Chapter 1

Troubleshooting Distillation Simulations

It may appear inappropriate to start a distillation troubleshooting book with a malfunction that did not even make it to the top 10 distillation malfunctions of the last half century. Simulations were in the 12th spot (255). Countering this argument is that simulation malfunctions were identified as the fastest growing area of distillation malfunctions, with the number reported in the last decade about triple that of the four preceding decades (252). If one compiled a distillation malfunction list over the last decade only, simulation issues would have been in the equal 6th spot. Simulations have been more troublesome in chemical than in refinery towers, probably due to the difficulty in simulating chemical nonidealities. The subject was discussed in detail in another paper (247).

The three major issues that affect simulation validity are using good vapor–liquid equilibrium (VLE) predictions, obtaining a good match between the simulation and plant data, and applying graphical techniques to troubleshoot the simulation (255). Case histories involving these issues account for about two-thirds of the cases reported in the literature. Add to this ensuring correct chemistry and correct tray efficiency, these items account for 85% of the cases reported in the literature.

A review of the VLE case studies (247) revealed major issues with VLE predictions for close-boiling components, either a pair of chemicals [e.g., hydrocarbons (HCs)] of similar vapor pressures or a nonideal pair close to an azeotrope. Correctly estimating nonidealities has been another VLE troublespot. A third troublespot is characterization of heavy components in crude oil distillation, which impacts simulation of refinery vacuum towers. Very few case histories were reported with other systems. VLE prediction for reasonably ideal, relatively high volatility systems (e.g., ethane–propane or methanol–ethanol) is not frequently troublesome.

The major problem in simulation validation appears to be obtaining a reliable, consistent set of plant data. Getting correct numbers out of flowmeters and laboratory analyses appears to be a major headache requiring extensive checks and rechecks. Compiling mass, component, and energy balances is essential for catching a
misleading flowmeter or composition. One specific area of frequent mismatches between simulation and plant data is where there are two liquid phases. Here comparison of measured to simulated temperature profiles is invaluable for finding the second liquid phase. Another specific area of frequent mismatches is refinery vacuum towers. Here the difficult measurement is the liquid entrainment from the flash zone into the wash bed, which is often established by a component balance on metals or asphaltenes.

The key graphical techniques for troubleshooting simulations are the McCabe–Thiele and Hengstebbeck diagrams, multicomponent distillation composition profiles, and in azeotropic systems residue curve maps. These techniques permit visualization and insight into what the simulation is doing. These diagrams are not drawn from scratch; they are plots of the composition profiles obtained by the simulation using the format of one of these procedures. The book by Stichlmair and Fair (472) is loaded with excellent examples of graphical techniques shedding light on tower operation.

In chemical towers, reactions such as decomposition, polymerization, and hydrolysis are often unaccounted for by a simulation. Also, the chemistry of a process is not always well understood. One of the best tools for getting a good simulation in these situations is to run the chemicals through a miniplant, as recommended by Ruffert (417).

In established processes, such as separation of benzene from toluene or ethanol from water, estimating efficiency is quite trouble free in conventional trays and packings. Problems are experienced in a first-of-a-kind process or when a new mass transfer device is introduced and is on the steep segment of its learning curve.

Incorrect representation of the feed entry is troublesome if the first product leaves just above or below or if some chemicals react in the vapor and not in the liquid. A typical example is feed to a refinery vacuum tower, where the first major product exits the tower between 0.5 and 2 stages above the feed.

The presentation of liquid and vapor rates in the simulation output is not always user friendly, especially near the entry of subcooled reflux and feeds, often concealing higher vapor and liquid loads. This sometimes precipitates underestimates of the vapor and liquid loads in the tower.

Misleading hydraulic predictions from simulators is a major troublespot. Most troublesome have been hydraulic predictions for packed towers, which tend to be optimistic, using both the simulator methods and many of the vendor methods in the simulator (247, 254). Simulation predictions of both tray and packing efficiencies as well as downcomer capacities have also been troublesome. Further discussion is in Ref. 247.

**CASE STUDY 1.1 METHANOL IN C3 SPLITTER OVERHEAD?**

**Installation**  Olefins plant C3 splitter, separating propylene overhead from propane at pressures of 220–240 psig, several towers.
Case Study 1.1  Methanol in C₃ Splitter Overhead?

Background  Methanol is often present in the C₃ splitter feed in small concentrations, usually originating from dosing upstream equipment to remove hydrates. Hydrates are loose compounds of water and HCs that behave like ice, and methanol is used like antifreeze. The atmospheric boiling points of propylene, propane, and methanol are −54, −44, and 148°F, respectively. The C₃ splitters are large towers, usually containing between 100 and 300 trays and operating at high reflux, so they have lots of separation capability.

Problem  Despite the large boiling point difference (about 200°F) and the large tower separation capability, some methanol found its way to the overhead product in all these towers. Very often there was a tight specification on methanol in the tower overhead.

Cause  Methanol is a polar component, which is repelled by the nonpolar HCs. This repulsion is characterized by a high activity coefficient. With the small concentration of methanol in the all-HC tray liquid, the repulsion is maximized; that is, the activity coefficient of methanol reaches its maximum (infinite dilution) value. This high activity coefficient highly increases its volatility, to the point that it almost counterbalances the much higher vapor pressure of propylene. The methanol and propylene therefore become very difficult to separate.

Simulation  All C₃ splitter simulations that the author worked with have used equations of state, and these were unable to correctly predict the high activity coefficient of the methanol. They therefore incorrectly predicted that all the methanol would end up in the bottom and none would reach the tower top product.

Solution  In most cases, the methanol was injected upstream for a short period only, and the off-specification propylene product was tolerated, often blended in storage. In one case, the methanol content of the propylene was lowered by allowing some propylene out of the C₃ splitter bottom at the expense of lower recovery.

Related Experience  A very similar experience occurred in a gas plant depropanizer separating propane from butane and heavier HCs. Here the methanol ended in the propane product.

Other Related Experiences  Several refinery debutanizers that separated C₃ and C₄ [liquefied petroleum gases (LPGs)] from C₅ and heavier HCs (naphtha) contained small concentrations of high-boiling sulfur compounds. Despite their high boiling points (well within the naphtha range), these high boilers ended in the overhead LPG product. Sulfur compounds are polar and are therefore repelled by the HC tray liquid. The repulsion (characterized by their infinite dilution activity coefficient) made these compounds volatile enough to go up with the LPG. Again, tower simulations that were based on equations of state incorrectly predicted that these compounds would end up in the naphtha.
In one refinery and one petrochemical debutanizer, mercury compounds with boiling points in the gasoline range were found in the LPG, probably reaching it by a similar mechanism.

**CASE STUDY 1.2 WATER IN DEBUTANIZER: QUO VADIS?**

**Installation**  A debutanizer separating C₄ HCs from HCs in the C₅–C₈ range. Feed to the tower was partially vaporized in an upstream feed-bottom interchanger. The feed contained a small amount of water. Water has a low solubility in the HCs and distilled up. The reflux drum was equipped with a boot designed to gravity-separate water from the reflux.

**Problem**  When the feed contained a higher concentration of water or the reflux boot was inadvertently overfilled, water was seen in the tower bottoms.

**Cause**  The tower feed often contained caustic. Caustic deposits were found in the tower at shutdown. Sampling the water in the tower bottom showed a high pH. Analysis showed that the water in the bottom was actually concentrated caustic solution.

**Prevention**  Good coalescing of water and closely watching the interface level in the reflux drum boot kept water out of the feed and reflux. Maximizing feed preheat kept water in the vapor.

**CASE STUDY 1.3 BEWARE OF HIGH HYDROCARBON VOLATILITIES IN WASTEWATER SYSTEMS**

Benzene was present in small concentration, of the order of ppm, in a refinery wastewater sewer system. Due to the high repulsion between the water and benzene molecules, benzene has a high activity coefficient, making it very volatile in the wastewater.

Poor ventilation, typical of sewer systems, did not allow the benzene to disperse, and it concentrated in the vapor space above the wastewater. The lower explosive limit of benzene in air is quite low, about a few percent, and it is believed that the benzene concentration exceeded it at least in some locations in the sewer system.

The sewer system had one vent pipe discharging at ground level without a gooseneck. A worker was doing hot work near the top of that pipe. Sparks are believed to have fallen into the pipe, igniting the explosive mixture. The pipe blew up into the worker's face, killing him.

**Morals**

- Beware of high volatilities of HCs and organics in a wastewater system.
- Avoid venting sewer systems at ground level.
Case Study 1.4  A Hydrocarbon VLLE Method Used For Aqueous Feed Equilibrium

CASE STUDY 1.4  A HYDROCARBON VLLE METHOD USED FOR AQUEOUS FEED EQUILIBRIUM

Contributed by W. Randall Hollowell, CITGO, Lake Charles, Louisiana

Installation  Feed for a methanol–water separation tower was the water–methanol phase from a three-phase gas–oil–aqueous separator. Gas from the separator was moderately high in H₂S and in CO₂. Tower preliminary design used a total overhead condenser to produce 95% methanol. Methanol product was cooled and stored at atmospheric pressure. Off gas from storage was not considered a problem because the calculated impurities in the methanol product were predominantly water.

Problem  Tower feed had been calculated with a standard gas-processing vapor–liquid–liquid equilibrium (VLLE) method (Peng–Robinson equation of state). A consultant noted that the VLLE method applied only to aqueous phases that behaved like pure water and only to gas-phase components that had low solubility in the aqueous phase.

The large methanol content of the aqueous phase invalidated these feed composition calculations. Every gas component was far more soluble in the tower feed than estimated. The preliminary tower design would have produced a methanol product with such a high H₂S vapor pressure that it could not be safely stored in the atmospheric tank.

Better Approach  Gas solubility in a mixed, non-HC solvent (methanol and water) is a Henry’s constant type of relationship for which process simulation packages often do not have the methods and/or parameters required.

Addition of a pasteurization section to the top of a tower is a common fix for removing light impurities from the distillate product. After condensing most of the overhead vapor, a small overhead vent gas stream is purged out of the tower to remove light ends. Most or all of the overhead liquid is refluxed to minimize loss of desired product in the purges. The pasteurization section typically contains 3–10 trays or a short packed bed, used to separate light ends from the distillate product. The distillate product is taken as a liquid side draw below the pasteurization trays. The side draw may be stripped to further reduce light ends. The vent gas may be refrigerated and solvent washed or otherwise treated to reduce loss of desired product.

Solution  An accurate, specific correlation (outside of the process simulation package) was used to calculate H₂S and CO₂ concentration in the methanol–water tower feed. Solubility of HC components was roughly estimated because they were at relatively low concentrations in the tower feed. A high-performance coalescer was used to minimize liquid HC droplets in the tower feed.

A pasteurization section was added to the top of the tower. The overhead vent gas purge stream was designed to remove most of the H₂S, CO₂, and light HCs. Downstream recovery of methanol from the vent gas and stripping of the methanol product side draw were considered but found to be uneconomical.
Moral Poor simulation and design result from poor selection of VLE and VLLE methods. Computer output does not include a warning when the selected VLE method produces garbage.

CASE STUDY 1.5 MODELING TERNARY MIXTURE USING BINARY INTERACTION PARAMETERS

Contributed by Stanislaw K. Wasylkiewicz, Aspen Technology, Inc., Calgary, Alberta, Canada

This case study describes a frequently encountered modeling problem during simulation of heterogeneous azeotropic distillation. Phase diagrams are invaluable for troubleshooting this type of simulation problems.

Distillation Simulation A sequence of distillation columns for separation of a mixture containing water and several organic alcohols was set up in a simulator. Since some of the alcohols are not fully miscible with water, a nonrandom two-liquid (NRTL) model was selected to model VLLE in the system. At atmospheric pressure, the vapor phase was treated as an ideal gas.

Problem Simulation of the sequence of distillation columns never converged, giving many warnings about flash failures.

Investigation For the three key components (methanol, water, and \( n \)-butanol) a phase diagram was created (508) (Fig. 1.1a). As expected, the water–methanol and methanol–\( n \)-butanol edges are homogeneous and the water–\( n \)-butanol edge contained an immiscibility gap. Surprisingly, the three-liquid region and three two-liquid regions covered almost the entire composition space. Since water and methanol, as well as butanol and methanol, are fully miscible, the diagram should have been dominated by a single-liquid region. Just looking at the phase diagram one can conclude that the model is not correct.

Analysis Binary interaction parameters for activity models used for VLLE calculations are published for thousands of components [see, e.g., DEHEMA (158) series]. They are regressed based on various experimental data and usually fit the experimental points quite well. NRTL, UNIQUAC, and Wilson models extend these binary data to multicomponent systems without requiring additional ternary, quaternary, and so on, interaction parameters. That is why these models are so popular for modeling VLE for strongly nonideal azeotropic mixtures. This extension, however, is not always performed correctly by the model.

For the ternary mixture methanol–water–\( n \)-butanol, the binary interaction parameters have been taken from DEHEMA (158). Some of them are recommended values. All of them describe all the binary pairs very well. But what they predict when combined together can be seen in Figure 1.1a. Notice that to create this VLLE diagram an extremely robust flash calculation with stability test is essential. Without a reliable global stability test, flash calculation can easily fail at some points in this component space or give unstable solutions (526).
Figure 1.1  Phase diagram for nonideal system methanol–water–n-butanol, based on extension of good binary data using NRTL model: (a) incorrect extension; (b) correct extension.
Solution Another set of binary interaction parameters was carefully selected and a new phase diagram was recreated (34). The VLLE changed dramatically (Fig. 1.1b). There is no more three-liquid phase region and only one two-liquid phase region covers only a small part of the composition space. After proper selection of interaction parameters of the thermodynamic model, the sequence of distillation columns converged quickly without any problems.

Morals
- To simulate multicomponent, nonideal distillation, the behavior of the mixture must be carefully verified, starting from binary mixtures, then ternary subsystems, and so on.
- Since there may be many pairs of binary interaction parameters of an activity thermodynamic model that describe behavior of a binary mixture equally well, it is recommended to select one with the lowest absolute values. It is our experience that such values extrapolate better to multicomponent mixtures.
- To correctly create a multicomponent, nonideal VLLE model, an extremely robust VLLE calculation routine with a reliable global stability test is a must [even if liquid–liquid (LL) split is not expected].
- Because of their visualization capabilities, VLLE phase diagrams are invaluable (for ternary and quaternary mixtures) for verification of thermodynamic models used in distillation simulations.

**CASE STUDY 1.6 VERY LOW CONCENTRATIONS REQUIRE EXTRA CARE IN VLE SELECTION**

**Contributed by W. Randall Hollowell, CITGO, Lake Charles, Louisiana**

**Problem**  Bottoms from a tower recovering methanol from a methanol–water mixture contained 6 ppm methanol, exceeding the maximum specification of 4 ppm required for discharging to the ocean.

**Investigation**  A consultant pointed out that unusual hydrogen-bonding behavior had been reported at very low concentration of methanol in water. He recommended use of the UNIQUAC equation.

Wilson’s equation is generally the method of choice for alcohol–water mixtures when there is no unusual behavior. The more complex NRTL equation is the usual choice for systems that cannot be handled by Wilson’s equation. The UNIQUAC equation often applies to systems with chemically like interactions (i.e., hydrogen bonding, which behaves like weak chemical bonding) that neither Wilson’s nor the NRTL equations can represent.

**Solution**  Schedule constraints precluded independently developing UNIQUAC parameters. Various process simulation packages were checked for methanol–water VLE with Wilson’s, NRTL, and UNIQUAC equations. All of the equations in all of the packages gave essentially the same VLE, except that UNIQUAC in one major
simulator gave lower methanol relative volatilities (by as much as 15%) at very low methanol concentrations. This package executed much slower than the other alternatives. The only methanol concentration predictions that were in line with the field data came from this UNIQAC equation.

**Postmortem** Exceptions to the typical choices of chemical VLE methods are often not reflected in process simulation packages. For this case, the same data base was probably used by all of the process simulation packages for the regression of UNIQUAC parameters. Predicting VLE for high-purity mixture often requires extrapolation of activity coefficients. Only one method and one simulation package did a good extrapolation to the low-methanol end. Cross checking of VLE equations and packages is a useful way to identify potential problems.

**CASE STUDY 1.7 DIAGRAMS TROUBLESHOOT ACETIC ACID DEHYDRATION SIMULATION**

Contributed by Stanislaw K. Wasylikiewicz, Aspen Technology, Inc., Calgary, Alberta, Canada

This case study describes a typical thermodynamic modeling problem in distillation simulation and an application of residue curve maps for troubleshooting and proper model selection. The problem described here happened far too many times for many of our clients.

**Dehydration of Acetic Acid** At atmospheric pressure, there is no azeotrope in the binary mixture of water and acetic acid. However, there is a tangent pinch close to pure water. This makes this binary separation very expensive if only a small concentration of acetic acid in water is allowed (high reflux, many rectifying stages). The difficult separation caused by the tangent pinch can be avoided by adding an entrainer that forms a new heterogeneous azeotrope, moving the distillation profile away from the binary pinch toward the minimum-boiling heterogeneous azeotrope. A decanter can then be used to obtain required distillate purity in far fewer stages than in the original binary distillation (525).

**Distillation Simulation** A column with top decanter was set up in a simulator to remove water from a mixture containing mostly water and acetic acid. N-Butyl acetate was selected as an entrainer. The vapor phase was treated as an ideal gas [*Idel* (227) option]. For the liquid phase, the NRTL model was selected.

**Problem** Even with an extreme reflux and a large number of stages, the simulation never achieved the required high-purity water in the bottom product of the column.

**Troubleshooting** For the three key components (water, acetic acid, and the entrainer) a distillation region diagram (DRD) was created (227) to examine the three-component space for multiple liquid regions, azeotropes, and distillation boundaries, as shown in Figure 1.2a.
Figure 1.2  Phase diagram for dehydration of acetic acid using \( n \)-butyl acetate (\( n \)-B-C2-oate) entrainer at 1 atm: (a) with ideal vapor phase, incorrect; (b) accounting for dimerization, correct.
Case Study 1.8  Everything Vaporized in a Crude Vacuum Tower Simulation

Analysis  By examining the DRD, one can easily conclude that there is something wrong with the model. We know that there is no binary acetic acid–water azeotrope at 1 atm. The model (ideal vapor phase) is not capable of describing the system properly. It is well known that carboxylic acids associate in the vapor phase and this has to be taken into account, for example, by vapor dimerization model (158) [Dimer option (227)].

Solution  Instead of Idel, the Dimer option was selected (227). The DRD for the system changed tremendously (see Fig. 1.2b). There are no more binary azeotropes between acetic acid and water or n-butyl acetate. After proper selection of the thermodynamic model, the distillation column converged quickly to the required high-purity water specifications in the bottoms.

Morals
- It is important to select the proper thermodynamic model and carefully verify the behavior of the mixture.
- Because of their visualization capabilities, DRDs are extremely useful for evaluating thermodynamic models for ternary and quaternary mixtures.

CASE STUDY 1.8 EVERYTHING VAPORIZED IN A CRUDE VACUUM TOWER SIMULATION

Contributed by W. Randall Hollowell, CITGO, Lake Charles, Louisiana

Problem  Atmospheric crude tower bottom was heated, then entered a typical, fuel-type vacuum tower. A hand-drawn curve estimated the atmospheric crude tower bottom composition from assay distillation data for a light crude oil. The simulation estimated that all of the vacuum tower feed vaporized in the flash zone. This was a preposterous result inconsistent with plant data.

Investigation  The heaviest assay cuts fell progressively lower than those from another assay of the same crude oil. The heaviest cut was at 850°F atmospheric cut point, compared to the other assay at 1000°F. The assay data were extrapolated on a linear scale to 100% at 1150°F atmospheric boiling point.

The high-boiling part of crude assay data must be carefully assessed. The last several assay points are often poor, particularly when coming from laboratories that cut back on quality control for increased productivity. Crude oils have very high boiling point material. Even light crude oils have material boiling above 1500°F. Extrapolation should be done with percent distilled on a probability-type scale, particularly for light crudes where the slope increases very rapidly on a linear scale.

Solution  A new boiling point curve was developed. Another assay was used up to 1000°F cut point, thus reducing the needed extrapolation range. Extrapolation and smoothing of assay data were based upon a probability scale for percent distilled.
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A 95% point (whole crude oil basis) of 1400°F was estimated by this extrapolation. Simulation based upon the new boiling point curve was in reasonable agreement with plant data.

Moral Crude oil high-boiling-point data are often poor and must be extrapolated. Experience, following good procedures, and cross checks with plant data are essential for reliable results.

CASE STUDY 1.9 CRUDE VACUUM TOWER SIMULATION UNDERESTIMATES RESIDUE YIELD

Contributed by W. Randall Hollowell, CITGO, Lake Charles, Louisiana

Problem Process simulation estimated much lower vacuum residue yields than obtained from plant towers and from pilot unit runs. Vacuum tower feed boiling point curves were based upon high-temperature gas chromatography (GC) analyses.

Investigation Vacuum tower feed boiling point curves from the GC fell well below curves estimated from assays. The GC analyses assumed that all of the feed oil vaporized in the test and was analyzed.

The highest boiling part of crude oil is too heavy to vaporize in a GC test. Thus the reported GC results did not include the highest boiling part (that above about 1250°F boiling point) of the feed. Simulations based upon this GC data estimated much higher vaporization than actual because they were missing the heaviest part of the feed.

Solution The GC method was modified to include a standard that allowed estimation of how much oil remained in the GC column and was not measured. New GC data and extrapolations of assay data indicated that 10–15% of the feed oil was not vaporized and thus had not been measured by the earlier GC method.

With this improved GC data, simulations agreed well with most of the pilot data. The agreement between simulation and plant data was much better than before but was still not good. This may have been due to poor plant data. Specifically, measured flash zone pressures were often bad.

Moral The analyses used for process simulations must be thoroughly understood.

CASE STUDY 1.10 MISLED BY ANALYSIS

Contributed by Geert Hangx and Marleen Horsels, DSM Research, Geleen, The Netherlands

Problem After a product change in a multipurpose plant, a light-boiling by-product could not be removed to the proper level in the (batch) distillation. The concentration
of the light-boiling component in the final product was 0.5%. It should have been (and was in previous runs) 200 ppm.

**Investigation** The feed was analyzed by GC per normal procedure. The concentration levels of different components looked good. No significant deviation was found. Then some changes in the distillation were performed, such as

- increasing the “lights fraction” in the batch distillation,
- increasing the reflux ratio during the lights fraction, and
- decreasing the vapor load during the lights fraction.

These changes yielded no significant improvement.

The off-specification product was redistilled. The purity was improved, but still the specification could not be met. The GC analysis was checked (recalibrated) again. Everything was OK.

As all of the above-mentioned actions did not improve the product quality, it seemed that something was wrong with the column. After long discussions it was decided to open the handhole at the top of the column and to have a closer look at the feed distributor. Nothing suspicious was found.

Then it was decided to have a closer look at the analysis again. A gas chromatography–mass spectrometry (GC-MS) analysis was performed. This method showed that the impurity was not the light-boiling component as presumed. This component was a remainder from the previous run in the multipurpose plant. Having a boiling point much closer to the end product, this component could not be separated in the column.

**Moral** It is a good idea to check the analysis with GC-MS before shutting down a column.

**CASE STUDY 1.11 INCORRECT FEED CHARACTERIZATION LEADS TO IMPOSSIBLE PRODUCT SPECIFICATIONS**

Contributed by Chris Wallsgrove

**Installation** A new, entirely conventional depentanizer, recovering a C₅ distillate stream from a C₅/C₆/C₇ raffinate mixture from a catalytic reformer/aromatics extraction unit, with some light pyrolysis gasoline feed from an adjacent naphtha-cracking ethylene plant. The column had 30 valve trays, a steam-heated reboiler, and a condenser on cooling water.

**Problem** The C₅ distillate was guaranteed by the process licensor to contain a maximum of 0.5% wt. C₆’s. Laboratory testing by the on-site laboratory as well
as an impartial third-party laboratory consistently showed about 1.0% of C₆’s in the distillate. Increasing reflux ratio or other operation adjustments did not improve distillate purity.

**Troubleshooting**  The tower was shut down after about 6 weeks of operation to inspect the trays. No damage was found and the trays were reported to be “cleaner than new.”

The design simulation was rerun with a variety of options: correlations, convergence criteria, and plant analysis data. The laboratory methods, which were established American Society for Testing and Materials (ASTM) test methods, were reviewed. It became apparent that the feed contained some low-boiling components, such as certain methyl-cyclo C₅’s which were analyzed (correctly) as C₆’s but whose boiling points are in the C₅ range. Since these components would end up in the distillate, it was thermodynamically impossible to achieve the specified performance.

**Solution**  The higher impurity level could be lived with without excessive economic penalty and was accepted.

**Moral**  Correct characterization of feed components is essential even for an “ideal” hydrocarbon mixture.

**CASE STUDY 1.12  CAN YOU NAME THE KEY COMPONENTS?**

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**Installation**  A stabilizer separating C₃ and lighter HC’s from nC₄ and heavier operated at its capacity limit. It was to be debottlenecked for a 25% increase in capacity. In addition, it was required to handle several different feedstocks at high throughputs. Due to the tight requirements, thorough tests were conducted and formed the basis for a simulation, which was used for the debottlenecking. We have seen very few tests as extensive and thorough as the stabilizer tests. Two tests were conducted: a high-reflux (HR) test and a low-reflux (LR) test.

**Simulation Versus Measurement**  With two seemingly minor and insignificant exceptions, all reliable measurements compared extremely well with simulated values. In most tests, the accuracy and reliability of the data would have made it difficult to judge whether the exceptions were real or reflected a minor test data problem. In this case, however, consistency checks verified that the exceptions were real. The high accuracy and reliability of the test data made even small discrepancies visible and significant.
The discrepancies occurred in the HR test, while the LR test showed no discrepancy. This was strange because the stabilizer was extremely steady and smooth during the HR test. Any data problems should have occurred in the LR test or in both tests, but not in the HR test alone.

The two exceptions were interlinked. For the HR test, the simulation predicted three times the measured C₅ concentration in the stabilizer overhead, which would lead to a warmer rectifying section. Indeed, the second exception was simulated rectifying section temperatures 2–5°F warmer than measured.

What Does the Stabilizer Do? At first glance, this question appears stupid. But it turned out to be the key for understanding the test versus the simulation discrepancy.

There was a tight specification on the content of C₃ in the stabilizer bottoms. An excessive amount of C₃ would lead to excessive Reid vapor pressure (RVP) in the bottom, which was undesirable. For similar reasons, it was desirable to minimize iC₄ in the stabilizer bottom, although there was no set specification. In the bottoms, nC₄ and heavier were desirable components and were to be maximized. Any C₅ and heavier, and even nC₄, ending up in the overhead product incurred an economic penalty because the bottoms were far more valuable than the overheads. There were no set specifications for any of these components.

With the above in mind, what is the stabilizer actually doing? Which pair is the key components? Initially, we thought it was iC₄/nC₄—but could it have been C₃/iC₄, nC₄/C₅, C₃/C₅, or maybe some other pair? Computer simulations do not answer such questions; Hengstebeck diagrams (211, described in detail in Ref. 251) do.

Hengstebeck diagrams (Fig. 1.3) were prepared from the compositions calculated by the simulation. The HR and LR tests each require one Hengstebeck diagram for each choice of key components: C₃/iC₄, iC₄/nC₄, and nC₄/iC₅. A Hengstebeck diagram for the iC₄/nC₄ separation was included in a more detailed description of the case (254) and showed that this pair behaved the same as the C₃/iC₄ pair.

Figure 1.3a shows that in the HR test, below the feed, the stabilizer effectively separated C₃ and lighter from iC₄ and heavier. The diagram also shows that a limited degree of separation of these components occurred in the top two stages of the rectifying section, but pinching occurred below these. Overall, very little separation of C₃ and lighter from iC₄ and heavier occurred in the rectifying section. The stabilizer essentially behaved as a stripper for separating C₃ and lighter from iC₄ and heavier.

Figure 1.3b shows that in the HR test, above the feed, the stabilizer effectively separated nC₄ and lighter from iC₅ and heavier. It also illustrates that some separation of these components took place in the bottom five stages of the stripping section, but pinching occurred above these.

Together, Figures 1.3a and b underscore that the stripping section of the stabilizer separated C₃ and lighter from iC₄ and heavier and, per Ref. 254, also iC₄ and lighter from nC₄ and heavier. The rectifying section of the stabilizer separated iC₅ and heavier from nC₄ and lighter.
Figure 1.3  Hengstebeck diagrams for stabilizer tests: (a) C$_3$–iC$_4$ separation, HR test; (b) nC$_4$–iC$_5$ separation, HR test; (c) nC$_4$–iC$_5$ separation, LR test. (From Ref. 254. Reproduced with permission. Copyright © (1995) AIChE. All rights reserved.)
In the LR test, the Hengstebeck diagrams for the C3/iC4 and iC4/nC4 separation were similar to those for the HR test (Fig. 1.3a). In this test, too, the stabilizer stripping section effectively separated C3 and lighter from iC4 and heavier and iC4 and lighter from nC4 and heavier.

Figure 1.3c indicates that in the LR test, above the feed, the separation of nC4 and lighter from iC5 and heavier was pinched. This is different from the HR test, where the rectifying section effectively separated nC4 and lighter from iC5 and heavier. The diagram also shows that, as in the HR test, the nC4/iC5 separation was pinched in the stripping section.

Overall, the stabilizer behavior in the LR test resembled that of HR test, with the exception that the rectifying section, which separated nC4 from iC5 in the HR test, was pinched and did little of this separation in the LR test.

**Why the Differences Between Measurement and Simulation?** There were two conceivable explanations to the high C5 concentration in the HR test simulation:

1. *Inaccuracies in VLE data.* Detailed checks of the VLE confirmed that the values used were very good and superior to those predicted by the commercial simulator program, but not perfect. Two relevant inaccuracies were a high C3/iC4 volatility prediction for the stripping section and a low C4/C5 volatility prediction for the rectifying section.

2. *Efficiency differences between different binary pairs.* This explanation was unlikely because the simulation would suggest a considerably higher efficiency for the higher volatility pair, nC4/iC5, than for the lower volatility pair, iC4/nC4. In contrast, test data (52, 379, 381) show that lower volatility pairs have a higher efficiency.

It was therefore concluded that VLE inaccuracy is the most likely explanation.

One unanswered question is why the differences between measurement and simulation were observed only in the HR test and not in the LR test. Again, the Hengstebeck diagrams provided the answer.

For the HR test, the Hengstebeck diagram (Fig. 1.3b) shows that the rectifying section rectifies C5 from the nC4 and lighter. Any error in the relative volatility of the nC4/iC5 and nC4/nC5 pairs is magnified at each separation stage. The final result is a large difference between measured and simulated top-product compositions.

For the LR test, the Hengstebeck diagram (Fig. 1.3c) shows very little separation of nC4 from C5 in the rectifying section. Because of the pinch, an error in the relative volatility of the nC4/iC5 and nC4/nC5 pairs is not magnified in each separation stage. Such an error, therefore, has little effect on the separation and the temperature profile. For this reason, the LR test simulation gave a good match to measured data.

**Would the Inaccuracy Affect the Debottlenecking Predictions?** The simulation predicted higher C5 in the top product, giving a conservative forecast of
the stabilizer performance under test conditions. The remaining question is whether the simulation will continue to give conservative predictions under different process conditions. The question of extrapolating test data into different process conditions is addressed rigorously on pp. 400–405 of Ref. 251. In fact, the analysis in Ref. 251 was part of the stabilizer-debottlenecking assignment. The conclusion reached was that when test data are simulated with too low a volatility the simulation compensates by using a greater number of stages (and, hence, higher efficiencies) to match the measured separation. In this case (e.g., the nC₄/C₅ pair in the stabilizer), the simulation will continue to give conservative predictions when extrapolated into different process conditions.

The converse occurs when test data are simulated with too high a relative volatility. The simulation compensates by using a smaller number of stages to match the measured separation. In this case (e.g., the C₃/iC₄ pair in the stabilizer), extrapolation to other process conditions will be optimistic, sometimes grossly so.

Based on the above, it was concluded that the simulation was a reliable basis for debottlenecking for the base case (similar feedstock to that used in one of the tests) and for alternative feedstocks that are not widely different from the base case. However, for those cases of feedstock variations where feed composition varied widely from the base case, the simulation could not be used with confidence until the inaccuracy in the C₃/iC₄ relative volatility was mitigated.

**Postmortem** The column was successfully debottlenecked. The same simulation (modified to account for the debottlenecking hardware modifications) was found to give superb predictions of the post-revamp performance.

**CASE STUDY 1.13 LOCAL EQUILIBRIUM FOR CONDENSERS IN SERIES**

Contributed by W. Randall Hollowell, CITGO, Lake Charles, Louisiana

This is my all-time favorite fractionation simulation problem. The entire refinery capacity was sometimes limited by the gas rate, which was calculated to be zero.

**Installation** An atmospheric crude distillation tower had an extremely broad boiling range overhead vapor with significant ethane, high propane, through full-range kerosene. There were three long, double split-flow condensers in series. The shells were flange to flange and located directly above the overhead accumulator.

**Problem** Simulation predicted a zero off-gas rate at peak summer temperatures. But actual off-gas rates were substantial, even in winter. Summer crude charge rate was sometimes reduced to avoid flaring of gas in excess of compressor capacity. There was a strong economic incentive to increase butane spiking of crude, but this was not done due to concerns that the gas rate would increase.
Component Balances  Earlier calculations had failed to obtain an adequate material balance of the lightest components in the overhead. The naphtha GC analyses were found to be poor. Procedures were corrected by the laboratory, and good material balance closures were obtained.

Simulations predicted that all of the exiting vapor off gas should have been absorbed into the naphtha stream at the operating temperature and pressure. The naphtha had much lower light-ends concentrations than predicted: 30% of the predicted for propane, 50% for butanes, and 75% for pentanes concentration. These low concentrations in the naphtha provided the vapor off-gas flow.

With many sets of data, each giving good material balance closure, it was obvious that the vapor exiting the overhead accumulator was not in equilibrium with liquid exiting the accumulator. Condensers fouled severely on the tube side, but this did not explain the large deviations from equilibrium.

Theory  Conventional process simulation assumes what can be called the “universal VLE model.” This model assumes that VLE is universal, that is, holds at every location, between the total vapor flow and the total liquid flow. In shell-side condensation, the liquid and vapor are usually close to equilibrium locally when the liquid condenses on the tube surface. But after the liquid drops off the tube (and to the bottom of the shell), there is not enough vapor–liquid mixing to maintain equilibrium with the downstream vapor. Thus there is usually “local VLE” at the tube surface, but not universal VLE for the system. This local equilibrium is responsible for the phenomena of subcooled refluxes coexisting with uncondensed vapor. Condensers designed for total condensation have frequently been partial condensers because of local VLE.

Deviations from universal equilibrium can be large for condensers in series with broad boiling range mixtures. Deviations are particularly high for mixtures with high light-ends content and for arrangements where the liquid stays largely separated from the downstream vapor. This case study represents an extreme example of these deviations.

For the overhead accumulator, universal VLE requires that the operating pressure and the exiting liquid bubble point pressure be equal. But bubble point pressure was half of the operating pressure. If the entire exiting vapor flow had been absorbed into the naphtha stream, the bubble point pressure would still have been less than the operating pressure.

Solution  A model was developed to more closely represent the condensation steps. Liquid condensed in each shell was assumed to be in equilibrium with the gas leaving that shell. After the liquid left the shell in which it condensed, it was assumed to have zero mass transfer with the gas phase but to be cooled to the local operating temperature. This model had only one-third of the total liquid (the one-third that condensed in the last shell) in equilibrium with the off gas. The other two-thirds of the liquid was much heavier and caused the overall liquid bubble point pressure to be about half that of the liquid that condensed in the last shell. The actual system was
more complex than the above model, in particular:

- The liquid condensed in each shell was heavier than the calculated liquid in equilibrium with the exiting vapor.
- Liquid condensed in an upstream shell experienced a moderate amount of mixing (and thus mass transfer) with downstream vapor.

The above two effects are in opposite directions and largely cancel each other for this case study (perhaps because of the double-split arrangement and three shells in series). This cancellation of errors caused the model to adequately match actual liquid composition and actual vapor rate leaving the overhead accumulator.

Morals  For broad boiling range mixtures, condensers (particularly condensers in series) have less capacity than estimated by conventional simulation with universal VLE. This is a failure in simulation and design rather than an equipment failure.

A simulation based upon good operating data can often be used to adequately model the effect of local equilibrium. Good heat and material balances and confidence in them are necessary to step away from universal VLE assumptions and obtain realistic simulations.

Process designers have compensated for their lack of understanding by using large design margins for condensers, by specifying off-gas compressors for zero calculated gas rates, and by greatly oversizing off-gas compressors. These practices can still result in lack of capacity for installations such as in this case study. Even very rough estimates of local equilibrium effects can be far better than conventional calculations for series condensation.

For a single shell and moderate deviations from universal VLE, a reasonable subcooling delta temperature can sometimes be used for simulation and design. In extreme cases, calculations for zones in each shell may be necessary to give good simulation or design. For this case study, the zone method would probably have been required if the condenser paths had been many times longer than in a double split-flow configuration.

CASE STUDY 1.14 SIMULATOR HYDRAULIC PREDICTIONS: TO TRUST OR NOT TO TRUST?

Henry Z. Kister, reference 254. Reproduced with permission. Copyright © (1995) AIChE. All rights reserved

In this case study, a simulator hydraulic calculation led a plant to expect a capacity gain almost twice as high as the tower revamp actually achieved.

History  A refinery vacuum tower was debottlenecked for a 30% capacity gain by replacing 2-in. Pall rings in the wash and heavy vacuum gas oil (HVGO) sections with 3-in. modern proprietary random packings. Only about 15–20% capacity gain was achieved. It was theorized that above this throughput vapor maldistribution set in
and caused the tower to lose separation. The refinery sought improvements to vapor distribution in an effort to gain the missing 10–15%.

**Troubleshooting**  A vacuum manometer pressure survey showed that at the point where the tower lost separation the pressure drop was 0.65 in. H₂O/ft packing. Based on air/water measurements, many suppliers’ packages take the capacity limit (or flood point) to occur at a pressure drop of 1.5–2 in. H₂O/ft packing. Work by Strigle (473), Rukovenia and Koshy (418), and Kister and Gill (257, 259) demonstrated that such numbers are grossly optimistic for modern, high-capacity random and structured packings. Using published flood data, Kister and Gill (257, 259) showed that, for random and structured packings, the flood pressure drop is given by

\[
\Delta P_{\text{flood}} = 0.115 F_P^{0.7}
\]

where \(\Delta P_{\text{flood}}\) is the flood pressure drop (in. H₂O/ft packing) and \(F_P\) is the packing factor (ft⁻¹). This equation was shown to give a good fit to experimental data (many of which were generated by suppliers) and was later endorsed by Strigle (473) with a slight change of coefficient. For the high-capacity packing in the vacuum tower, the packing factor was 12. Equation 1 predicts that \(\Delta P_{\text{flood}}\) was 0.65 in. H₂O/ft packing, which coincided with the limit observed by the refinery.

For hydraulic calculations, gas velocity usually is expressed as a \(C\)-factor \((C_S)\), (ft/s), given by

\[
C_S = \frac{\rho_G}{\rho_L - \rho_G} U_S^{0.5}
\]

where \(U_S\) is the gas superficial velocity based on tower cross-sectional area (ft/s), \(\rho\) is the density (lb/ft³), and the subscripts G and L denote gas and liquid, respectively. The \(C\)-factor essentially is a density-corrected superficial velocity. The fundamental relevance of the \(C\)-factor is discussed elsewhere (251).

Based on a flood pressure drop of 0.65 in. H₂O/ft packing derived from Equation 1, the maximum efficient capacity of the new 3-in. random packing calculated by the Kister and Gill method (251) was at a \(C\)-factor of 0.38 ft/s. This is about 17% higher than the maximum efficient capacity for the previous 2-in. Pall rings, just as the refinery observed.

According to the supplier’s published hand correlation, which we believe was similar to the one in the computer simulation, the maximum efficient capacity of the packing was at a \(C\)-factor of 0.43 ft/s, which is 13% higher than observed. This high \(C\)-factor matched a pressure drop of between 1 and 1.5 in. H₂O/ft packing, well above the value where the packing reached a capacity limit.

**Epilogue**  Based on the hydraulic calculation in the computer simulation, the refinery expected that changing the 2-in. Pall rings to the 3-in. high-capacity random packing would increase capacity by 30%. In real life, just over half of the capacity increase materialized. The half that did not materialize is attributed to the optimistic prediction from the simulation.
Chapter 1  Troubleshooting Distillation Simulations

CASE STUDY 1.15  PACKING HYDRAULIC PREDICTIONS: TO TRUST OR NOT TO TRUST

**Background**  This case presents a number of experiences which were very similar to Case Study 1.14. In each one of these, vendor and simulator predictions for a packed tower were optimistic. In each one of these, the Kister and Gill equation \((257, 259)\) gave excellent prediction for the maximum capacity. The Kister and Gill equation is

\[
\Delta P_{flood} = 0.115 F_P^{0.7}
\]

where \(\Delta P_{flood}\) is the flood pressure drop (in. H\(_2\)O/ft packing) and \(F_P\) is the packing factor (ft\(^{-1}\)).

**Tower A**  This was a chemical tower, equipped with wire-mesh structured packing with a packing factor of 21. The tower ran completely smoothly until reaching a pressure drop of 1 in. H\(_2\)O/ft packing, then would rapidly lose efficiency. This compares to a flood pressure drop of 0.97 in. H\(_2\)O/ft packing from Equation 1. Simulation prediction (both vendor and general options) predicted a much higher capacity.

**Tower B**  This was a chemical tower equipped with random packing with a packing factor of 18. This column would rapidly lose efficiency when the pressure drop increased above 0.67 in. H\(_2\)O/ft packing. This compares to a flood pressure drop of 0.87 from Equation 1. The measurement was slightly lower than the prediction because the vapor load varied through the packings, so much of the bed operated at lower pressure drop. Simulation prediction (both vendor and general options) predicted a much higher capacity. Similar to Case Study 1.14, the plant initially theorized that the shortfall in capacity was due to vapor maldistribution.

**Tower C**  This was a chemical absorber equipped with random packing with a packing factor of 18. The highest pressure drop at which operation was stable was 0.8 in. H\(_2\)O/ft packing. Above this, the pressure drop would rapidly rise. This compares to a flood pressure drop of 0.87 from Equation 1. Simulation predictions (both vendor and general options) were of a 20% higher capacity.

**Tower D**  Random packing installed in a chemical tower fell short of achieving design capacity. The vendor method predicted flooding at a pressure drop of 1.5 in. H\(_2\)O/ft packing. With a packing factor of 18, Equation 1 predicted that the packing would flood much earlier at a pressure drop of 0.8 in. H\(_2\)O/ft packing. The packing flooded at exactly that pressure drop.

CASE STUDY 1.16  DO GOOD CORRELATIONS MAKE THE SIMULATION HYDRAULIC CALCULATIONS RELIABLE?

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What follows is an actual letter circulated by an engineer working for a reputable company. The names of the correlations cited, as well as a few sentences, were changed to protect those involved.

We have had a problem recently with the prediction of flooding in packed towers using the Smith correlation for packed tower capacity in the Evertrue Simulator. We used this for sizing a packed tower at 400 psia. The program predicted a percentage flood of 56 percent using the Smith correlation. The vendor predicted 106 percent of flood, and 123 percent of the packing useful capacity.

The Evertrue calculation is based on an article by Smith in Quality Chemical Engineering magazine. Smith’s method, in turn, depends on an earlier correlation by Jones, also published in an article in Quality Chemical Engineering.

These correlations are neither well developed nor tested. Neither of these articles (Smith’s and Jones’) have undergone very close scrutiny, nor are the correlations from well-known textbooks or journals that have a tradition of peer review. One of the failings is the use of the correlation at high pressure with hydrocarbon systems. Smith’s correction factor for high pressures produces numbers that are unreasonably high. There is no indication that this factor is supported either by correlation or by theory. In addition to the lack of credibility of Smith’s values, the correlation of Jones, used as the basis of the Smith method, appears inaccurate for the high-pressure systems.

For these reasons, I would not recommend use of the Evertrue Smith correlation, regardless of the system pressure, for predicting whether or not a packed tower will work. Instead, the 1960 correlation included on Evertrue should be used. This correlation is based on well-known methods, and can be found in “Perry’s Handbook.” It predicts the tower would be at 96 percent of flood, compared to the 106 percent predicted by the vendor, which is much closer than the Smith correlation.

In either case, calculations must be verified by the packing vendor. I recommend that the vendor verifies the results even for estimates.

What Really Happened

In our experience, both the Smith and the Jones correlations are excellent. The correlation that leaves a lot to be desired for modern packing calculations is the 1960 one. Nevertheless, the letter’s author appeared to have reached the converse conclusion.

It is a sad fact of life that correlation authors always examine their correlations for good statistical fit but seldom properly explore and clearly define their correlation limitations. On page 39 of Ref. 259, Kister and Gill remark: “An excellent fit to experimental data is insufficient to render a packing pressure-drop correlation suitable for design. In addition, the correlation’s limitations must be fully explored.”

In contrast to the letter writer’s comment, the problem is more acute in articles that are peer reviewed. These contain correlations based on fundamental models that are inherently complex. This complexity makes it very difficult to properly identify the limitations. A peer review offers little help unless the reviewer spends several days checking the calculations. This rarely happens.

The Smith correlation works very well for vacuum and atmospheric pressures, perhaps up to 50 psia. It was never intended to apply to 400 psia. Unfortunately, Smith’s article only contained a hint of the pressure limitation but no firm statements to that effect. It, therefore, went into the Evertrue simulator without a warning flag.
above 50 psia. In this case, the 1960 correlation was found to work well. This appears to be a case of two wrongs making a right.

**Epilogue**  There are many correlations in the published and proprietary literature for which the limitations are neither well explored nor well defined. Limitations unflagged in the original articles remain unflagged in the simulator version.

Despite the letter writer’s wrong conclusion, his bottom line is broadly valid. A simulator correlation cannot be trusted, even when the correlation is good, unless the correlation’s limitations are known and included in the simulation. An independent verification, say, by a supplier or an independent method, is a good idea. When *Distillation Design* (251) was compiled, special effort was made to talk to authors of good correlations, with the objective of exploring their limitations and filling in the missing blanks. For instance, the pressure ranges for the application of Smith’s correlation were listed in *Distillation Design* almost two years before the above letter was written.