Validation of Acid Gas Cleaning in Aspen HYSYS[®] for Liquid Hydrocarbons

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Introduction

In recent years, LPG (liquefied petroleum gas) and NGL (natural gas liquids) production has increased in tandem with the rapid expansion in natural gas production. LPG and NGL are used as feedstocks for petrochemical plants, burned for heating and cooking and blended into fuels for vehicles. Natural gas producers are increasingly focusing on the production of liquids-rich supply basins as a lower-cost alternative to crude oils. Over the past few years, the world has set all-time high production rates of these products, increasing the need for processing capacity, including gas and liquid sweetening.

This white paper will provide an overview of the process of sweetening liquid hydrocarbons, the challenges with predicting the performance of the process and product quality, the solution offered in Aspen HYSYS[®], and the results of Aspen HYSYS compared to experimental and plant data.

The Case for Removing Acid Gases in Liquid Hydrocarbons

The contaminants in the sour LPG and NGL include H_2S , CO_2 , mercaptans, COS, CS_2 and elemental sulfur. Each of these contaminants can cause problems within the products for producers, consumers and the environment and should be removed.

- Hydrogen sulfide (H₂S) is corrosive, toxic and its presence in hydrocarbon products and flared gas is regulated by most governments. H₂S can be converted to free sulfur or form mercaptans for easier storage and sale. In general, most liquid hydrocarbon products must meet a 1A copper strip corrosion test which corresponds to less than 4 ppm H₂S.
- Sulfur dioxide (SO₂) emissions are also regulated, as high amounts in the atmosphere can lead to acid rain.
- High quantities of CO₂ in liquid hydrocarbons is undesirable. For instance, CO₂ can raise the LPG's vapor pressure and lower its heating value. If the product is treated with caustic, the presence of CO₂ can cause large caustic losses.
- Although mercaptans are used in small quantities for odorizing products, an excess amount will impart strong odors in the product, as well as in the combustion products that follow.

COS and CS_2 are not overly corrosive in liquid hydrocarbons, but they can hydrolyze slowly to H_2S in the presence of free water, which can cause a product that may have initially passed the copper strip to then fail after storage. In general, heightened levels of dissolved acids (such as H_2S and SO_2 in liquid products) can increase corrosion rates in piping and equipment. Removal of these acids from liquid sales products is important to maximize equipment life, particularly for pipelines and transportation.

Benefits of Using a Simulator for Acid Gas Removal from Liquid Hydrocarbons

Aspen HYSYS Acid Gas Cleaning for liquid hydrocarbons brings value to both design and operations use cases. A simulator is typically used to model a process when physical phenomena cannot be intuitively explained, when trying to predict process changes on operations and specifications or when designing a grassroots model to meet the requirements of the plant.

Aspen HYSYS Acid Gas Cleaning for liquid hydrocarbons can be used in design and business studies to:

- Ensure a reliable operation across operating windows
- Determine which process configuration is most effective
- Discover which solvent is most effective, and at what rate
- Analyze how energy consumption can be reduced
- · Assess which column internals are most efficient
- Determine if a water wash section is needed

Aspen HYSYS Acid Gas Cleaning for liquid hydrocarbons can also be used to simulate and make decisions based on the impact of operations issues, such as:

- Inadequate inlet separation
- Poor temperature control
- Inadequate regeneration of lean amines
- · Lack of instrumentation, data collection and adequate analysis data
- Excessive rich solution loadings
- Impact of heat stable salts
- Monitoring process degradation
- Assessing impact of feed changes

Process Overview of Sweetening Liquid Hydrocarbons

There are several commercial processes used to sweeten light hydrocarbon liquids, the most common of which are amine treating systems, caustic washes and molecular sieves. For significant amounts of dissolved acid gases, a caustic wash may not be the best option due to the cost of the caustic, waste and salt disposal challenges, and the efficacy of the process to meet liquid sales specifications. Molecular sieve drawbacks include large capital and operating costs, undesirable COS formation if both H_2S and CO_2 are present, and an inability to meet ppm-level concentrations in sales products. Thus, amine-based treatment is usually the most cost-effective and technologically sound choice for liquid sweetening when significant amounts of acid gases are present.

The popularity of using amines to treat liquid hydrocarbons is increasing, alongside the growth in production of unconventional feedstocks and natural gas. This is especially true when an amine gas treater is already onsite. In such cases, amines are also being used to sweeten the gas stream before processing the liquid hydrocarbon stream. A common stripper can be used to regenerate the amine, and the liquid extractor can often be operated by using a slipstream of amine from the gas treating unit.

Amine-based liquid hydrocarbon treating processes are similar to those of gas treating. A flow diagram of a typical LPG treating system is shown in Figure 1. The countercurrent, liquid-liquid contactor is a column with three beds of random packing. The liquid hydrocarbon enters the bottom of the column, while a filtered lean amine is fed to the top of the column. The liquid hydrocarbon feed is distributed evenly and formed into droplets by injection into the continuous amine phase at the bottom of the column. The lean amine is distributed across the top of the packing where it joins the continuous amine phase. The density difference between the two phases causes the dispersed liquid hydrocarbon to flow upward through the continuous amine phase. The treated liquid hydrocarbon leaves the contactor and flows to a gravity settler or coalescer where entrained droplets of amine are removed from the liquid hydrocarbon. Figure 1 also shows a typical LPG water wash system.



Figure 1: Typical LPG amine treating system with gravity settler and LPG water wash¹. The combined water and liquid hydrocarbon stream flows through a static mixer or other mixing device and then flows to the gravity settler. A portion of the water-amine stream from the settler is recycled to the liquid hydrocarbon stream upon entering the water wash mixer. Washing the treated liquid hydrocarbon with water improves the recovery of the entrained amine and also removes the dissolved amine from the liquid hydrocarbon.

A single-stage contactor system is often used when high efficiency carbon dioxide removal is not required. Figure 2 shows a single-stage liquid hydrocarbon CO_2 removal system, liquid hydrocarbon and an amine that are contacted in either an educator or a static mixer where the intimate mixture of the two liquid phases is sent to a settling tank and separated. A relatively large flow of rich amine is then recycled through the educator to ensure an adequate surface area for the transfer of CO_2 from the liquid hydrocarbon to the amine.





The operating temperatures and pressures of the liquid hydrocarbon treater must be maintained within narrow limits to keep the hydrocarbon in the liquid state, minimize hydrocarbon and amine entrainment and optimize amine-hydrocarbon separation.

The operating temperature must be below the liquid hydrocarbon bubble point throughout the treating system to ensure that the hydrocarbon remains in a liquid state. Typical design margins between the liquid hydrocarbon bubble point pressure and the liquid hydrocarbon treater operating pressure are often 100 psi or greater, and the difference between the liquid hydrocarbon bubble point pressure and the minimum operating pressure in the liquid hydrocarbon treating system is often set at 50 psi or more.

To assure effective phase separation, Veldman recommends that the lean amine temperature be controlled so that the viscosity is around two centipoise at the amine and liquid hydrocarbon interface². Changela and Root reported that low amine operating temperatures (60-70° F) increased the viscosity of the lean amine solution which resulted in a significant amount of LPG entrainment in the rich amine³. Additionally, DuPart and Marchant reported that an excessive amine was entrained in the liquid hydrocarbon product due to low temperatures⁴. In those cases, improving the operating temperatures reduced the liquid hydrocarbon and amine losses.

Amine Solvents

The commonly used alkanol amines, including MEA, DEA, DGA, MDEA and MDEA-based specialty solvents, usually perform satisfactorily for liquid treating. Since the contact time between the two liquid phases is relatively long, more than adequate time is available for the relatively slow reaction between CO₂ and the amines, such as with MDEA. Therefore, it is possible to accurately model these systems using a theoretical stage approach, or discounting actual stages for realized efficiency. All the amines are degraded to some extent by COS and CO₂. However, DEA is degraded to a lesser extent. In addition, less reboiler heat is required to regenerate DEA due to higher solution concentrations, higher loading and lower heat of absorption. Thus, DEA is usually the best choice of solvent for a liquid treating process, unless a neighboring gas-liquid treating amine unit can provide a slipstream of an amine.

Rigorous calculation for the minimum required amine flow rate, the maximum product purity attainable and the relationship between amine flow rate and number of theoretical trays all need to be considered during design. The maximum LPG or NGL purity that's possible for a given process scenario would assume that equilibrium is reached in the extractor with the lean amine solution. In practice, it is necessary to regenerate the amine to acid gas concentrations below the levels that would be in equilibrium with the desired liquid hydrocarbon product purity.

The theoretical, minimum amine flow rate occurs when a rich amine that's leaving the contactor is in equilibrium with the entering liquid hydrocarbons. However, to provide an adequate driving force for mass transfer over the entire contactor, it is necessary to use an actual flow rate greater than the minimum. As a result, the rich solution loading is always below the equilibrium value.

Once the lean and rich amine solution loadings have been selected, the required solution flow rate can be calculated by a simple material balance. In addition, the volumetric flow rate ratio of the continuous phase (amine) to the dispersed phase (liquid hydrocarbon) should be more than a 1:30 ratio to ensure good mass transfer.

Modeling Liquid-Liquid Treatment in Aspen HYSYS

Acid Gas Cleaning is an integral functionality of version 8.3 or higher of Aspen HYSYS. The "Acid Gas – Chemical Solvents" property package in Aspen HYSYS provides thermodynamics based on the Electrolyte NRTL model with all the necessary aqueous-phase equilibrium and kinetics reactions required for rigorous calculations of the process⁵. The "Acid Gas - Physical Solvents" property package is available in version 8.6 and higher of Aspen HYSYS and is based on the Perturbed Chain Statistical Association Fluid Theory. Similar validation papers were published for the "Acid Gas - Chemical Solvents" and "Acid Gas - Physical Solvents" property packages. In version 9 of Aspen HYSYS, the Acid Gas Cleaning functionality has been extended with a new "Acid Gas - Liquid Treating" property package, which allows users to model the sweetening of liquid hydrocarbons with amine solvents.

The Acid Gas Cleaning property packages from AspenTech have been developed based on a wealth of phase equilibrium and other property data and proprietary models. These property packages have been shown to accurately predict experimental results over a range of operating conditions for the supported amine blends. The thermodynamic package technology for chemical solvent modeling is based on the Electrolyte Non-Random Two-Liquid (NRTL) model for electrolyte thermodynamics and the Peng-Robinson Equation of State for vapor phase and liquid hydrocarbon phase properties. Regression has been performed with available VLLE, VLE and LLE data for many major amine solvents used in the industry, such as MDEA, MEA, DEA, DGA and PZ+MDEA. (See Appendix I for proper names of these amines).

Aspen HYSYS has an equilibrium-stage model (liquid-liquid extractor in Figure 3) to simulate the liquid-liquid contactor (column or mixer) that provides the efficiency factor which allows users to match plant data. It also has two rate-based models for the simulation of the regenerator that are called "Efficiency" and "Advanced Modeling". The flowsheet shown in Figure 3, as well as additional models, are available pre-built within Aspen HYSYS (under the "Resources" tab). Tuning capabilities and factors are available for both the extractor and regenerator columns for making small corrections to the results for the purpose of matching plant data and operations.



Figure 3: LPG amine treating flowsheet in Aspen HYSYS simulation.

Column Analysis is a new functionality available in Aspen HYSYS V9. Aspen HYSYS was updated with the latest hydraulic correlation for trays and packing, as well as updated with an interactive, visual interface for inputs and results. To learn more about the features and how the results compare to experimental data, please refer to the white paper, **"Column Analysis in Aspen Plus® and Aspen HYSYS®: Validation with Experimental and Plant Data."**

Physical Properties Validation: Modeling Phase Equilibria in Liquid-Liquid Treatment

VLLE, LLE and VLE data from a broad range of pressures and temperatures were used for the development and validation of various systems. For the purpose of giving an example in this paper, the following systems related to propane (C_3H_8), which is usually the main component in the LPG stream, are shown in this section:

- C₃H₈-H₂O
- C₃H₈-MDEA-H₂O
- C₃H₈-MDEA-H₂O-CO₂

Literature References Used for Experimental Data

A list of references and the ranges of temperatures and pressures used in validation are presented in Tables 1-3.

Data Type	Т, К	Pressure, kPa	# of Data Points	Reference
VLLE	278-369	560-4400	13	Kobayashi ⁶
VLE	310-427	20690-21000	78	Kobayashi ⁶
LLE	310-369	1400-20000	57	Kobayashi ⁶

Table 1: C_3H_8 - H_2O experimental data used in this work.

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Data Type	Т, К	Pressure, kPa	MDEA Molefrac	# of Data Points	Reference
VLLE	273-370	470-4700	0.075	11	Carroll ⁷
VLLE	298-333	950-2100	0.048-0.131	11	Mokraoui ⁸
VLE	273-423	190-19000	0.075	33	Carroll ⁷
LLE	273-348	1000- 20000	0.075	24	Carroll ⁷

Table 2: C_3H_8 -MDEA- H_2O experimental data used in this work.

Data Type	Т, К	Pressure, kPa	MDEA Molefrac	CO ₂ Loading	# of Data Points	Reference
VLLE	298-313	960-5000	0.075	0-1.2	27	Jou ⁹

Table 3: C_3H_8 -MDEA- H_2O - CO_2 experimental data used in this work.

Aspen HYSYS Results Compared to Experimental Data

The fit of water content in the liquid propane phase, propane content in the aqueous phase and CO₂ content in the liquid propane phase are shown in Figures 4-9, respectively. These results indicate that the acid gas liquid-treating property package can adequately represent the phase behavior of these systems.



Figure 4: VLLE of C_3H_8 - H_2O water content in the propanerich phase. The circles represent the experimental data⁶ while the curves represent the results given by Aspen HYSYS.



Figure 5: VLLE of C_3H_8 - H_2O propane content in the aqueous phase. The circles represent the experimental data⁶ while the curves represent the results given by Aspen HYSYS.





Figure 6: VLLE of C_3H_8 -MDEA- H_2O water content in the propane-rich phase. The circles represent the experimental data⁷ while the curves represent the results given by Aspen HYSYS. The water solubility in this ternary system is close to that in the binary system of C_3H_8 - H_2O .



Figure 7: VLLE of C_3H_8 -MDEA- H_2O propane content in the aqueous phase. The circles represent the experimental data⁷ while the curves represent the results given by Aspen HYSYS. Propane solubility in the aqueous MDEA solution is higher than that in pure water.

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Figure 8: VLLE of C_3H_8 -MDEA- H_2O -CO₂ and CO₂ content in the propane-rich phase. The circles represent the experimental data⁹ while the curves represent the results given by Aspen HYSYS.



Figure 9: VLLE of C_3H_8 -MDEA- H_2O -CO₂ propane content in the aqueous phase. The circles represent the experimental data⁹ while the curves represent the results given by Aspen HYSYS.

Beside the above systems, many other systems were also regressed or validated against the experimental data for the liquid-liquid treating package. The quaternary systems of hydrocarbon-amine-water-acid gas and their subsystems (hydrocarbon-amine-water and hydrocarbon-water) were studied. The hydrocarbons in those systems included $CH_{4'}$, $C_2H_{6'}$, $C_3H_{8'}$, $n-C_4H_{10'}$, $i-C_4H_{10'}$, $n-C_5H_{12'}$, $n-C_6H_{14'}$, C_6H_{12} (cyclohexane), $C_6H_{6'}$, C_7H_8 (toluene) and C_8H_{10} (p-xylene), the amines included MDEA, MEA, DEA and DGA, and the acid gases included CO₂ and H₂S.

Flowsheet Validation

In addition to validating the thermodynamic model with physical properties data, the simulation model has also been studied against published data.

Static mixer contactor

In this case, a static mixer is used to treat an LPG stream containing 85% ethane and 0.6% CO_2 . The unit operating data is shown in Table 4, along with simulation results.

The mixer separator has a theoretical maximum efficiency equivalent to one ideal stage. Due to less than ideal mixing, the mixer usually achieves less than one ideal stage. As shown in Table 4, the static mixer achieved an efficiency of about 98.9% of one ideal stage, which compares favorably with the 98.7% efficiency obtained by Fleming et al¹⁰. When given a reasonable amine to LPG flowrates, a well-designed mixer can usually achieve 98% to 99% efficiency. However, efficiencies as low as 70% have been observed¹¹.

	Data	Simulation Assuming Theoretical Stages	Simulation Using Actual Tray Efficiency
Hydrocarbon Rate, gpm	240	240	240
T, F	110	110	110
P, psig	900	900	900
CO ₂ in, ppm	6000	6000	6000
CO ₂ out, ppm	100	10.4	104
Amine	DGA	DGA	DGA
wt%	30	30	30
Flow, gpm	85	85	85
Lean Loading	-	0.06	0.06
Rich Loading	-	0.21	0.21
Ideal Stages	1	1	1
Stage Efficiency, %	-	100	98.9

Table 4: Comparison of operating data for a static mixer¹¹ with simulation results.

Structured packing column

The use of packing increases the mass transfer in the LPG contactor by increasing the residence time of the LPG droplets, reducing the possibility of back-mixing and renewing the droplet surface film.

Random packing is usually less expensive to install than trays. In addition, the efficiency is usually higher with packing because the complex meanders in the packing act to continuously stir and break up LPG droplets that work their way up through the column. Each eight to twelve feet bed of random packing is approximately equivalent to one theoretical stage. Structured packing is an alternative that retains the advantages of random packing and sieve trays without the disadvantages, but is typically more expensive.

Rogers reported that for structured packing, the height of a theoretical stage is six to eight feet¹. However, lower efficiency is also observed. For instance, Table 5 shows a case where 20 feet of structured packing behaves as one ideal stage with 98.7% efficiency.

	Data	Simulation Assuming Theoretical Stages	Simulation Using Actual Tray Efficiency
Hydrocarbon Rate, gpm	1750	1750	1750
T, F	60	60	60
P, psia	800	800	800
CO ₂ in, ppm	6100	6100	6100
CO ₂ out, ppm	<300	183	300
Amine	MDEA	MDEA	MDEA
wt%	35	35	35
Flow, gpm	210	210	210
Lean Loading	-	0.08	0.08
Rich Loading	-	0.21	0.21
Structured Packing Height, ft	20	-	-
Ideal Stages	1	1	1
Stage Efficiency, %	-	100	98.7

Table 5: Comparison of operating data for a structured packing column¹ with simulation results.

Sieve tray column

While the vast majority of LPG treaters utilize packing, sieve trays are occasionally used. The operating data and simulation results are given in Table 6. In this case, a column with 20 sieve trays was used to treat a LPG stream containing 0.3% H₂S. As shown in Table 6, the performance of this sieve tray column corresponds to roughly two ideal stages. This is consistent with the report from Holmes and co-workers stating that a 10-sieve tray column achieved a CO₂ removal efficiency of one idea stage¹². Usually, 10 to 20 trays are required to achieve the equivalent of one ideal stage.

	Data	Simulation Using Two Ideal Stages	Simulation Using One Ideal Stage
Hydrocarbon Rate, gpm	671	671	671
T, F	110	110	110
P, psig	150	150	150
H ₂ S in, ppm	3000	3000	3000
H ₂ S out, ppm	<4	4.38	229
Amine	MDEA	MDEA	MDEA
wt%	40	40	40
Flow, gpm	60	60	60
Lean Loading	0.002	0.002	0.002
Rich Loading	0.1	0.1	0.096
No. of Trays	20	-	-
Ideal Stages	-	2	1
Stage Efficiency, %	-	100	100

Table 6: Comparison of operating data for a sieve tray column with simulation results¹.

Conclusion

The acid gas liquid-treating property package and related functionality in Aspen HYSYS is based on the electrolyte NRTL thermodynamic model and the equilibrium-stage simulation for liquid-liquid contactors. The thermodynamic package and the simulation model in Aspen HYSYS were tested against experimental and plant data. The results show a good match at a wide range of operating conditions.

Do you need help validating your models? AspenTech can help meet your business objectives, while improving the technology. If you would like us to compare your plant data with our model predictions, please get in touch with Jennifer Dyment by emailing **Jennifer.Dyment@aspentech.com**.

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Appendix I

Abbreviations

MDEA	Methyldiethanolamine
MEA	Monoethanolamine
DEA	Diethanolamine
PZ	Piperazine
DGA	2-(2-Aminoethoxy) Ethanol (Diglycolamine)

AspenTech is a leading supplier of software that optimizes process manufacturing — for energy, chemicals, engineering and construction, and other industries that manufacture and produce products from a chemical process. With integrated aspenONE[®] solutions, process manufacturers can implement best practices for optimizing their engineering, manufacturing, and supply chain operations. As a result, AspenTech customers are better able to increase capacity, improve margins, reduce costs, and become more energy efficient. To see how the world's leading process manufacturers rely on AspenTech to achieve their operational excellence goals, visit www.aspentech.com.

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