

Modeling the HF alkylation chemistry

An OLI Joint Industry Project (JIP) beginning April 2019

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Corrosion in the HF alkylation process

The HF alkylation process converts alkene hydrocarbons into premium, high octane alkylate blending stock, using hydrofluoric acid (HF) as the catalyst. This process typically includes various fractionation systems (Isostripper/desisobutanizer), depropanizer, debutanizer and HF stripper, and associated pre-heating, condensing and acid recycling operations. The HF catalyst can become 'rich', that is, it can contain water; during the alkylation process the water-rich HF can become entrained in droplets in the reactor effluent to the fractionation section. Corrosion from this water-rich HF is a problem for this process.

Water-rich HF corrosion is associated with the phase changes of the process. This includes water-rich HF condensing out of a vapor or liquid hydrocarbon stream, in which the first drops of condensate are highly concentrated with HF, or the water-rich HF becoming soluble or vaporizing during heating. One best practice for mitigating the water-rich HF corrosion is to set integrity operating windows (IOW) that prevents phase changes outside the heat exchangers. If IOWs are used, it is typically set by experience.¹

Current modeling challenge

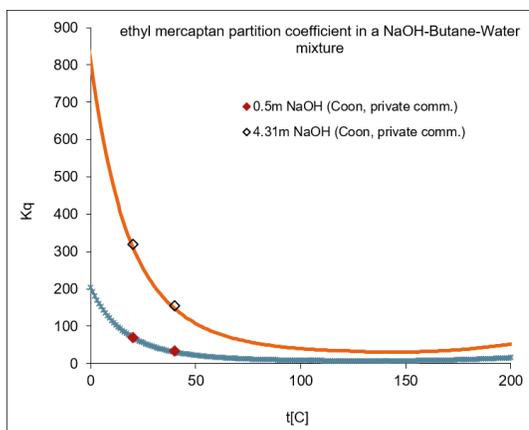
Ideally, the IOW for a given HF alkylation process would be fine-tuned using process simulation: Rigorous process simulation predicts the phase change temperature and pressure and these conditions can be controlled to avoid the phase changes outside the heat exchangers.

The current modeling challenge is that simulators designed to model hydrocarbon processes cannot predict accurately, the rich HF phase changes. On the other hand, simulators that model electrolytes and hydrocarbons lack the molecule-molecule interactions among hydrocarbons, HF, and water that are required for accurate phase prediction.

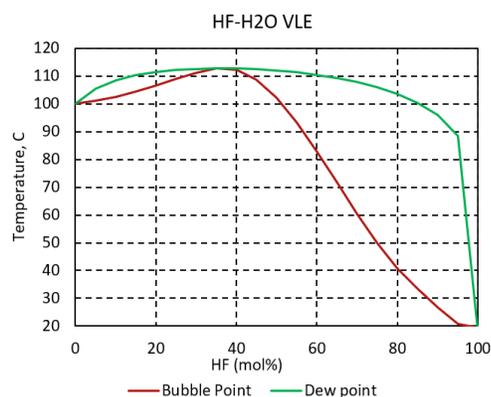
Many significant benefits will be realized once an accurate thermodynamic model is available for this process. Benefits would include: measurable improvements such as longer equipment life, process optimization in terms of optimal yield and heating / cooling savings, resource savings in terms of increased productivity of corrosion engineers and less corrosion consulting time, lower replacement/maintenance costs and perhaps most important, lowered risk on catastrophic unit failures.

OLI Systems framework

The OLI electrolyte thermodynamic framework is a robust and proven model that accurately predicts the behavior of electrolytes in any process.



This model has been applied successfully in predicting the amine-hydrochloride behavior for the CDU overheads, carbonate-ammonia speciation in sour water strippers, phase distribution in sulfur recovery, acid-base interactions in gas sweetening, etc.



¹ Gysbers, A. (2018) "HF/Water/Hydrocarbon Modelling, Presentation, NACE CTW STG34 (206X)

In addition, when the necessary binary and higher order molecular interactions are defined, OLI can successfully model mixed hydrocarbon-electrolyte systems.

One such mixed electrolyte and hydrocarbon system is the Merox process, in which mercaptans are converted to disulfides. The OLI model accurately reproduces the mercaptan partitioning between hydrocarbons and caustic water liquids.

Proposed Joint Industry Project (JIP)

OLI proposes a JIP to develop a model that will predict the chemistry and phase properties between the hydrocarbons and water-rich HF. This project has two primary objectives:

1. To develop the necessary interaction parameters between HF, hydrocarbons, and H₂O

This objective is to extend OLI's existing database beyond the HF-H₂O binary system, and develop HF – hydrocarbon and HF-Hydrocarbon-H₂O interactions where water is a minor component.

2. To develop case studies and case templates using this updated model to simulate the alkylate and HF recovery process

The project team will work with JIP members to set up template cases in the OLI software. Attention will be given to individual stream chemistry analysis in the OLI Studio, as well as flowsheet analysis within OLI Flowsheet: ESP.

The successfully completed JIP will give the engineers ionic modeling capabilities for the HF alkylation process, to facilitate the development of accurate IOWs for the minimization of phase change driven water rich HF corrosion, as well as for process optimization.

Project approach

OLI will use a combination of thermophysical modeling and process simulation to meet the project objectives:

1. MODELING

Develop the necessary interaction parameters for the HF alkylation process

- 1.1 Perform a literature search for published experimental data on vapor-liquid equilibria (VLE) and liquid-liquid equilibria (LLE) in mixtures containing HF and hydrocarbons, focusing on C1-C5 alkanes and alkenes
- 1.12 Request data for VLE or LLE from members which could be used in this project for parameter development or validation
- 1.13 Perform a literature search for the acid soluble oils and organic fluorides that are associated with circulating acid in the reaction system
- 1.2 Regress thermodynamic parameters to match the experimental data where data exists
- 1.3 Develop correlations for the thermodynamic parameters where data does not exist, using correlations based on 'anchors' found in the literature search and the number of carbons in the hydrocarbon families
- 1.4 Validate predictions for the ternary systems / adjust as necessary
- 1.5 Identify key transitions such as the presence of upper critical endpoints for LLE

2. SIMULATION

Develop case studies and case templates in the OLI software for simulation of the HF alkylation chemistry / process

- 2.1 Make a recommendation to each member company on where simulation is possible / advantageous for (one of) that member's alkylation unit(s)
- 2.2 Perform 3 case studies submitted by member companies on their HF alkylation processes, sharing the results of these studies with project stakeholders
- 2.3 Develop case templates in OLI Studio: Stream Analyzer for chemistry analysis of water-rich HF hydrocarbon streams for use by project stakeholders
- 2.4 Develop case templates in OLI Flowsheet: ESP for process analysis of the HF alkylation process for use by project stakeholders

Project feasibility

This project is technically feasible.

MODELING: OLI completed a literature search (tasks 1.1, see Appendix 1) in advance to assure that there is sufficient published data to anchor the necessary correlation work, since an experimental program with HF is expensive and dangerous. Correlations for hydrocarbons based on the number of carbons is a reliable and proven method for estimating missing data for organic components. The thermophysical modeling and correlation modeling skills required to develop HF – hydrocarbon – water parameters, are part of OLI Systems' core competency.

SIMULATION: The process simulation skills required to develop the chemistry and process simulations of **key parts** of the HF alkylation process (excluding the actual alkylation reactor) are well developed at OLI Systems, practiced by a team of process simulation consultants on hundreds of other simulation studies. In addition, Andy Gysbers of Becht Engineering will join the process simulation team in the role of HF Alkylation Technical Consultant to bring his experience and insights to the simulation work.

This project is operationally feasible. OLI has the necessary resources and skills to start and complete this project in 2019.

Finally, **this project is economically feasible.** OLI is seeking a minimum of 7 companies to join this JIP in order to have sufficient funding for this modeling and simulation work.

Pricing and deliverables

JIP membership requires a one-time \$15,000 USD investment from each member company.

In return, members receive at least \$24,100 USD benefit, and more for new clients.

Benefits/ Value	JIP Members
Database & Thermodynamic Models Updates	No fee for 2 years for named, individual copy * or no fee for 1 year for network copy ** <i>\$10,000 USD value</i>
Validation spreadsheets	No fee (included in database fee)
Application Templates	No fee (included in database fee)

Software License for OLI Flowsheet ESP and OLI Stream Analyzer	<p>Two 4-month evaluation copies of Stream Analyzer and Flowsheet ESP (individual key), activated at any point during the project or upon delivery.</p> <p><i>\$8,400 USD value</i></p> <p>Promotional pricing for annual lease of OLI Software for new customers: \$10,000 for an individual key* for Stream Analyzer; and / or \$10,000 for an individual key* for Flowsheet ESP <i>\$24,000 USD bundled price. \$4,000 USD savings</i></p>
Consulting Services	<p>2 days application building and review assistance for each member, applying the application templates to a specific HF alky unit,</p> <p><i>\$4,800 USD value</i></p> <p>For the first 3 members who sign contract a complete case study which will be used to build the case templates.</p> <p><i>Extra \$7,200 USD value for 3 members</i></p>
Training and support	<p>Two, live 3-hour web-based training sessions; First training on chemistry and corrosion and second on process and corrosion; access to the on-demand training</p> <p><i>\$900 USD value</i></p>

This project offers a unique combination of benefits for both extension of the OLI database and thermodynamic modeling capability, combined with practical expert simulation guidance in deploying the technology on members' particular HF alkylation process.

It is not necessary to be an existing OLI client to benefit from this project. OLI will offer 4-month evaluation copies to either (or both) the OLI Studio: Stream Analyzer (for chemistry studies) and OLI Flowsheet: ESP (for process studies), so that clients can apply the new model to existing questions / HF alkylation units. Also, incentive pricing is available for those members who decide to include this technology in their toolset going forward.

Members who have existing HF alkylation data at their companies are invited to bring this data as part of OLI's validation phase of the project. This data will be held confidentially for validation analysis only.

Finally, in addition to the training and 2 days of simulation consulting that are part of this project for every member, OLI offered an additional 3 days of simulation consulting to the first three members to join this JIP. These more in-depth cases will be held confidentially by OLI for use only by the company submitting the data. However, the general layouts from these cases will be used to develop the case templates that will be available to members only.

JIP details

Cost	\$15,000 USD
Commitment	OLI Systems is looking for commitments to this project by the end of Q1 2019
Contract signed by	OLI is seeking contracts signed for this project by April 2019
Start date	OLI plans to start this project April 2019, upon contract signing from a minimum of 7 companies
Duration	Project is expected to complete in 12 months from start date
Early signing bonus	The first three members will receive one-on-one assistance from the Simulation team on their own HF alkylation process simulation case

Payment	Members will be invoiced for the project fee upon signing the contract. Terms are NET 30 from invoice day
Fixed cost basis	OLI will work on a fixed cost basis for this JIP. OLI will absorb any cost overrun
Project management	Project management will be provided by Pat McKenzie
Project meetings	Project meetings will be held periodically by web, with an optional breakfast meeting planned for NACE CORROSION 2019 on 24 March 2019
Release of data	OLI will offer the private databank for an HF alkylation application licensing fee to other non-participating members at the end of this project, along with a paid simulation study service
Software licensing	Two, 4-month licenses for a named individual copy of OLI Studio: Stream Analyzer (chemistry analysis) and OLI Flowsheet: ESP (process analysis)
Advantageous lease pricing	\$10,000 USD for one year for either the OLI Studio: Stream Analyzer or OLI Flowsheet: ESP, for an individual named user copy for one year, for those participants whose companies are not already OLI clients

Why choose OLI?

Simulation has been proven time and again to cut cost and reduce risk of physical operations. A one-time investment in OLI simulation will reap years of benefits. OLI Systems framework for electrolyte thermodynamics is a proven delivery vehicle for complex and reactive HF chemistry, for alkanes and alkenes in water (LLE) and for electrolyte – hydrocarbon interactions such as was done for the Merox process. There is literally no other company in the world who shares this position with OLI Systems. We are the only simulation company with the talent and capabilities to tackle this system.

Membership in this OLI Systems JIP will increase your competitive edge and guarantee that you have the earliest path to optimization for your HF alkylation units. You and your colleagues will learn how to apply ionic modeling to refining problems, saving time and cutting costs in refining operations. OLI will also grant access to the closely-held, OLI validation spreadsheet for this system. Along with this underlying data, OLI technologists will explain the significance of the data and the simulation. No other clients will receive the benefit of this private data, nor of the underlying explanation of ‘why?’

Finally, the JIP team is a collection of highly trained and experienced scientists, researchers, and consultants who will be available to you, including:

Dr. Andre Anderko, OLI’s Chief Technical Officer, architect of the OLI MSE and the OLI corrosion framework, Fellow of NACE

Dr. Anthony J (A.J.) Gerbino, OLI’s Vice President Client Success, a process simulation consultant, the lead OLI trainer, recipient of the NACE Technical Award in 2015 and elected this year as Vice Chairperson for ACPC at NACE

Mr. James Berthold, MSc, OLI’s Vice President Client Support, a process simulation consultant with 33 years of experience in electrolyte process simulation

Mr. Andy Gysbers, Becht Engineering, a highly qualified engineer who brings over 40 years refinery experience, including experience with troubleshooting HF alkylation unit processes, recipient of NACE Technical Award in 2017

Ms. Pat McKenzie, OLI’s Vice President Global Sales, a process simulation software developer by background and a project manager who has led several OLI and AQSim special projects

OLI Systems, Inc: Proven Modeling Leadership

Most comprehensive electrolyte chemistry based solutions

- 80 elements of the periodic table; 6,000 species
- Rigorous and accurate models
- Extensive data validation
- Simulation software, consulting services

Sustained innovation research & development

- 30 years of modeling innovation
- 10 Joint industry Research programs
- \$150M Investment in the OLI platform
- Properties database for 10,000 applications

**Think simulation!
Getting the chemistry right**

Expertise and resources

- 10 Ph.Ds.; NACE Fellow 2016
- Leadership in technical standards
- Applications expertise in 10 industrial markets
- 100 man years of consulting and training

Global recognition

- Presence in 35 countries, 6 continents
- 500 clients; 95% renewal rate
- R&D100 Award for OLI Corrosion Analyzer
- Partner integrations, Channel Partner ecosystem



Appendix 1: Preliminary literature search results

Hydrogen Fluoride (HF) / Hydrocarbon Phase Equilibrium Data September 2018, Literature search performed by OLI			
Hydrocarbon	T Range, C	Data Type	Reference
Octane	25 - 65	Solubility of HF in hydrocarbon	Simons (1931)
Benzene	20 - 75		
Propane	0 - 40	Mutual solubility of HF and hydrocarbon	Butler et al. (1946)
Butane	5 - 40		
Isobutane	0 - 50		
Pentane	-25 - 40	Mutual solubility of HF and hydrocarbon	Marcus et al. (1970)
Hexane	-25 - 40		
Heptane	-25 - 40		
Propane	30 - 90	Mutual solubility of HF and hydrocarbon	Chen et al. (1994)
Butane	30 - 90		
Isobutane	30 - 90		
Butene ₁	30 - 90		
Benzene	30 - 90		
Propane	20, 30		

References

- Simons J. H., "The Solubility of Hydrogen Fluoride in Benzene and in Octane", *Journal of the American Chemical Society*, 53, (1), 83-87, 1931.
- Butler E. B., Miles C. B., Kuhn Jr. C. S., "Hydrogen Fluoride Paraffin Systems. Significance of Liquid Phase Equilibria in the Hydrogen Fluoride Alkylation Process", *Industrial and Engineering Chemistry*, 38, (2), 147-155, 1946.
- Marcus Y., Shamir J., Soriano J., "Mutual Solubility of Anhydrous Hydrogen Fluoride and Aliphatic Hydrocarbons", *Journal of Physical Chemistry*, 74, (1), 133-139, 1970.
- Chen X., Lee C., Wu Z., "The Measurement of Mutual Solubility Data for Hydrogen Fluoride Systems", *AIChE DIPPR Data Series*, (2), 28-33, 1994.
- Kang Y. W., "Phase Equilibria for the Binary Mixtures Containing Hydrogen Fluoride and Non-Polar Compound", *Fluid Phase Equilibria*, 154, (1), 139-151, 1999.

Notes

- The amount of data in the literature is small but provides the necessary core information to develop a predictive model. Considering the small amount of data, a major focus area in modeling will be to develop prediction techniques for the HF – hydrocarbon systems for which no experimental data are available.
- If members have knowledge of datasets that are not on this list, please inform OLI so that we can add them to this list.
- OLI will evaluate any member company existing (proprietary) experimental data on HF and hydrocarbons as possible validation for the model predictions. Data will be held confidentially.
- Project stakeholders may wish to consider a second phase of the project, which would commission an experimental program to extend the database and validate phase I predictions. Given the dangers and expense of working with HF, combined with the high likelihood of success with the correlations, OLI has excluded an experimental program in this project at this time.

Credits

OLI acknowledges **Andy Gysbers, Becht Engineering**
Mike Cayard, Flint Hills Resources for their technical insights into the HF Alkylation processes

For more Information

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