

The Formation and Disposition of Cyanide Ion Degradation Products in Refinery DEA Solutions

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ABSTRACT

Hydrogen cyanide is a low-level byproduct of the coking and fluid catalytic cracking of nitrogen containing heavy oil molecules. This byproduct is processed in the wet gas compression and separation stages of a typical gas plant following the cracking operation. HCN is well known to be a corrosion accelerator in parts of the gas processing equipment requiring use of water washes in main fractionator condensation and wet gas compression stage aftercoolers to prevent localized cyanide buildup.

While HCN is somewhat soluble in water, the limited amount of fresh water fed to a water wash system, as described by Hatcher and Weiland¹, is usually insufficient to remove a significant amount of HCN from the gas stream that eventually goes to an amine system for H₂S and CO₂ removal. Alkanolamines such as Di Ethanol Amine (DEA) will remove the HCN from the gas stream as well as the H₂S and CO₂ as the HCN is an acid gas. Removal of the proton from HCN in solution forms cyanide ion (CN⁻).

Solution data taken over a period of 16 months from 5 different DEA systems were examined for the content of various DEA degradation products. These are DEAH⁺ HCOO⁻, DEA formamide, and THEED. The paper will discuss the relationship between cyanide ion and the formation of these degradation products and will discuss the equilibrium boundaries on the accumulation of these degradation species.

THE FORMATION AND DISPOSITION OF CYANIDE ION DEGRADATION PRODUCTS IN REFINERY DEA SOLUTIONS

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Introduction

The Origin of Sulfur and Nitrogen in Crude Oil and Distillates

One time living tissue, containing nitrogen and sulfur in the proteins assembled from amino acids and sulfur, was buried and pressure cooked for millions of years to become petroleum-literally rock-oil. Part of the living matter may have been affected by microbes or chemical processes before or during the burial and cooking process. This left the petroleum with varying amounts of sulfur and nitrogen compounds in the matrix of mainly hydrocarbons that constitute petroleum.

As the size of the hydrocarbon molecules in petroleum get larger, the propensity to have sulfur and nitrogen compounds increases. Transportation fuel boiling range hydrocarbons, gasoline, kerosene, and diesel generally do not have heavy coke forming compounds and are typically sent to hydrodesulfurization (HDS) units straight from atmospheric pressure distillation. These streams have sulfur removed by conversion to hydrogen sulfide over cobalt-nickel-molybdenum catalysts by using high temperatures and high hydrogen partial pressures. Similarly, nitrogen compounds are converted to ammonia by the same means. The bottoms product from the initial atmospheric pressure distillation contains coke forming precursors and must be distilled further to prepare the oil for conversion to transportation fuels.

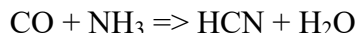
In order to utilize the atmospheric distillation bottoms for transportation fuels, the hydrocarbon molecules must be reduced in size so that they fit the desired distillation specifications for each fuel. The two most common molecular size reduction techniques handle the atmospheric and vacuum gas oils (boiling range 750 °F to 1050 °F) and the vacuum distillation residual oil (boils at >1050 °F).

Sources of HCN in the Refinery

Gas oil fractions may also undergo desulfurization and denitrification directly. Whether they do or not, the next processing step for gas oils is usually a Fluid Catalytic Cracking Unit (FCCU). The FCCU uses heat and modified zeolite catalyst to reduce the hydrocarbon chain size and boiling range of the gas oil molecules. Vacuum residual oil conversion to transportation fuels usually takes place in a coking unit. Delayed cokers and fluid cokers basically use high temperatures to disproportionate the carbon in the vacuum residual oil feed. The resulting higher hydrogen to carbon ratio, smaller molecules are distilled from the coker effluent while the very low hydrogen to carbon portion is collected as “coke” solids.

While the major products of these processes are gasoline to diesel range distillates, smaller amounts of lower molecular weight alkanes and alkenes are produced as byproducts in both processes. In the FCC, H₂S and NH₃ are produced as byproducts from cracking reactions of sulfur and nitrogen containing molecules. CO and CO₂ are produced from air combustion of coke on the

spent catalyst. When FCC catalyst containing adsorbed CO contacts feed oil, cracking takes place forming NH₃. At the elevated temperature ~1000 °F in the FCC reactor pipe and separator, some of the CO and NH₃ react to form HCN.



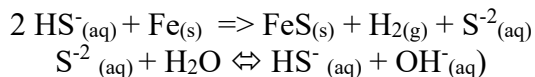
Low MW alkanes, alkenes, CO, CO₂, NH₃, H₂S, mercaptans along with N₂ and O₂ adsorbed on the FCC catalyst at regeneration leave the reaction with the HCN formed above. The amount of HCN made is very small, usually less than about 10 lb. mole/day. However, the small amount of HCN can cause significant issues in downstream equipment.

Normal processing of the light ends produced in the FCCU are directed to a “wet gas” compressor, then to a series of distillation towers which separate uncondensed gases, propane-propylene, butane-butylene, and stabilized gasoline. HCN volatility forces it into the uncondensed gas product.

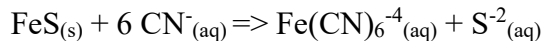
In coking, the HCN is generally believed to result from cracking nitrogen containing molecules into smaller aliphatic and olefinic chains, distillate boiling range fractions, and polycyclic aromatics. Again, a wet gas compressor-fractionation gas plant is used to separate lighter products into gas, propane-propylene, butane-butylene, and stabilized gasoline. HCN goes out with the gas product.

Downstream Effects of HCN-Hydrogen Blistering and Cracking

As part of the gas plant operation, water washes must be used strategically to prevent HCN in the streams being processed from accumulating in stagnant water in the presence of H₂S. Liquid water contacting gases containing ammonia will readily absorb the ammonia providing a basic solution, Acid gases, H₂S, CO₂ and HCN will dissolve into the liquid water aided by conversion to ammonia salts, NH₄HS, NH₄HCO₃, and NH₄CN. HS⁻ will oxidize carbon steel according to the reaction:



Nominally the FeS deposited on the surface of the steel will slow the oxidation reaction down as deposit thickens. However, cyanide ion in water will compete with the sulfide in FeS to form the very stable Fe(CN)₆⁻⁴ and displace the sulfide via the second equation above.



Unfortunately, the removal of the FeS protection, combined with surface and wall defects in carbon steel can allow the accumulation of atomic hydrogen formed in the iron oxidation reaction in cracks and crevices leading to cracking and hydrogen blistering.

Disposition of the HCN

Water washes in the gas and LPG recovery systems of FCCs and cokers, as shown in Reference 1, are ineffective due to the typical design used for these washes. A typical water wash system will consist of a water circulation pump taking water from separator drums in the gas plant, and

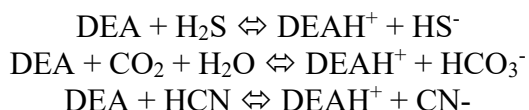
several injection points for the pumped water to enter the heat exchangers in main fractionator overhead systems and in the compressor aftercoolers in the compression section. A portion of the water pumped through the system is purged to control the production of sour water from the unit, and makeup water is added to replace the volume of water purged. Simulation of these systems using ProTreat[®] showed that the makeup water rates to these systems is low enough that the water becomes HCN saturated. Thus, almost all the HCN entering these water wash zones will move on with the gases to the final gas product.

As the final gas product from the FCC and coker gas plants is normally directed to use as refinery fuel gas, it must be amine treated to reduce the H₂S content of the fuel gas to the customary level required by the prevailing air quality enforcement jurisdiction. The commonly applied gas treating alkanolamines, MEA, DEA, DIPA, DGA, or MDEA, react with the H₂S. CO₂ is removed almost completely by the first four amines, and only partially removed by MDEA. The small concentration of HCN in these gases likely assures almost complete HCN removal by the amine as there is generally a large reserve of unreacted amine in solution even after H₂S and CO₂ removal.

The Fate of HCN in Refinery DEA Systems

DEA-Acid Gas Reactions

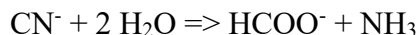
DEA reacts with the acid gases to form DEA salts.



The operation of an alkanolamine system requires the first two equations are reversible so that the acid gases can be expelled for further processing. However, the operation is not necessarily geared toward nor explicitly dependent on the third equation. H₂S and CO₂ should be relatively “inert” as they are transported from absorber to regenerator. But this is not totally the case for systems dealing with the ingress of HCN or HCN and oxygen.

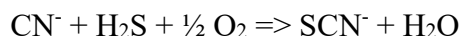
CN⁻ Reactions Forming HSS Anions

Cyanide ion reacts with water to form formate ion and ammonia



Ammonia is stripped from the amine solution in the amine regenerator ending up dissolving in the regenerator reflux. Without a purge of water from the reflux, ammonia can buildup in the reflux attracting H₂S from the acid gas expelled from the rich amine. High concentration of ammonia, and subsequently H₂S in the reflux leads to high corrosion rates for carbon steel.

Cyanide Ion Reacts With Oxygen and H₂S to Form Thiocyanate Ion



The division between water reaction and oxygen reaction dictates the ratio of formate to thiocyanate as both anions accumulate in solution. Since DEAH^+ (as well as any other protonated alkanolamine) is associated with CN^- , DEAH^+ serves as the counter cation to these heat stable salt anions. The $\text{DEAH}^+\text{HCOO}^-$ and $\text{DEAH}^+\text{SCN}^-$ cannot be converted to HCOOH and HSCN and DEA in the regenerator, hence the designation as heat stable salts.

Reference 2 gives a summary of the effects of HSS anion accumulation on acceleration of corrosion rate of carbon steel by HSS anions. Reference 2 also covers the benefit of allowing HSS anions to build to a certain level before participating in accelerating corrosion rates. Many refineries choose between several methods to control the accumulation of the HSS anions.

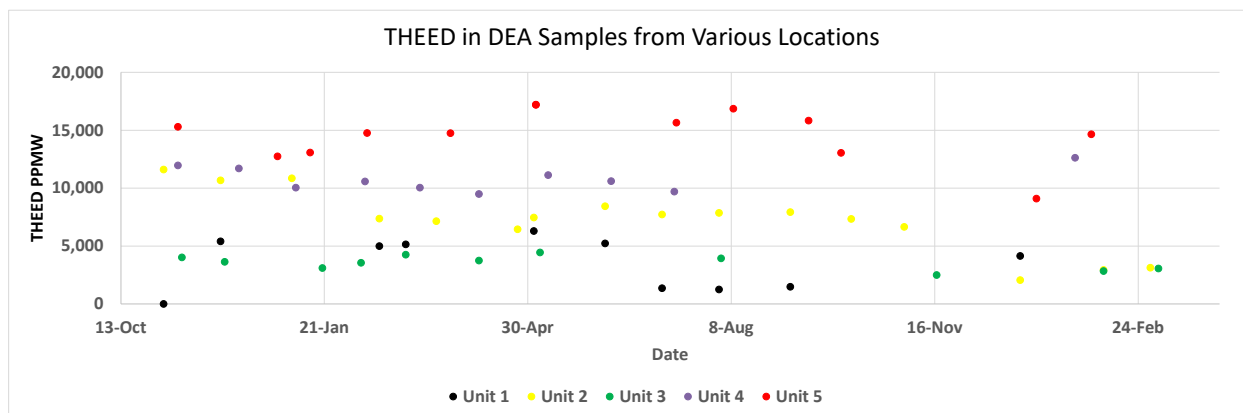
A Client's Concern

A client operating a DEA system was well aware of the problems with HCN incursion into the amine solution, The client tracked the accumulation of HCOO^- and SCN^- anions and routinely took action to remove the accumulation to acceptable levels. In scheduling the anion removal, the presence of another DEA system contaminant, Tris HydroxyEthyl Ethylene Diamine or THEED was also shown in the analysis. Reference 3 gives a quick summary of the occurrence of THEED in DEA and the recommended method of removing it from the amine solution, vacuum distillation. The client's concern was the timing of doing an HSS anion removal and doing the vacuum distillation for THEED removal. While the vacuum distillation method can be used to remove HSS anions, it is not as economical as removing them via ion exchange or electrodialysis. Even though these anion removal techniques are superior economically to vacuum distillation, they are incapable of reducing THEED.

In the author's experience, THEED had been measured by amine supplier laboratories, but the values did not appear to give as routine trends as did the major HSS anion species, HCOO^- and SCN^- . The author's previous employer had, at the author's request, managed to get hold of standards for THEED and another DEA degradation product, DEA formamide, to determine if there was a discernable trend in their accumulation. Monthly lean amine samples from 5 DEA systems were evaluated over a period of 16 months for the normal HSS anions, DEA formamide, and THEED.

Figure 1 is a graph of the amount of THEED accumulated in these systems over the 16 month period.

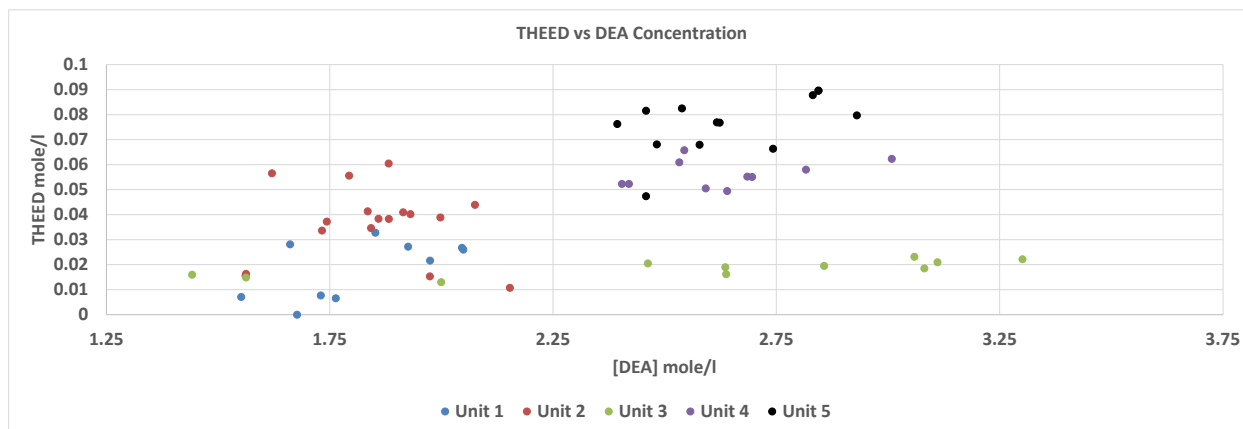
Figure 1



Two units, 4 and 5 had permanent HSS anion removal facilities. Two Units, 1 and 2 practiced “bleed and feed” HSS anion control. Unit 3 had periodic visits by an HSS anion removal contractor. Two units, 1 and 3, did not treat FCC gases, and the other three units treated FCC gases. Unlike HSS anion accumulation, Figure 1 shows THEED accumulation did not monotonically increase.

In Figure 2, THEED was found in 4 systems to be related linearly to DEA content of the solution. The other system showed little relationship to amine concentration.

Figure 2



Recommendation to the Client

Three observations of the data in Figures 1 and 2 aided in making a recommendation to not do the vacuum distillation THEED removal.

- Even where HSS anions were continuously removed, THEED levels remained relatively stable
- THEED levels after a bleed and feed rapidly returned to stable level
- Monotonic climbs in HSS anion content did not coincide with monotonic increases in THEED

At this point the subject might have gone back to dormancy had there not been a couple of questions in the author's mind about THEED and the other major diluent contaminant in DEA, DEA formamide.

THEED Formation Chemistry

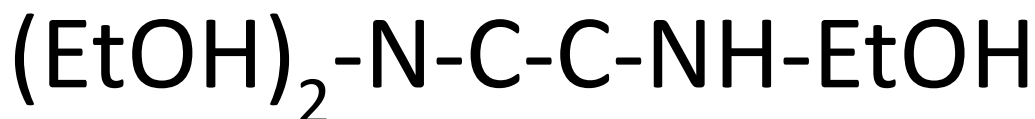
A couple of questions came to mind. One, how was THEED supposed to be formed? The other, Were the origins of these two degradation products totally separate, or could they be related to contamination by HCN?

Well, obviously, DEA formamide will hydrolyze in basic conditions to DEAH^+ and HCOO^- . This can either be done by caustic addition or by removing HCOO^- ions by ion exchange and returning the solution to the system where the formamide, HCOO^- and DEAH^+ equilibrium is readjusted. Since HCN is the source of HCOO^- , the origin of the formamide comes via HCN contamination.

THEED on the other hand does not give an obvious answer. The pattern of THEED accumulation did appear to make clear that THEED formation was likely limited by equilibrium. What components need to be measured to check for an equilibrium relationship? First, we need to see the structure of THEED in Figure 3 to get an idea how it could be formed.

Figure 3

THEED

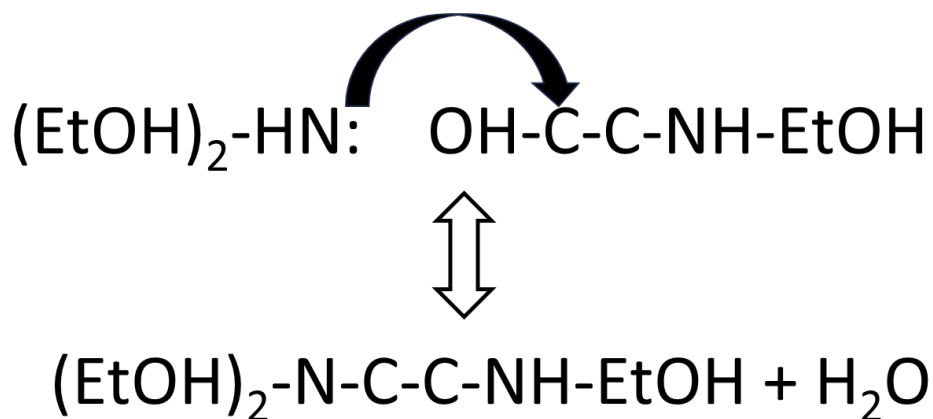


EtOH=Hydroxy Ethyl group

It would appear THEED is the merger of two DEA molecules. A simple way to describe this is shown in Figure 4

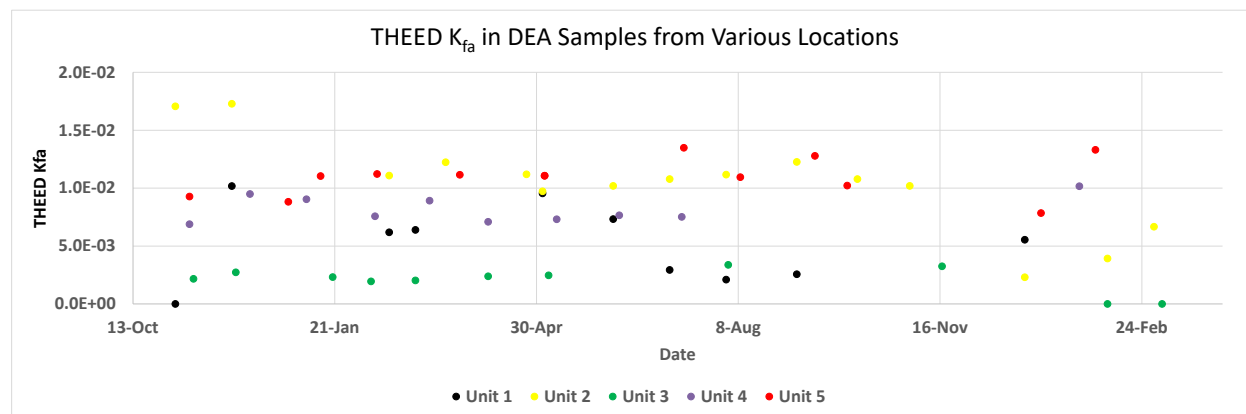
Figure 4

THEED Formation from DEA with DEA as the Nucleophile



The equilibrium relationship would be $K_f = [\text{THEED}][\text{H}_2\text{O}]/[\text{DEA}]^2$. However, since $[\text{H}_2\text{O}] \gg [\text{DEA}] \gg [\text{THEED}]$, the $[\text{H}_2\text{O}]$ will be incorporated in the K_f and a K_f apparent (K_{fa}) will be used. Figure 5 gives a graph of K_{fa} computed for each of the 5 systems.

Figure 5



While not exactly a constant, the values for 4 out of the 5 systems hover at about the same value of 0.01. The outlier system in Figure 2, Unit 3, further demonstrates its outlier status. The variation could be, as Reference 4 points out, amine samples with H_2S are vulnerable to air exposure, and samples that sit for long periods of time may not accurately represent the amine status in the unit at the time of sampling.

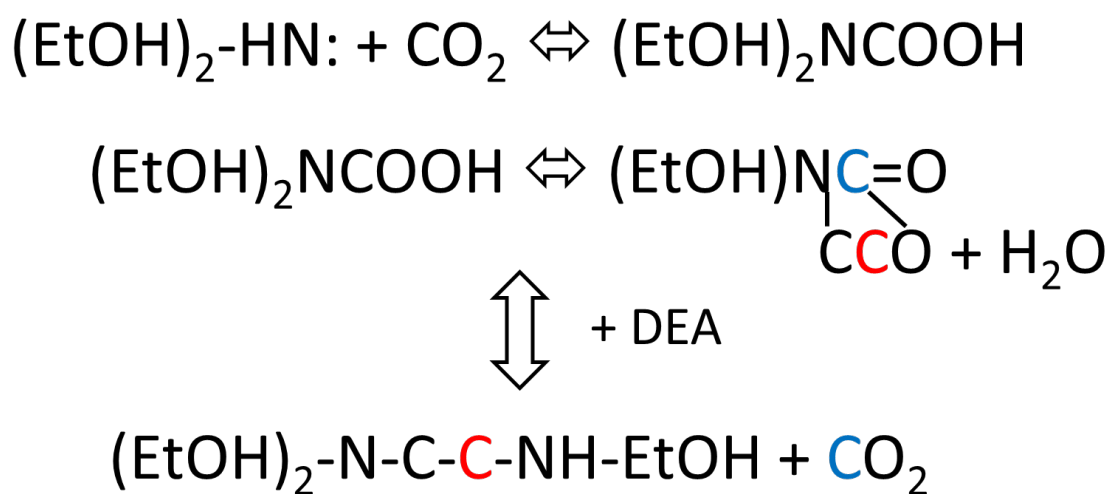
If we ignore the obvious errors that could be introduced by poor sampling technique, aging, and laboratory handling procedures, we can see that the data is saying THEED formation is likely governed by this equilibrium expression. If this were not the case, all the DEA would react to form THEED making the solution useless! Part of this can be seen from the simple substitution reaction from Figure 4. DEA is a bulky nucleophile and the OH group on the ethanol arm of DEA

is expected to be stable so that the amine can be recirculated. The reaction seems rather unlikely to go to much extent.

Reference 5 provides an alternate formation route for making THEED from DEA. This route used the fact that DEA, a secondary amine, will form a carbamic acid by reacting with CO₂. The resultant carbamic loses water in the formation of an oxazolidone ring. It is stated that the oxazolidone ring will then react with another DEA to form THEED while rejecting the CO₂ from the carbamic acid formation. This is shown in Figure 6.

Figure 6

THEED Formation via Carbamate-Oxazolidone-DEA



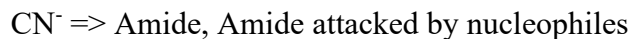
This is the most frequently used explanation for THEED formation, but there are some concerns. First the bulky DEA nucleophile must attack the aliphatic C attached to O in the oxazolidone ring to end up with the correct THEED structure. However, the carbonyl carbon is usually a better site for substitution as there is more electron withdrawing capability by the double bonded O. Second, the carbamic acid is itself unstable. What are the competing rates of carbamic acid decomposition and oxazolidone formation? Lastly, what if no CO₂ is in the gases being treated?

CN⁻ and THEED

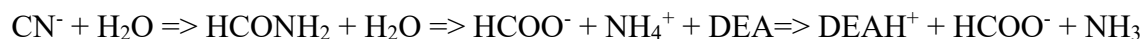
In the examination of these 5 systems, it will be hypothesized that cyanide ion is a participant in THEED formation. Data from the systems will be reviewed to determine if the hypothesis can be confirmed.

The method for the interaction will be built upon looking at analogous reaction with CN⁻ in the DEA solution. The pattern for the analog is posed as follows:

General Reaction:



Formate ion HSS formation:



DEA formamide formation:



Possible THEED formation:



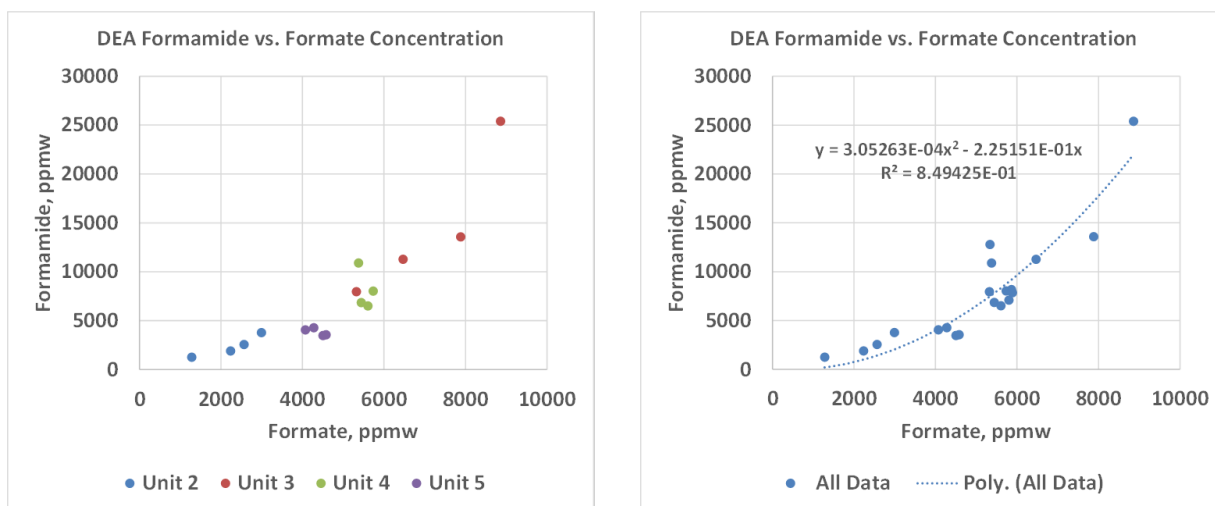
Certain advantages may apply to this analog over the carbamate-oxazolidone-DEA route for THEED formation.

CN^- ion is stabilized as it enters the amine solution as a non-volatile DEA salt. It will stick around until it is reacted into some byproduct.

Different amides can form as data shows the buildup of HCOO^- and DEA formamide are simultaneous. (See Figure 7)

Figure 7

DEA Formamide Accumulation vs Formate Ion Accumulation



The relationship in the graph led to testing the formamide decomposition equation to see if it was governed by equilibrium.



$$K_{app} = [\text{DEAF}] / [\text{HCOO}^-][\text{DEAH}^+], [\text{H}_2\text{O}] \text{ constant}$$

Averaged Over 4 sites, $K_{app} = 3.54 \pm 0.49$

The computed K_{app} from the site data was used to estimate $[\text{DEAF}]$ from $[\text{HCOO}^-]$ and $[\text{DEAH}^+]$ data where DEAF was not directly measured.

The hypothetical involvement of CN^- ion THEED formation then consisted of reviewing the buildup of the CN^- related contaminants in each system followed by testing the data sets according to a consistent set of hypothetical rules governing accumulation.

Tracking Rules

$$[\text{HCOO}^-]_{\text{tot}} = [\text{HCOO}^-]_{\text{direct hydrolysis}} + [\text{HCOO}^-]_{\text{THEED}}$$

Assign $[\text{HCOO}^-]$ to THEED formation, then direct hydrolysis

Assign THEED to cyanide analogue first, then to alternate mechanisms

$$\% \text{HCN}_{\text{dh}} = 100 * ([\text{HCOO}^-]_{\text{dh}} / ([\text{HCOO}^-]_{\text{dh}} + [\text{HCOO}^-]_{\text{THEED}} + [\text{DEAF}]))$$

$$\% \text{HCN}_{\text{THEED}} = 100 * ([\text{HCOO}^-]_{\text{THEED}} / ([\text{HCOO}^-]_{\text{dh}} + [\text{HCOO}^-]_{\text{THEED}} + [\text{DEAF}]))$$

$$\% \text{HCN}_{\text{DEAF}} = 100 * ([\text{DEAF}] / ([\text{HCOO}^-]_{\text{dh}} + [\text{HCOO}^-]_{\text{THEED}} + [\text{DEAF}]))$$

Method

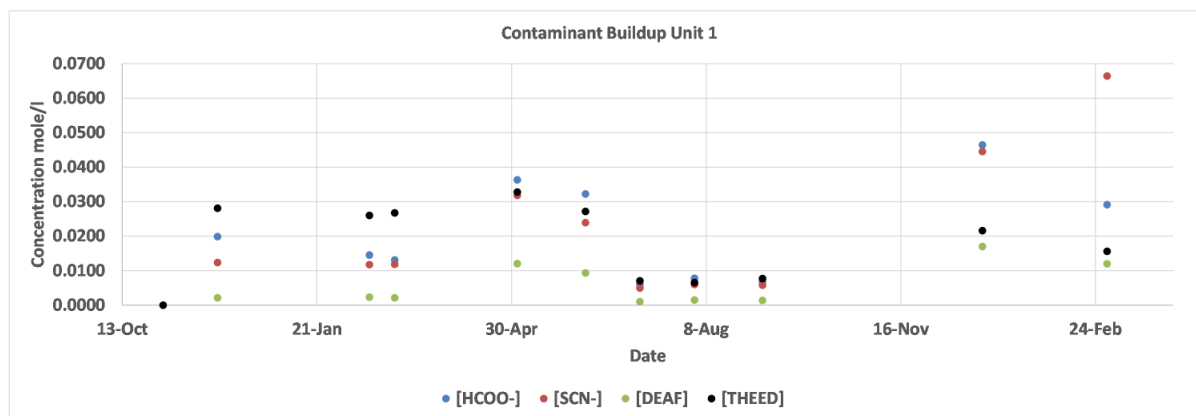
The data will be examined by looking at graphs for contaminant buildup over time, the analog product accumulation over time using the tracking rules, and tracking all the analogs versus formate ion and DEA formamide accumulation.

Figures 8, 9, and 10 represent a system that treats very low CO_2 containing gases. A small ingress of O_2 is noted by the accumulation of SCN^- . Figures 11, 12, and 13 represent a system that treats both FCC and coker gases. Figures 14, 15, and 16 represent a system that treats coker and hydrotreater gases but no FCC gases. Figures 17, 18, 19, and figures 20, 21, and 22 represent systems that treat FCC and coker gases.

It should be noted for the review of the data that HCOO^- attributed to the direct hydrolysis of CN^- and HCOO^- attributed to the THEED analog are chosen by rule and not measured by any type of measurable marker. Formate ion can form in DEA solutions from ingress of oxygen in the sampling of the DEA solution. All samples are considered to have been exposed to air and do not represent exactly the composition of amine taken from each system. Finally, there was no attempt to measure DEA carbamate in any of the solutions.

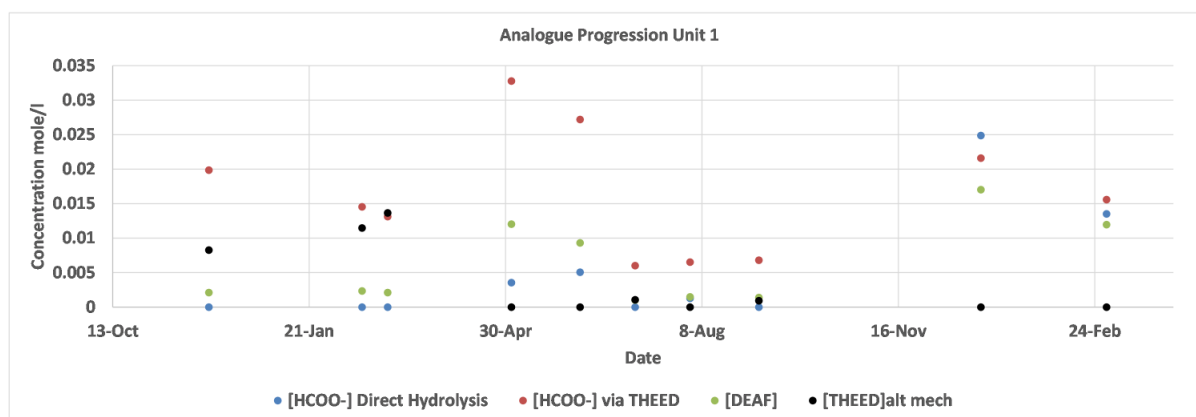
Figure 8

System characteristics: Low CO_2 , normally low ingress of O_2 , Bleed/Feed
HSS anion removal



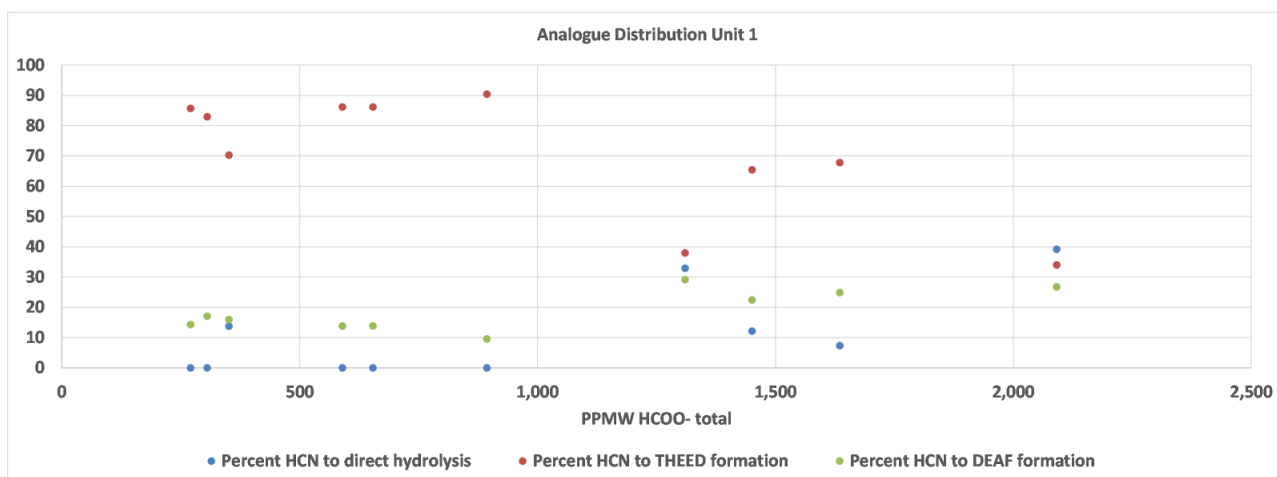
Observation: THEED builds after bleed/feed then plateaus. Higher O_2 ingress at last two points (SCN^- buildup)

Figure 9



Observation: Both THEED mechanisms active at low HCOO^- levels.
Alternate mechanism THEED disappears at next bleed/feed.

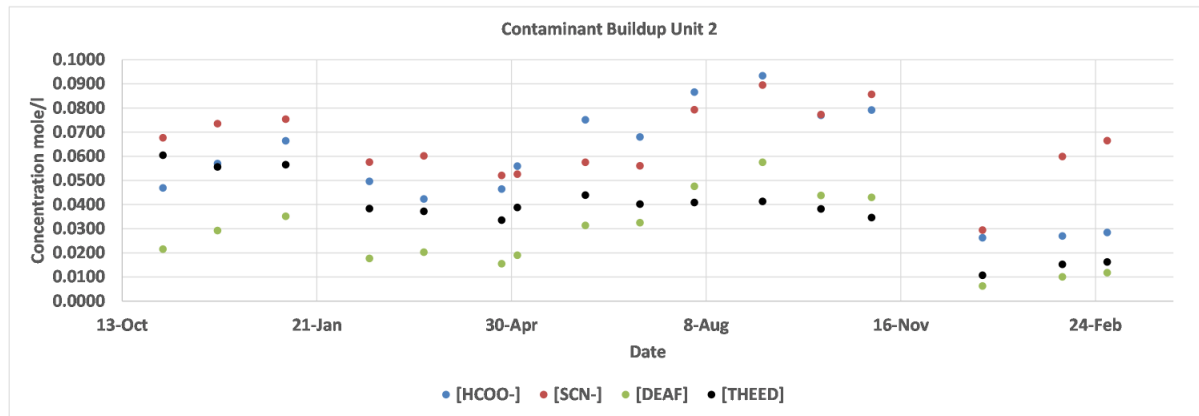
Figure 10



Observation: THEED percentage by cyanide analog seems active at low HCOO⁻ content, but percentage drops as THEED plateaus.

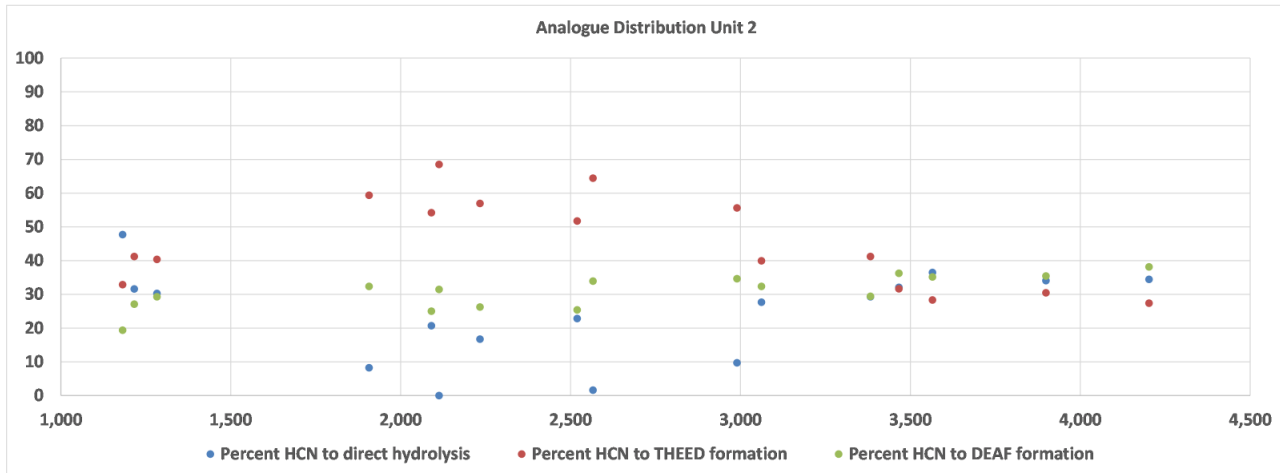
Figure 11

System characteristics: Treats FCC gas with CO₂ and O₂, Bleed/Feed HSS anion removal



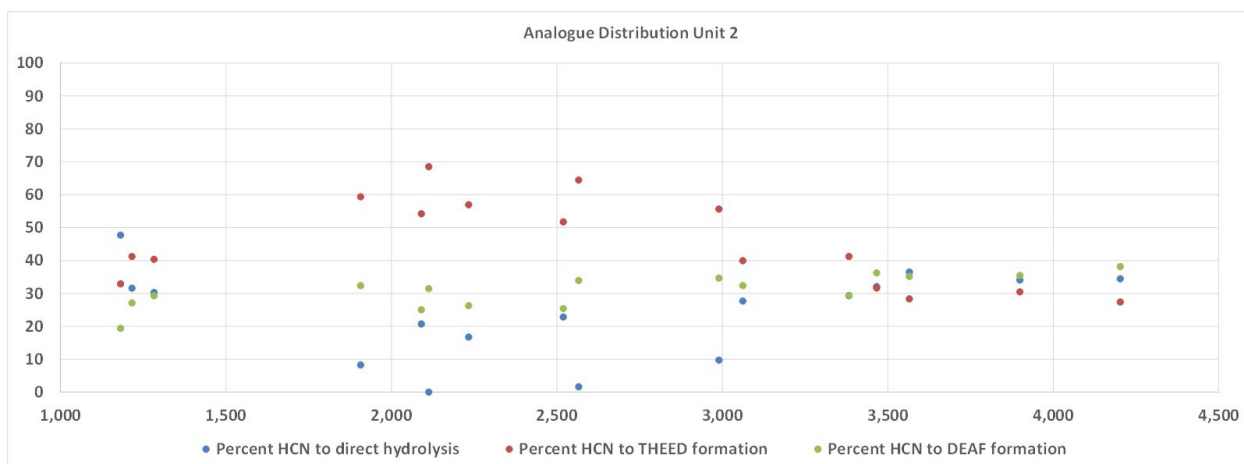
Observation: THEED relatively steady but builds after large bleed/feed.

Figure 12



Observation: THEED percentage by cyanide analog seems active at low HCOO⁻ content, but percentage drops as THEED plateaus.

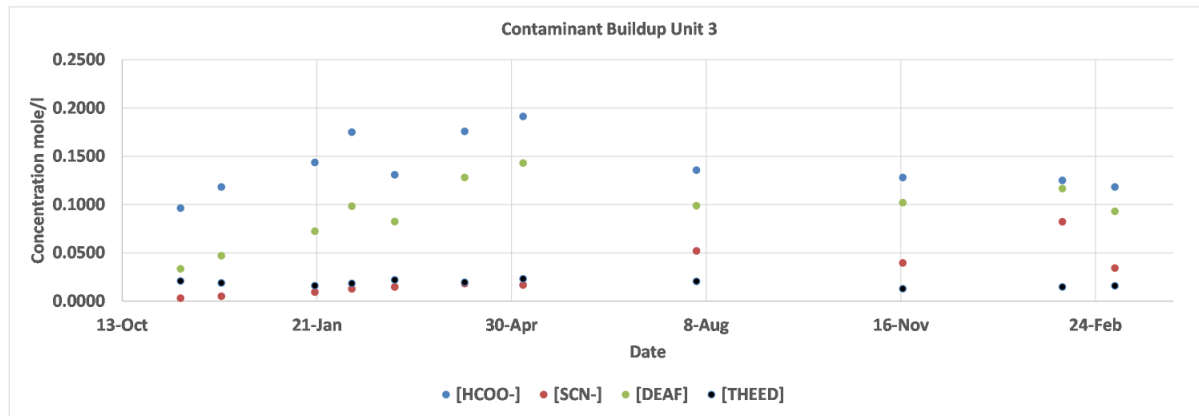
Figure 13



Observation: THEED percentage by cyanide analog seems active at low HCOO^- content, but percentage drops as THEED plateaus.

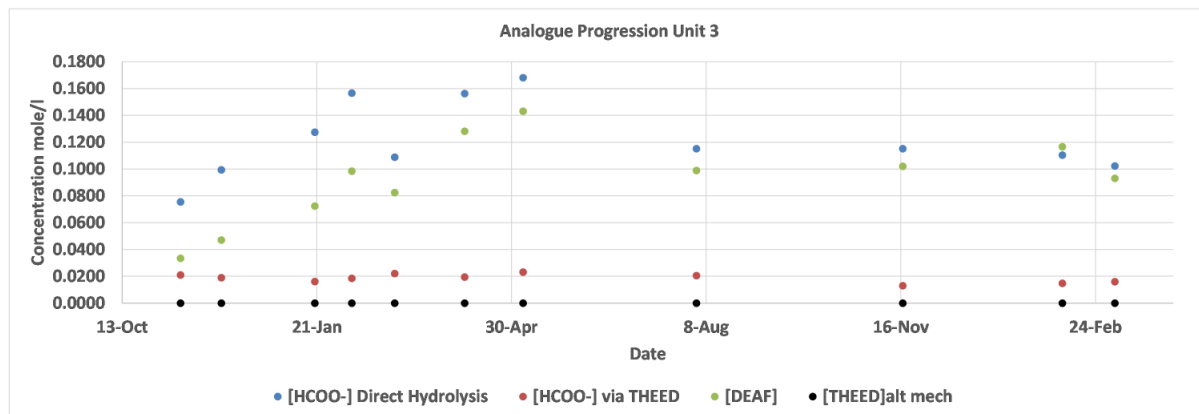
Figure 14

System characteristics: Low CO₂, Low O₂, Occasional HSS anion removal



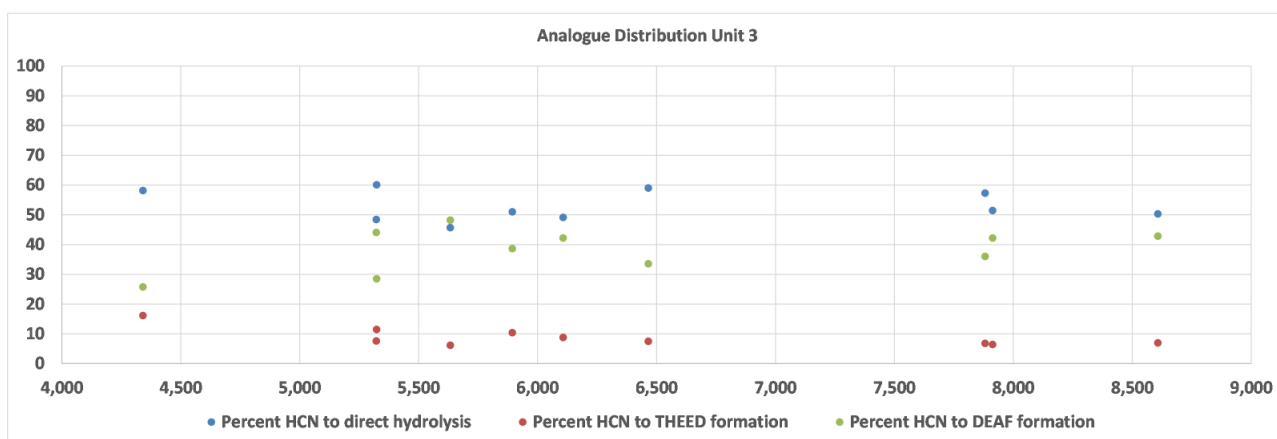
Observation: THEED builds slowly as HCOO⁻ and DEAF accumulate monotonically after cleaning.

Figure 15



Observation: THEED byproduct HCOO⁻ steady. DEAF and HCOO⁻ by direct hydrolysis rise monotonically from cleaned levels.

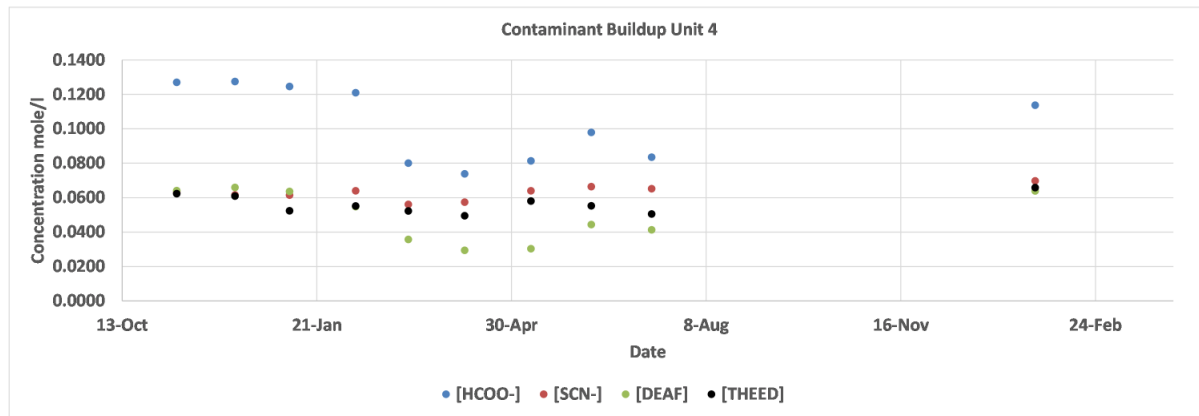
Figure 16



Observation: THEED by cyanide analog seems arrested at higher average HCOO⁻ levels.

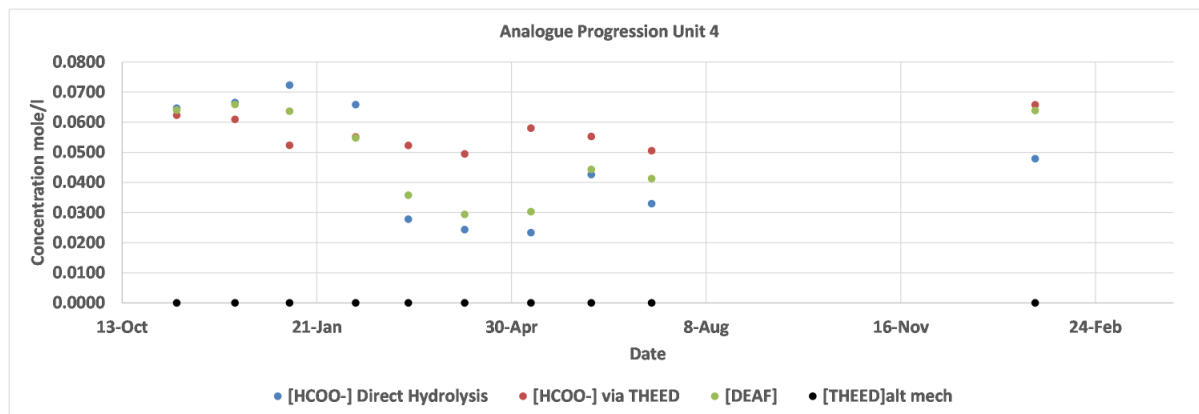
Figure 17

System characteristics: Treats FCC gas with CO₂ and O₂, Permanent HSS anion removal unit



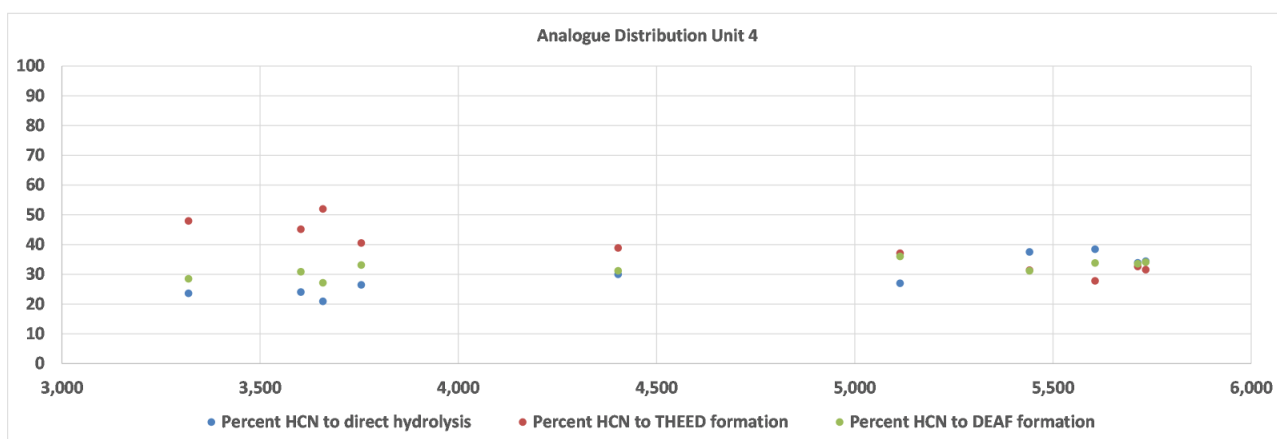
Observation: THEED levels steady. DEAF goes down as HCOO⁻ and DEAH⁺ are reduced via anion removal.

Figure 18



Observation: Baseline THEED HCOO⁻ steady while variable hydrolysis HCOO⁻ and DEAF vary with HSS anion removal.

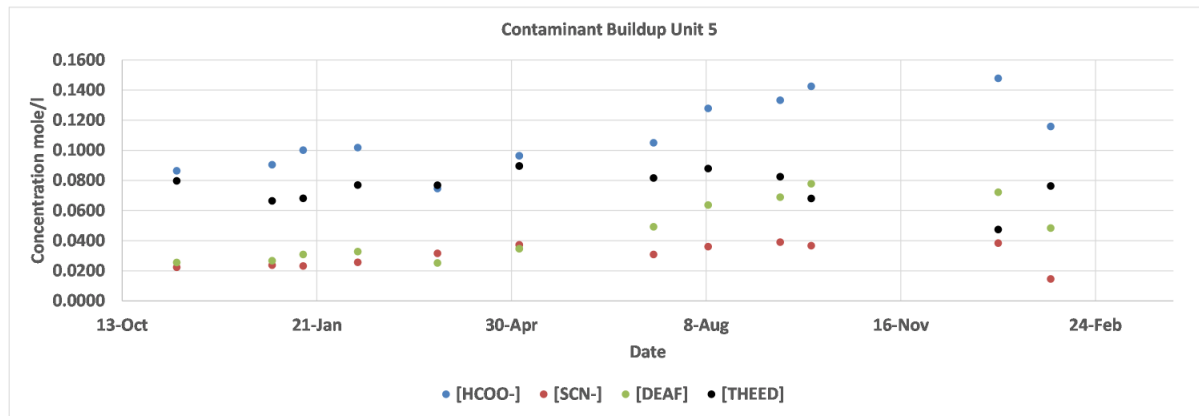
Figure 19



Observation: THEED by cyanide is greater percentage at low HCOO^- concentrations.

Figure 20

System characteristics: Treats FCC gas with CO₂ and O₂, Permanent HSS anion removal unit



Observation: Unit observations are close to the previous unit due to permanent anion removal system.

Figure 21

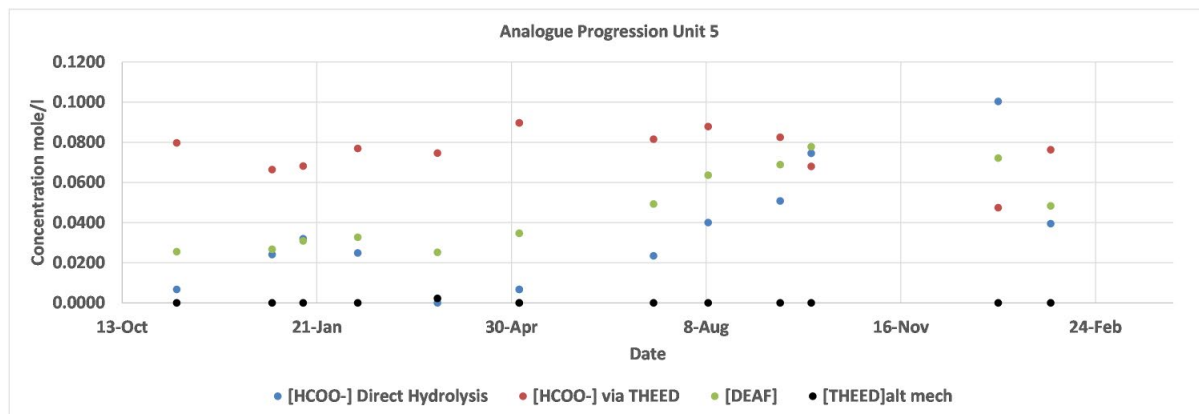
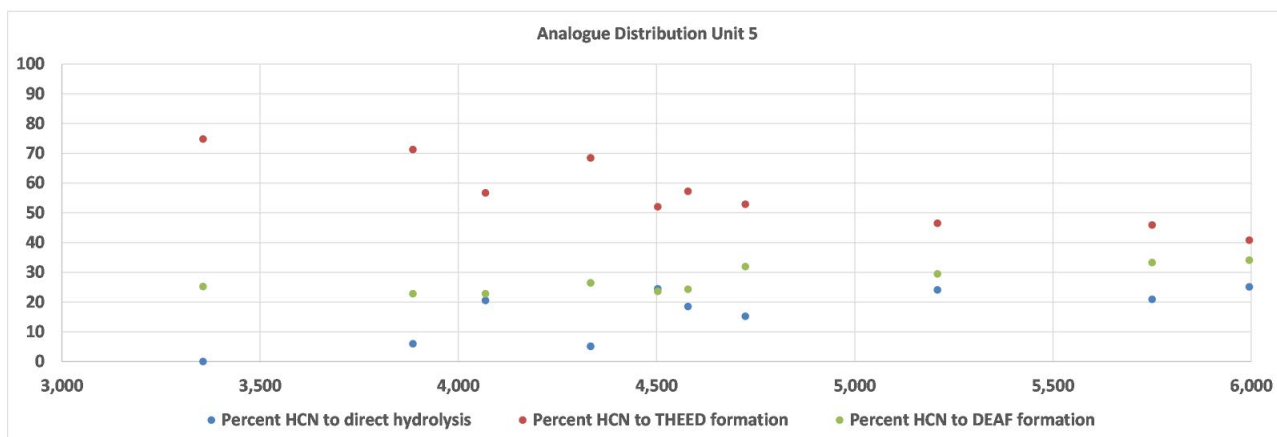


Figure 22

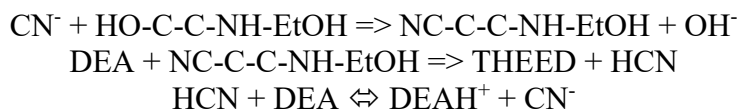


Discussion and Conclusions

THEED Formation by Cyanide Analog

In systems that have very little CO₂ available to make the DEA carbamate, THEED appears, and its formation seems to be weakly related to the buildup of other cyanide ion related species. The main advantages for cyanide ion displacement of hydroxyl on one ethanol group of DEA over straight replacement by DEA would be the small size and negative charge of the cyanide ion versus the bulky, neutral DEA molecule itself.

The mechanism of cyanide substitution, amide formation, and substitution as proposed has the same disadvantage that the carbamate-oxazolidone in that a nucleophile like DEA should go after the carbonyl carbon in the amide preferably over the aliphatic carbon in the ethyl group of the DEA where cyanide ion attacked. A possible way to overcome this is to simply ignore the intermediate amide formation. Thus:



In this case, instead of an analog reaction, CN⁻ simply acts as a catalyst. However, it becomes impossible to distinguish, with these data sets, which mechanism(s) occur. In the case of any of the competing mechanisms, equilibrium eventually sets the limit for THEED formation.

Conclusions

The data does not show a definitive tendency for cyanide ion to aid in the formation of THEED. Trends in the data tend to show:

- THEED formation via the cyanide-amide-nucleophile (CAN) analog to direct cyanide ion hydrolysis and DEAF formation is *possible* as THEED can be produced without DEA carbamate and subsequent oxazolidone
- THEED formation may be more favorable via CAN analog at low HCOO^- concentrations
- THEED accumulation is equilibrium limited and tends to plateau at higher HCOO^- levels

The most important conclusion is answering the client's original question, should an extra effort to remove THEED be used to along with HSS anion removal? The data clearly shows that such an effort may be futile.

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