

Modelling Electrolytic Hydrofluoric Acid in the Fractionation Phase Change Corrosion Zone of HF Alkylation Units

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ABSTRACT

Electrolytic hydrofluoric acid (HF containing water) continues to be a significant carbon steel corrosion concern in the industry, particularly in the regime where water/HF undergoes phase changes as it is heated and cooled in the fractionation section of the HF alkylation process. This corrosion may be attributed to the formation of a water enriched electrolyte phase. An industry sponsored Joint Industry Project (JIP) was undertaken to better understand this corrosion relationship by developing an electrolyte thermodynamic database and relationships of HF/Water/Hydrocarbon interactions that could be used in process models to evaluate the impact of operating changes on the corrosion potential in these systems. This paper will discuss the creation of the electrolyte thermodynamic model and its application in evaluating the phase transitions that occur in user plants as a function of operating conditions through process simulation. This work identified the complexity of this water/HF phase change corrosion phenomenon which can be significantly affected by changes in operating conditions. It further confirms the difficulty in trying to manage this corrosion by operational controls alone. Examples of user experiences with the modelling tool combined with plant corrosion experiences are used to demonstrate how the modelling helped explain the corrosion observed and how process changes can significantly impact corrosion. This work supported the need for rigorous corrosion monitoring of these HF alkylation processes. It further highlights the value of implementing targeted continuous onstream ultrasonic thickness monitoring sensors and the use of alloy upgrades such as Alloy 400 in water/HF phase change locations.

Key Words: Hydrofluoric Acid corrosion, Carbon Steel, Alkylation, Electrolyte Thermodynamic Modelling, Ionic Modelling, Process Modelling, Corrosion Monitoring, Alloy 400

INTRODUCTION

Hydrofluoric acid (HF) is used as a catalyst in the alkylation process to react isobutane with olefin feeds to manufacture a high octane alkylate product used in gasoline blending. The HF catalyst is added in its anhydrous liquid form (< 400 ppmw H₂O) but as it circulates in the reaction system, residual water in the

liquid hydrocarbon feed is absorbed by the acid such that the circulating reaction acid builds up a small percentage (0.5 to 2.0 mass%) of water. This water/HF mixture is also referred to as rich HF (RHF). In addition, the alkylation reactions also will generate fluorocarbons and acid soluble oils (ASOs). A portion of the circulating reaction HF acid, containing water and ASO, is sent for regeneration (heating and stripping) to remove a portion of the built up water and ASO to maintain targeted levels of water and acid strength. The circulating reaction emulsion is cooled (reaction is exothermic) and the hydrocarbon and RHF is separated by gravity in a settler vessel where the acid is returned (pumped or convective flow) to further react with incoming hydrocarbons. As separation efficiency is never perfect, some RHF will be entrained in the liquid hydrocarbon withdrawn from the settler. The liquid hydrocarbon effluent from the settler then requires separation of the propane, isobutane (recycled), and normal butane from the alkylate product via fractionation. Products will contain organic fluorocarbons (fluorides) that may be removed in the product streams via a heated defluorination process. A block diagram of the HF Alkylation process is shown in Figure 1.

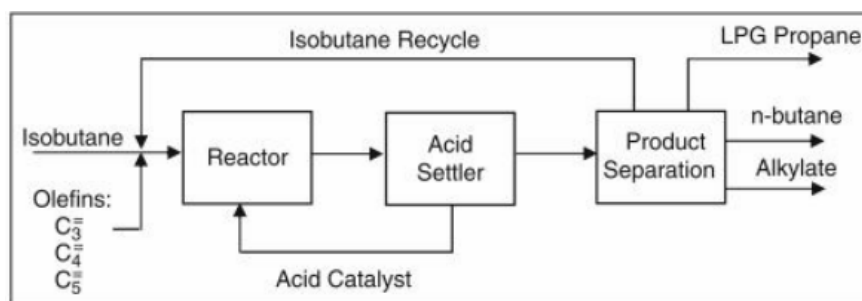


Figure 1: Simplified Block Outline of the HF Alkylation Process

Carbon steel is the primary materials of construction used in this process as within the majority of the plant the operating conditions exposed to the concentrated HF will generate a protective iron fluoride scale and inhibit corrosion. There are aspects of the process that can significantly impact the HF associated corrosiveness to carbon steel throughout the unit, particularly as the circulating HF now contains 0.5 to 2.0 mass% water (RHF). The various forms of corrosion that can occur are described in API Recommended Practice 751¹ which has defined five corrosion zones that are impacted by different HF corrosion mechanisms. One of the most problematic zones of corrosion in HF Alkylation plants is known as the Phase Change corrosion zone where RHF is either heated or cooled. When the RHF alone is heated / cooled the corrosion is due to the azeotropic nature of the HF-water system as shown in Figure 2 which was created per the model developed for this work. So this would be the source of concentration change such as seen in heating / cooling RHF in a plant's regeneration system. It should be recognized that this figure represents only ambient water/HF mixtures with no hydrocarbons. The implications of what happens with residual entrained RHF in a primary hydrocarbon stream has not been well understood, and how this impacts the water/HF interaction, particularly at varying operating conditions, was one of the major drivers for this work.

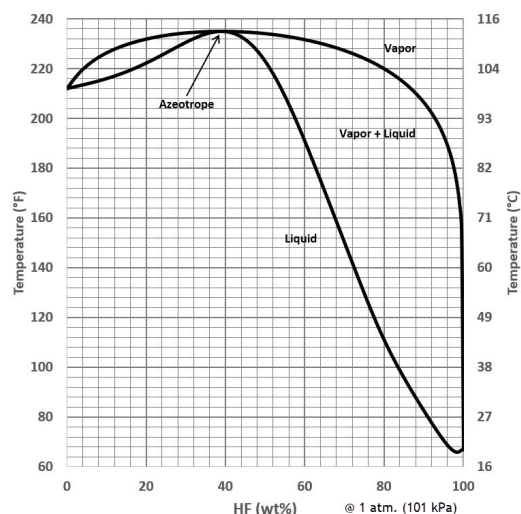


Figure 2: HF Acid/Water Phase Diagram: Showing azeotropic nature of HF-water mixture.

The significance of this water/HF mixture phase change can be seen in the estimated carbon steel corrosion rates versus HF/water concentration in Figure 3 which was generated with data per Degman² and superimposed with the data curve from NACE⁽¹⁾ Publication 5A171³. The red and blue arrows have been superimposed on the figure to represent the heating and cooling of the water/HF mixture and how the corrosion escalates rapidly as the water is enriched as the heated or initially cooled RHF phase changes. It is important to recognize that this figure applies to corrosion only up to 100°F (38°C) and the implications for warmer operations will be discussed further in this paper.

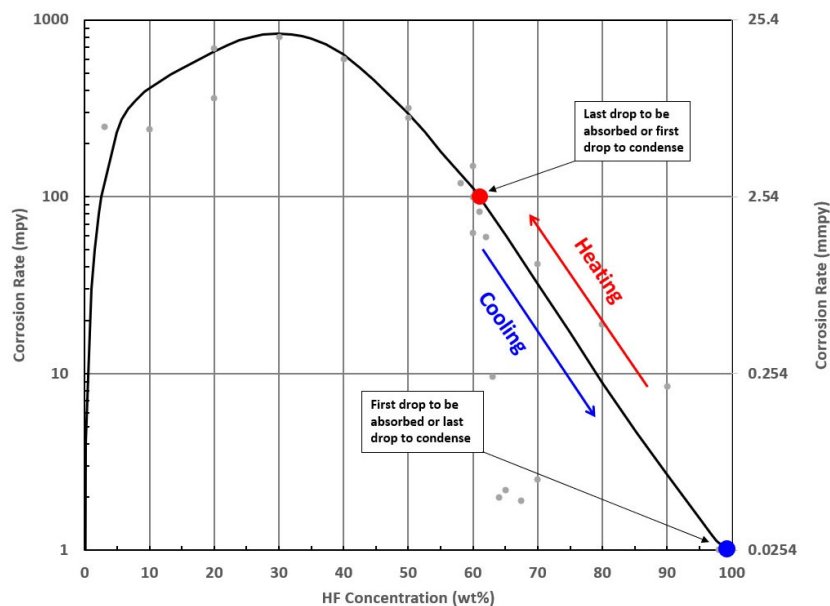


Figure 3: Carbon Steel Corrosion at 100°F (38°C) as a function of HF Concentration.

The most corrosive example of this phase change corrosion mechanism occurs in the RHF sent to the regenerator for removal of water and ASO. The operation has the highest temperature increase of an

⁽¹⁾ NACE (Now AMPP, The Association of Materials Protection and Performance), 15835 Park Ten Place, Houston, Tx, 77084

RHF stream in the HF alkylation unit. Alloy 400 is commonly used in this service as it is significantly more resistant to HF corrosion, yet not immune.

The settler hydrocarbon liquid effluent primarily contains soluble HF and a very small amount of soluble water with some entrained RHF droplets. Carbon steel is the primary choice for material as the amount of entrained RHF in the effluent hydrocarbon liquid should be minimized by good settling operations. As such, heating, and cooling of this stream during fractionation should not be expected to produce significant corrosion of carbon steel in the feed/tower/overhead system. Nevertheless, the industry has experienced considerable corrosion to carbon steel and more disconcerting is that this corrosion appears to be highly variable with subtle changes in operating conditions (water in acid content, settler performance leading to increased RHF entrainment, temperatures, and pressures) causing significant changes in both the rate and location of the corrosion. The corrosion can be highly localized in nature for the heated or cooled stream undergoing a phase change. This behavior will be discussed further in this paper. Despite ongoing attempts to monitor and to control operating conditions ^{1,4} as Integrity Operating Windows (IOWs), the predictability and control of this type of corrosion has proven to be elusive.

JOINT INDUSTRY PROJECT

The determination of how operating conditions will impact this RHF phase change and hence corrosivity has been inhibited by the fact that the current process simulators designed to model hydrocarbon processes could not predict accurately, the RHF phase changes. Those simulators which model electrolytes and hydrocarbons lacked the molecule-molecule interactions among hydrocarbons, HF, and water that are required for accurate phase prediction. Therefore, a joint industry project (JIP) was initiated to complete the following three phases:

- Build an electrolyte thermodynamic model by collecting and analyzing public literature experimental data and input data from JIP members. The model included H₂O/HF/HC interactions for C₃ to C₁₂ alkanes, C₃ to C₄ alkenes, representative alkylate molecules, some simple acid soluble oils (ASO) variants, C₁ to C₅ organic fluorides and of course HF and H₂O.
- Integration of the developed electrolyte thermodynamic model into a process simulator to evaluate operating exposure conditions and determine how liquid-liquid equilibrium (LLE) (heated reactor effluent to fractionators) and vapor-liquid equilibrium (VLE) (fractionator overhead vapor) conditions were impacted by various operating conditions for several JIP member plants.
- Comparison of these model assessments with actual plant corrosion experiences to determine how the operating conditions as modelled could be used to explain the corrosion reported by the plant.

Electrolyte Thermodynamic Modelling

A Mixed Solvent Electrolyte (MSE)⁵ model was applied in the development of a comprehensive framework to provide the foundation for the HF alkylation process simulation. The model has been developed based on a detailed analysis of the chemistry involved and on a critical evaluation of available literature data ^{6,7,8,9,10} combined with information provided by JIP members for the key components and their mixtures in the HF alkylation process. The model, established on a sound theoretical basis and supported by experimental data and information from JIP members, provides predictions of chemical speciation (e.g., dissociation of the acid) and phase equilibria (liquid-liquid and vapor-liquid equilibria) in mixtures containing hydrocarbons (C₃-C₁₂ alkanes, C₃-C₄ alkenes and selected branched hydrocarbons that represent the alkylate), HF, water, C₁-C₅ fluorocarbons and representative acid soluble oils (ASOs) to facilitate effective HF alkylation process simulation.

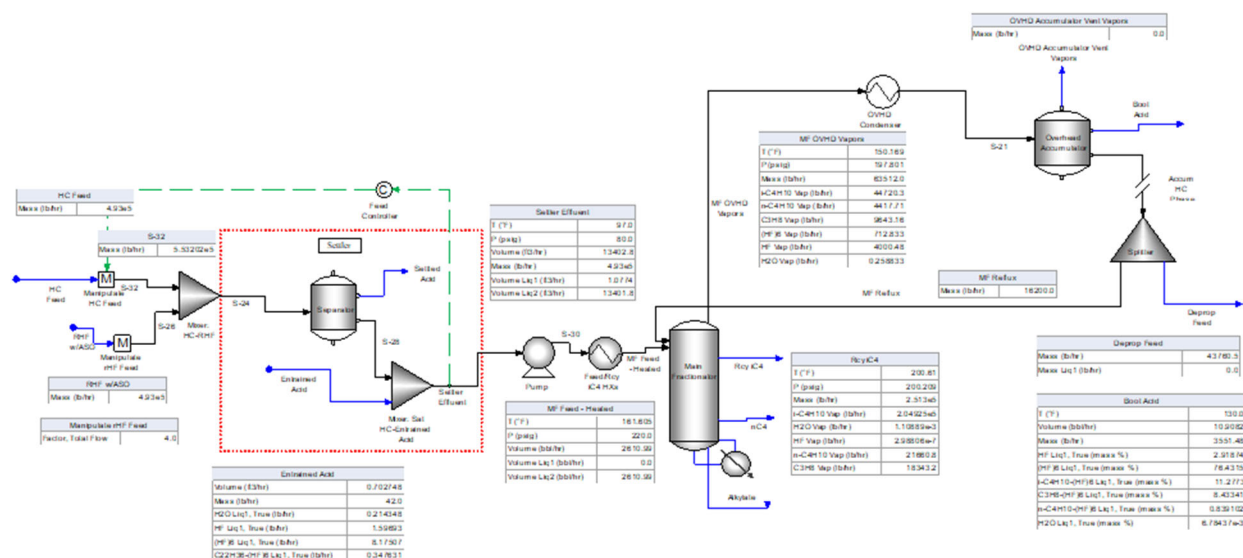
The HF alkylation thermodynamic model defines properties of each component and interactions between any two components in the mixtures including the HF-hydrocarbon, HF-water, hydrocarbon-water, HF-ASO, hydrocarbon-ASO, water-ASO, HF-fluorocarbon, fluorocarbon-water, and fluorocarbon-hydrocarbon combinations. Appropriate definition of these interactions allows accurate prediction of

phase equilibria under varying conditions of temperature, pressure, and mixture composition during process modelling. Specifically, the model accurately captures phase behavior in mixtures of HF with water as shown in Figure 2,⁵ as well as trends of solubilities of HF and water in hydrocarbons as a function of temperature and pressure which are critical to determine the phase transition as the process condition changes. In addition, chemical speciation due to acid dissociation (i.e., $\text{HF} + \text{H}_2\text{O} = \text{F}^- + \text{H}_3\text{O}^+$) is also taken into consideration in the modelling. The change of process conditions not only affects phase equilibria, but also chemical speciation (i.e., the amount of H_3O^+ present in RHF can vary with temperature and composition of the RHF phase). Increased concentration of H_3O^+ will result in an enhanced corrosivity. Accurate prediction of chemical and phase equilibria in such mixtures would be necessary to determine if process conditions can be defined to avoid exposure to the transition temperature where the most corrosive RHF phase may be occurring.

The results of this work have been incorporated into the thermodynamic database used in the OLI Systems Inc.[†] process modelling and simulation tools: OLI Flowsheet:ESP[†] and the OLI Studio[†].

Process Simulation

The process simulation incorporating the thermodynamic database within the model was performed on four user plants using process information provided by the end user for the plant in question. An example of the process modelling flowsheet is shown in Figure 4. The modelling was focused on providing the process conditions (P, T, rates), phases (vapor, Liquid 1 (aqueous), Liquid 2 (hydrocarbon)) and composition for the streams of interest; heated fractionator feed, fractionator overhead, recycle iC_4 draw) representing the areas where there are exposure potentials to reaching corrosive RHF phase change conditions. The process modelling was converged using actual plant data as closely as possible. Once the process model was converged, the three process streams of interest were exported to a separate mixed solvent electrolyte model to perform a sensitivity study on how varying important process conditions (water content, P and T) may impact the phase change profile in the systems.



Importantly, since the JIP was completed, two simulated plants have initiated onstream ultrasonic thickness monitoring that is providing real time corrosion loss evaluations that were compared to the modelled plant operating conditions to evaluate how the process is affecting the corrosion observed.

RESULTS

Electrolyte Thermodynamic Modelling

Sufficient property data was available to provide adequate modelling between the light hydrocarbons, HF and water as indicated by testing the database with the plant process models in our initial investigation. Further model improvement has been made by addition of a wider variety of alkylate molecules and heavier hydrocarbons (to C₁₂, to cover a broader boiling range), and a better definition of ASO contribution based on information provided by the users. This model, with the extended database, provides process modelling results with an improved match to plant conditions, and the convergence of the plant process modelling can now adequately address the phase interactions in the tower feed and light overhead systems which was the most critical aspect of this corrosion study.

The most significant aspect of the electrolyte thermodynamic model was the degree of solubility of HF and the very limited solubility of H₂O in the hydrocarbon phase which was determined to be the primary mechanism for the degree of water enrichment of the RHF rather than the azeotropic nature of the mixture that causes water enrichment. Based on the modeling conducted on the user plants and correlation with corrosion behavior, the thermodynamic model appeared to accurately predict the solubility of HF and water in hydrocarbons, thus ensuring the adequacy and reliability of the process modeling results.

It was found that organic fluorides do appear to affect the phase equilibria with increased fluorides leading to a greater increase of solubility of HF than H₂O into the hydrocarbon phase amplifying the concentration of water in the remaining RHF and causing an increase in the transition temperature. This was felt to be due to the result of hydrogen-bonding or dipole-dipole interactions. Another important observation was that increased fluorides also appeared to increase the solubility of water in the iC₄ recycle stream that can contribute to an elevated transition temperature and the onset of corrosive RHF formation in this stream.

The amount of ASO dissolved in the circulating acid can be modelled to qualitatively match data from laboratory tests by JIP members to ensure appropriate process modeling results in the operation units that may be most affected by their presence. The primary impact of ASO was found not to directly impact the HC/HF/H₂O equilibrium but rather improved the model convergence of the tower thereby improving the accuracy of the predicted tower top HC/HC/H₂O constituents.

Process Modelling

Process models for three of the four plants were able to be converged and compared reasonably well to measured plant parameters. The fourth plant (high pressure depropanizer) had difficulty in convergence attributed primarily to the uncertainty of the measured fractionator boot acid quantity from the plant and the estimated impact it had on entrained RHF in the settler effluent.

It became readily apparent in the plant assessments that the most critical aspect of process modelling was the need to understand the amount of entrained RHF that is exiting the settler since the electrolyte thermodynamic modelling defining the degree of water enrichment is due to H₂O's limited solubility verses HF in the hydrocarbon. The total mass of water entering the fractionation section is a function of both the water in RHF content (controlled in the circulating reactor system via regeneration) and the amount of entrained RHF exiting the settler. The amount of H₂O will determine the transition temperature, which is the point where all the water becomes soluble in the hydrocarbon in LLE or stays as vapor in VLE conditions. As there is no possible way to measure the amount of entrained RHF exiting the settler, the only means to estimate this quantity is by measuring the amount of the RHF collected in the fractionator overhead accumulator boot (boot acid). This boot acid quantity is largely due to hydrocarbon soluble HF (very little hydrocarbon soluble H₂O) being stripped from the hydrocarbon, plus some soluble

hydrocarbon and the small amount of entrained RHF. Process modelling requires measurement of the amount of boot acid to start the process of estimating the entrained RHF. The boot acid quantity was used in a manual iteration cycle in estimating the amount of entrained RHF by subtracting the model's prediction of the soluble HF amount and the amount of soluble hydrocarbon, then manually entering the difference as entrained RHF amount back into the settler hydrocarbon and entrained RHF mixer. This process was used to converge the process model so that the modelled overhead boot acid quantity was nearly equal to the measured quantity. The primary issue in the four cases modelled, was the lack of flowmeters on the boot acid effluent streams, such that measured boot acid quantity were based on manually timed boot acid fill rates. Reasonable closure was achieved in three of the four plants while one plant did not converge probably related to the measured boot acid quantity estimates.

Process modelling was completed for evaluating the fractionation feed (LLE), the fractionation overhead (VLE) as well as the liquid recycle iC_4 draw from the fractionator (LLE). No extended modelling was completed within the four plants for downstream fractionation such as the depropanizer feed/overhead (two tower systems) or HF stripper, although there is capability for extending the modelling to these locations.

The process modelling provided the ability to perform a parameter assessment and comparison to the plant actual operating envelope to identify what extent the plant may be operating into the critical transition zone regime where the most corrosive water concentrated RHF phase exists. A contour plot that varied temperature and pressure for different amounts of water available in the stream (estimated via the process model for a given water in acid content in the RHF and entrained RHF quantity). Figure 5 is a typical contour plot of temperature verses pressure for a given amount of total water in the effluent stream going to the tower. The color coding represents the changing amount of water in the rich HF phase as it is heated (or cooled) with the legend shown to the left. There are three zones of exposure in these plots; the left zone where a second phase entrained RHF phase is gradually changing in water content, the middle transition zone where the highest water concentration exists before complete solubility of all water in the hydrocarbon occurs which is represented on the right. The two zones with free RHF represent electrolytic corrosion while the fully soluble zone represents a direct HF corrosion reaction on carbon steel (i.e., no water involved in the corrosion reaction). The transition zone will shift to higher temperatures as water content in the effluent increases.

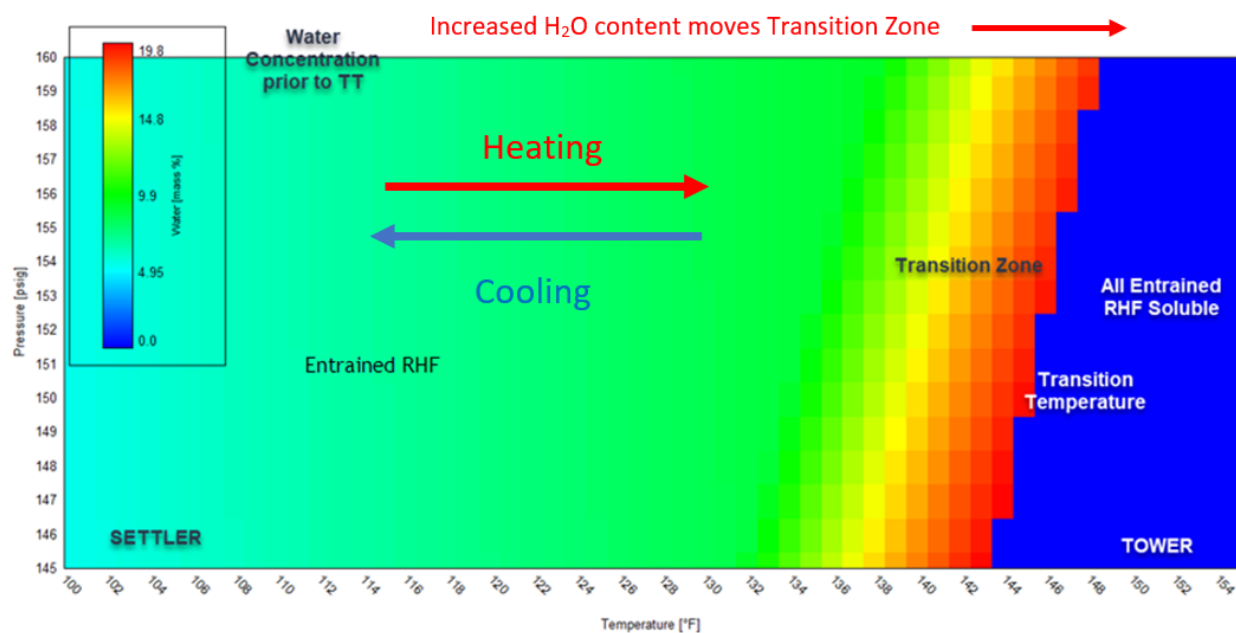


Figure 5: Parameter Contour Plot: Demonstrates P/T Impact on Phase Changing RHF