrates the same contactor operating with approximately the same LPG rates with biodiesel being fed to the FCC.

Figure 6

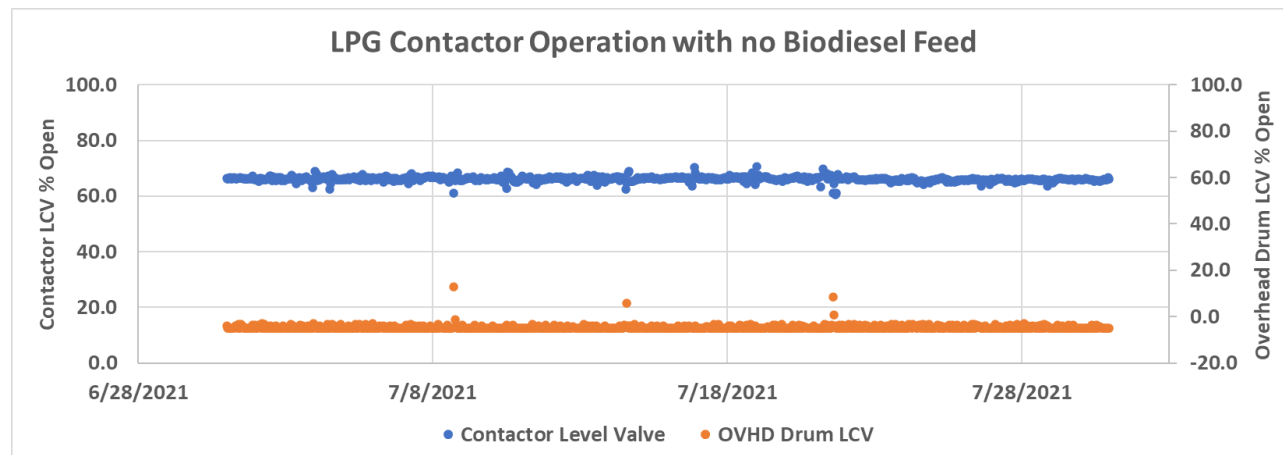
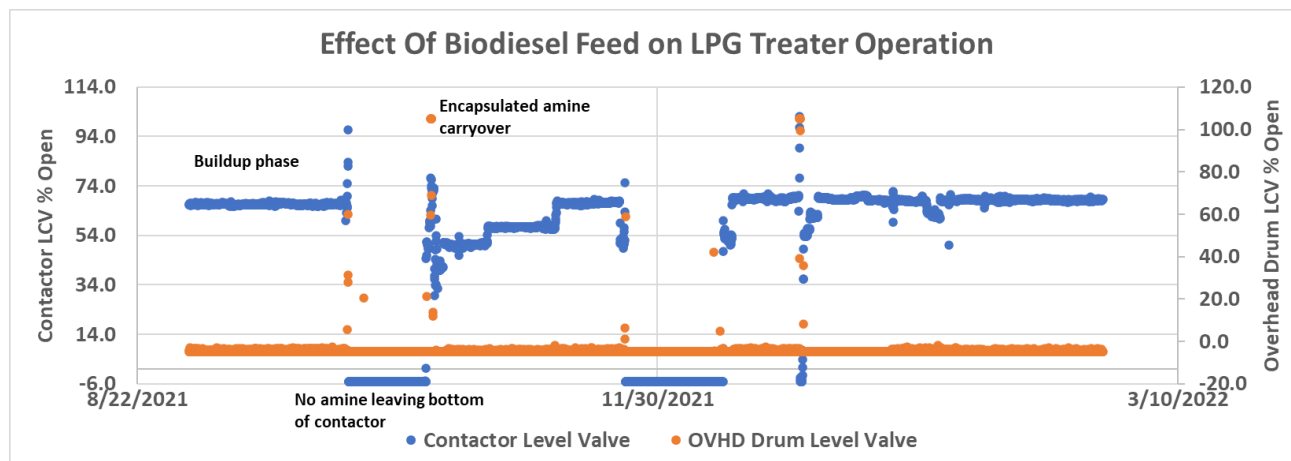


Figure 7



Back comes the strawman. "Oh!", he says, "We do have some amine carryover in our LPG treaters when running with petroleum-based stocks. Is this consistent with what is proposed for biodiesel operation?"

LPG amine treater carryover has pre-dated biodiesel feed to the FCC. In fact, many LPG treaters have been retrofitted with water wash drums on the treater overhead systems to recoup the amine being lost this way. What is normally seen is that the carryover is tied to petroleum-based hydrocarbons in two ways. The first is poor separation of gasoline boiling range components from the LPG feed to the treater. The second is the contamination of the amine with very heavy (gas oil boiling range) components that are not removed by carbon filtration. These much heavier oils then go to the LPG treater where they become trapped at the amine solution LPG interface and cause rag layer formation in the treater.

Biodiesel induced carryover is most likely only a micro-transport problem, one of moving small quantities of contaminant over time via the LPG until the accumulation causes an acute event in the treater. Petroleum based carryover can result from a micro-transport of contaminants by the amine solution, or the macro-transport of contaminants by the LPG due to poor upstream operations.

Conclusions

The first conclusion is that this proposed explanation needs a lot of sampling and analytical work for validation. There are pieces of the puzzle which have been incorporated in the analysis above, but the puzzle is nowhere near complete.

The second conclusion is that increased biodiesel production is going to come with unforeseen consequences. Surface activity is not something that can be readily modeled, so it is hard to account for these circumstances beforehand.

References:

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4. Keller, A. and Hatcher, N. “*Busting a Myth- Analyzing the Effectiveness of Lean Amine / Sour Gas Differential Temperature Control*”, Laurance Reid Gas Conditioning Conference, Norman, OK, 2006