Modeling of an Ethanol – Water- LiBr Ternary System for the Simulation of Bioethanol Purification using Pass-Through Distillation

By

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APPROVED

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Abstract

Accurate modeling of mixed solvent electrolyte systems is difficult and is not readily available in property modeling software such as Aspen Plus. Support for modeling these systems requires the knowledge and input of parameters specific to the compounds in question. The need for these parameters is particularly relevant in simulating new designs based upon recent developments in a concept known as pass-through distillation (PTD). In support of a specific application of PTD, this work determines and validates with existing experimental data, accurate user-parameters for the eNRTL property model in the ternary system of ethanol, water, and lithium bromide. Furthermore, this work creates the foundation for simulating this new PTD process by modeling the removal of bioethanol from a fermentation broth using low temperature evaporation in conjunction with absorption and stripping units to omit the need of a condenser requiring refrigeration. This will enable future investigations into the applications of PTD as well as provide a foundation for modeling the ternary system of ethanol, water and lithium bromide.

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1. Introduction

As the need for new sources of energy continues the grow the demand for alternatives energies, such as biofuels and bioethanol will also grow. As ethanol is produced in a fermentation broth it must be removed as a product from this fermentation broth. This can pose a number of different problems. For example, as organics are part of the mixture the temperature that the separation occurs at is of critical importance. If the temperature is too high it will cause degradation to the organics and is likely to result in fouling. Another problem is the energy requirements, this is exacerbated by the fact that water makes up the majority of the mixture composition and forms an azeotrope with ethanol. This means that some adaptations are required and a single distillation column cannot be implemented and although multi column distillation is one of the most common methods for bioethanol separation it can be energy intensive.[1]

However, there is another potential scheme that has been developed known as Pass-Through Distillation (PTD). This process enables the separation of ethanol from the rest of the mixture through a series of low pressure units in order to minimize degradation of the organics as well as the addition of an electrolyte in order to remove the azeotrope that forms between ethanol and water and avoid the need for a refrigeration unit to condense the low pressure vapor stream. In addition PTD has another added advantage of the reuse of heat throughout the system in order to minimize energy costs in conjunction with a custom unit.

Currently the PTD process has been built and tested on a pilot scale using a mixture of water, ethanol and lithium bromide. There is considerable interest from those working on the process to find a more accurate way to model the process using something other than Microsoft Excel based calculations. Therefore, there was desire to use a program such as Aspen Plus to provide a framework simulating PTD specifically applied to the separation of bioethanol from a fermentation broth. The modeling of this system poses some challenges, for example the process makes use of a custom unit and an accurate method of simulating its operation must be determined. In addition, the keystone of this process is the use of an electrolyte to absorb the bioethanol and water present. This requires a property method capable of accurately modeling the ternary relationship between ethanol, water and lithium bromide.

2. Modeling of a Ternary Water-Ethanol-LiBr System

The modeling of an electrolyte system can prove difficult with simply aqueous electrolyte systems. The use of a solvent instead of, or in addition to, water complicates this as many parameters do not exist to model certain collections of solvents and salts. Such is the case of water-ethanol-lithium bromide. There are accurate temperature dependent models for aqueous lithium bromide systems but no models that are able to immediately model an ethanol and lithium bromide system, let alone the ternary system that also includes water. In addition to accurately taking into consideration the relationship between the solvent and the electrolyte the model would also need to properly account for the polar interactions between the two solvents of interest: water and ethanol. Therefore it was imperative to find and use an appropriate property method in conjunction with appropriate parameters to accurately represent experimental data of the ternary water-ethanol-lithium bromide system. Aspen Plus V8.8 was used both to determine which property methods were available as well as to evaluate the accuracy of the model when compared against experimental data.

2.1 Background

Aspen Plus V8.8 is equipped with a large database of various property methods for many different components and component mixtures, including property methods for the system of interest here, electrolytes. By default Aspen Plus uses ELECNRTL for use with electrolytes, however there are a total of ten different property methods recommended by Aspen that are either listed when using the method filter for ELECTROL or when searching through all available methods. Most of the available options are simply variations on three primary methods and all options and their associated tooltip in Aspen Plus V8.8 are summarized in Table 2.1. These various property methods are all variations on the three methods of Pitzer, OLI and ELECNRTL. For example PITZ-HG and B-PITZER are both variations on the Pitzer model and ENRTL-HF, ENRTL-HG, NRTL-SAC, ENRTL-RK and ENRTL-SR are all variations on ELECNRTL.

Table 2.1: Summary of property methods available for electrolyte modeling in Aspen Plus V8.8.

Property Method	Tooltip
ELECNRTL	Electrolyte NRTL model with Redlich-Kwong equation of state. For aqueous and mixed solvent applications.
ENRTL-HF	Electrolyte NRTL model with HF equation of state. For mixed solvent applications.
ENRTL-HG	Electrolyte NRTL model with Redlich-Kwong equation of state. Uses Helgeson model for equilibrium constants estimation and for standard properties.
PITZER	Pitzer model for aqueous electrolyte systems.
PITZ-HG	Pitzer model for aqueous electrolyte systems. Uses Helgeson model for equilibrium constants estimation and for standard properties.
NRTL-SAC	NRTL-SAC with Ideal gas and Henry's law.
ENRTL-RK	Unsymmetric electrolyte NRTL model with Redlich-Kwong equation of state and Henry's law for electrolyte systems under unsymmetric reference state for ionic species.
ENRTL-SR	Symmetric electrolyte NRTL model with Redlich-Kwong equation of state and Henry's law for electrolyte systems under symmetric reference state for all components.
B-PITZER*	Bromley-Pitzer model for aqueous electrolyte systems.
OLI*	OLI property method for electrolytes applications. Required special license from OLI Systems Inc.

*Property methods not included under the ELECTROL method filter.

There exist other methods for modeling electrolyte solutions but they are not available as options in Aspen Plus V8.8 and are primarily precursors to the models listed in Table 2.1. One such example is the model developed in 1923 by Peter Debye and Erich Huckel used to theorize the interactions occurring in a solution containing dissolved strong electrolytes.[2] One of the expressions developed for use in their model is for the Debye-Huckel constant:

$$A = \frac{1}{2.303}\left(\frac{e}{\sqrt{DkT}}\right)^3 \sqrt{\frac{2\pi d N_A}{1000}} \tag{2.1}$$

Where D is the dielectric constant of the solution, e is the electronic charge and equal to 4.8029 x 10^{-10} e.s.u. Or 1.60206 x 10^{-19} coulomb, k is Boltzmann's constant 1.38045 x 10^{-16} erg/deg, T s the absolute temperature, N_A is Avogadro's number equal to 6.0232 x 10^{23} $mole^{-1}$, and d is the density of the solvent. This piece of the model they developed has since been incorporated into both the Pitzer model as well as the eNRTL model.[2]

The Pitzer model was an improvement on a model proposed by Guggenheim in 1935 and 1955 but was only successful in modeling low concentrations of electrolytes. The Pitzer model expanded the Debye-Huckel method and added terms to take into consideration the ionic strength and effect of these forces. The constant *A* defined in Equation 2.1was altered slightly and became known as the Debye-Huckel constant for osmotic coefficients as seen in Equation 2.2:

$$A_\phi = \frac{1}{3}\left(\frac{e}{\sqrt{DkT}}\right)^3 \sqrt{\frac{2\pi d_0 N_A}{1000}} \tag{2.2}$$

The reason that the Pitzer model, as well as those based upon it, can be ruled out as a potential option to model the water-ethanol-LiBr system is that it can only be used for aqueous systems and not a mixed solvent system.[2] A variation of the Pitzer model, the Bromley-Pitzer model, abbreviated as B-PITZER is another option but can only model aqueous electrolyte systems up to 6 molal ionic strength. Therefore it was quickly ruled out as an option to model the ternary system of ethanol-water-lithium bromide.[3]

Unlike the Pitzer model, the OLI model has the capability to model a mixed solvent system and is oftentimes referred to as OLI-MSE as opposed to its aqueous solution counterpart. The OLI-MSE model is ion-specific and includes binary-interaction parameters based upon the UNIQUAC model.[4] Unfortunately the exact details as to how the OLI-MSE model works are not readily available. In addition, the OLI-MSE model model requires additional licences in Aspen plus to use it, limiting its usefulness. The extra cost is justified because the OLI models are a product of OLI Systems and therefore include a large database of electrolyte parameters far exceeding Aspen's built-in of the models.[5] However, lack of widely available access is a primary

concern in this research and therefore the OLI model and its variations were excluded from further consideration.

The eNRTL-HF and eNRTL-HG models could quickly be removed as candidates for modeling as eNRTL-HF is the HF Hexamerization model and is only recommended by the Aspen Help Manual for the modeling of HF and its strong vapor association in any liquid. Similarly, the eNRTL-HG was ruled out due to its recommend use only in modeling aqueous solutions, and its uncommon reliance on the Helgenson model as the equation of state compared to other models under consideration.

The NRTL-SAC method is a semi-predictive segment contribution activity coefficient model generally used with polymer systems but has been extended to use with electrolytes as well.[6] It is a method that estimates interactions based on five segments: the hydrophobic segment, solvation segment, polar segment, strength segment, and hydrophilic segment. These segments can then be used to predict phase behavior. As this method does not deal with the specific properties of lithium bromide it was considered an option less favorable than options such as eNRTL-RK and eNRTL-SR.

The general ELECNRTL model is the forerunner to eNRTL-RK and eNRTL-SR. Although ELECNRTL is the default and most commonly used of the three of these models eNRTL-RK is a direct improvement to the method where when there are no electrolytes present the model can reduce to the NRTL method. The difference between eNRTL-RK and eNRTL-SR is that the eNRTL-RK model is an unsymmetric model whereas the eNRTL-SR model is a symmetric model. Simply put: an unsymmetric model means that the the method is normalized against a reference state of infinite aqueous dilution, therefore this model is only for aqueous solutions or mixed solvents including water. Conversely, the symmetric reference state normalizes the eNRTL-SR method using pure liquids and pure fused salts. For this reason this method can be used with non aqueous and mixed solvent systems.

Ultimately eNRTL-RK was chosen as it enabled a mixed solvent system to be modeled and would be adaptable to the components of interest: ethanol, water, and lithium bromide. In addition, eNRTL-RK is an updated version of the original ELECNRTL or eNRTL method. The eNRTL method was developed in the early 1980s and works by expressing the excess Gibbs free

energy and activity coefficients as a sum of a long range interaction contribution and a short range interaction contribution as seen in Equation 2.3 and 2.4 respectively.[7]

$$\frac{g^{ex*}}{RT} = \frac{g^{ex*,pdh}}{RT} + \frac{g^{ex*,lc}}{RT} \tag{2.3}$$

$$\ln(\gamma_i) = \ln(\gamma_i^{pdh}) + \ln(\gamma_i^{lc}) \tag{2.4}$$

The long range interaction contribution is taken from the Pitzer model and is the extended form of the Debye-Huckel equation. It is labeled as *pdh* for the Pitzer-Debye-Huckel formula and models the repulsive forces occurring between the ions.

$$\frac{g^{ex*,pdh}}{RT} = -\left(\sum_k x_k\right)\left(\frac{1000}{M_s}\right)^{1/2}\left(\frac{4A_\phi I_x}{\rho}\right)\ln\left(1+\rho I_x^{1/2}\right) \tag{2.5}$$

$$\ln\left(\gamma_i^{pdh*}\right) = -\left(\frac{1000}{M_s}\right)^{1/2} A_\phi \left[\left(\frac{2Z_i^2}{\rho}\right)\ln\left(1+\rho I_x^{1/2}\right) + \frac{\left(Z_i^2 I_x^{1/2} - 2I_x^{3/2}\right)}{\left(1+\rho I_x^{1/2}\right)}\right] \tag{2.6}$$

In Equations 2.5 and 2.6, ρ is the closest approach parameter and is generally set equal to 14.9. Z is the absolute value of the charge on the species of interest and is set equal to zero when the component is the solvent. I_x is the ionic strength parameter as defined in Equation 2.7:

$$I_x = \left(\frac{1}{2}\sum Z_i^2 x_i\right) \tag{2.7}$$

The second part of the eNRTL model is the short range interaction contribution superscripted as *lc* for the local composition concept and is based upon the NRTL model and reduces to the NRTL expression when there is no electrolyte present in the solution. There were two assumptions made in the development of the model, the like-ion repulsion assumption and the local electroneutrality assumption.The like-ion repulsion assumption assumes that no ions of the same charge will be present near each other in solution and therefore interactions occurring

between two cations or two anions can be ignored. The local electroneutrality assumption assumes that around a given solvent molecule there is an equal distribution of cations and anions so that the net ionic charge is equal to zero. These two assumptions are best illustrated by Figure 2.1.

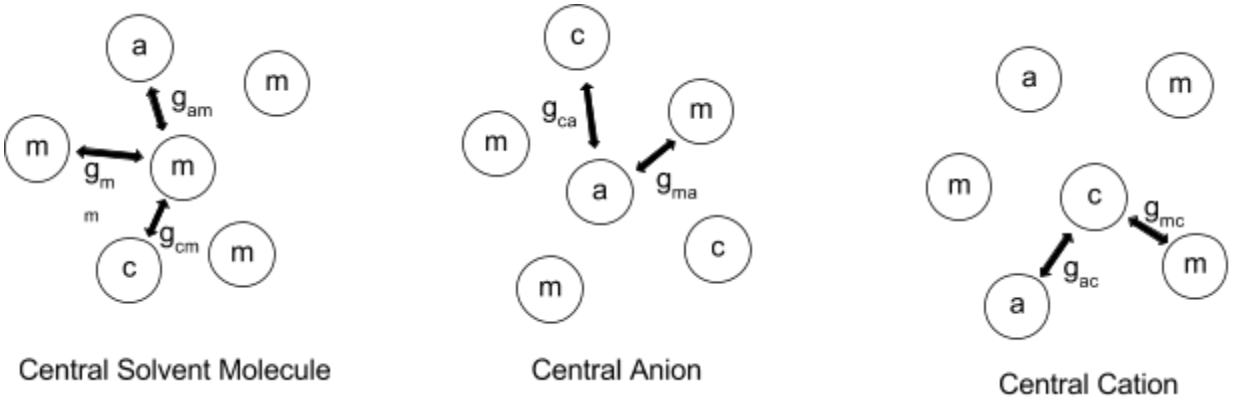


Figure 2.1: Illustration of the solvent, cation and anion interactions based upon the assumptions made by the eNRTL local composition concept.[7]

These cells allow the definition of the relationship between the mole fractions of each unit cell defined as follows:

$$x_{cm} + x_{am} + x_{mm} = 1 \tag{2.8}$$

$$x_{ma} + x_{ca} = 1 \tag{2.9}$$

$$x_{mc} + x_{ac} = 1 \tag{2.10}$$

The equation itself for the excess Gibbs energy as well as the equation for activity coefficients are based upon the above illustration where the parameters that can ultimately be adjusted to fit the experimental data of a given solvent and electrolyte are τ_{ij} and τ_{ji}. Initially these values were defined as seen in Equation 2.11 and for a given electrolyte values for τ_{ij} and τ_{ji} could be obtained via regression with experimental data but they do not vary with temperature, which can be a disadvantage depending on the system of interest. Thus the definition of τ_{ij} was updated so that the parameters could vary with temperature which is visible in Equation 2.12.[5]

$$\tau_{ji} = \frac{(g_{ji} - g_{ii})}{RT} \tag{2.11}$$

$$\tau_{ij} = c_{ij} + \frac{d_{ij}}{T} + e_{ij}\left(\frac{T_{ref} - T}{T} + \ln\frac{T}{T_{ref}}\right) \tag{2.12}$$

These values of τ_{ij} and τ_{ji} or alternatively the temperature dependent parameters of a_{ij}, a_{ji}, b_{ij}, b_{ji}, c_{ij} and c_{ji} are then used in order to calculate the excess Gibbs energy for each pair using Equation 2.13 in conjunction with α which is known as the non randomness factor. Often this value is set equal to 0.2. Unlike τ_{ij} and τ_{ji} where $\tau_{ij} \neq \tau_{ij}$ in the case of α, $\alpha_{ij} = \alpha_{ij}$. These calculated excess Gibbs energy values are then used in the calculations of both the overall excess Gibbs energy for the system as well as the activity coefficient models along with the respective mole fractions for each component which can be seen in Equations 2.14 and 2.15, 2.16 and 2.17, respectively.[7]

$$G_{ji} = \exp(-\alpha\tau_{ji}) \tag{2.13}$$

$$\frac{g^{ex*,lc}}{RT} = x_m(x_{cm} + x_{am})\tau_{ca,m} + x_c x_{mc} Z_c \tau_{m,ca} + x_a x_{ma} Z_a \tau_{m,ca} - x_c(Z_c\tau_{m,ca} + G_{cm}\tau_{ca,m}) - x_a(Z_a\tau_{m,ca} + G_{ma}\tau_{ca,m}) \tag{2.14}$$

$$\ln\gamma_c^{lc*} = \frac{x_m^2\tau_{cm}G_{cm}}{(x_cG_{cm} + x_aG_{am} + x_m)^2} - \frac{Z_a x_a \tau_{ma} x_m G_{ma}}{(x_c + x_m G_{ma})^2} + \frac{Z_c x_m \tau_{mc} G_{mc}}{(x_a + x_m G_{mc})} - Z_c\tau_{mc} - G_{cm}\tau_{cm} \tag{2.15}$$

$$\ln\gamma_a^{lc*} = \frac{x_m^2\tau_{am}G_{am}}{(x_cG_{cm} + x_aG_{am} + x_m)^2} - \frac{Z_c x_c \tau_{mc} x_m G_{mc}}{(x_a + x_m G_{mc})^2} + \frac{Z_a x_m \tau_{ma} G_{ma}}{(x_c + x_m G_{ma})} - Z_a\tau_{ma} - G_{am}\tau_{am} \tag{2.16}$$

$$\ln\gamma_m^{lc} = x_{cm}\tau_{cm} + x_{am}\tau_{am} + \frac{Z_c x_c G_{mc}\tau_{mc} x_a}{(x_a + G_{mc}x_m)^2} + \frac{Z_a x_a G_{ma}\tau_{ma} x_c}{(x_c + G_{ma}x_m)^2} - \frac{x_c x_m G_{cm}\tau_{cm}}{(x_cG_{cm} + x_aG_{am} + x_m)^2} - \frac{x_a x_m G_{am}\tau_{am}}{x_cG_{cm} + x_aG_{am} + x_m)^2} \tag{2.17}$$

Where x_{ij} is equal to:

$$x_{im} = \frac{x_i G_{im}}{(x_a G_{am} + x_c G_{cm} + x_m)} \tag{2.18}$$

$$x_{ac} = \frac{x_a}{(x_a + x_m G_{mc,ac})} \tag{2.19}$$

$$x_{ca} = \frac{x_c}{(x_c + x_m G_{ma,ca})} \tag{2.20}$$

Finally, the relationships between values of τ can be simplified through the following relationships due to the two assumptions previously made so that:

$$\tau_{am} = \tau_{cm} = \tau_{ca,m} \tag{2.21}$$

$$\tau_{mc,ac} = \tau_{ma,ca} = \tau_{m,ca} \tag{2.22}$$

In the instance where a mixed, rather than a single solvent is used an additional term is added to the overall excess Gibbs energy calculation in the form of the Born correction that uses the dielectric constants for the long range interactions and takes the form of Equation 2.23.[8]

$$\frac{\Delta G^{born}}{RT} = \frac{NQ_e^2}{2kT}\left(\frac{1}{\epsilon_s} - \frac{1}{\epsilon_w}\right)_i \frac{x_i Z_i^2}{r_i} 10^{-2} \tag{2.23}$$

One of the primary advantages of using the eNRTL and eNRLT-RK property method, especially with mixed solvents is that the calculations are all based off of binary interactions between the various components. Therefore one can obtain the parameters of interest separately for the electrolyte and each solvent in the mixture. This is important as it allows experimental data of a binary pair, for example, just ethanol and lithium bromide to be used to calculate the necessary parameters and then separately obtained experimental data to find the parameters for aqueous lithium bromide. These separately obtained binary parameters can then be used to calculate the behavior of the ternary mixture, though ideally this can be compared to experimental data of the mixture.

2.2 Methodology

As of Aspen Plus V8.8 there exists no parameters in the databases in order to describe a binary ethanol and lithium bromide system or, by extension, the ethanol-water-lithium bromide system of interest. Fortunately the eNRTL-RK, which will henceforth be referred to simply as the eNRTL method, models a ternary system using binary interactions. Therefore, experimental data of the three binary sets could be used in conjunction with a ternary data set to determine the parameters to accurately model the ethanol-water-lithium bromide system using the regression tools available in Aspen Plus. The resulting ternary model could then be compared against the experimental model to determine overall accuracy.

2.2.1 Setting Up Aspen Plus V8.8 for Regressions

The procedure of using Aspen Plus in a regression analysis to determine the parameters of a ternary electrolyte system is based upon the work of Wang et. al. in 2016.[5] The first step is to add the components of interest, in this case ethanol, water, lithium bromide as well as the lithium ion Li+ and the bromide ion Br- as seen in Figure 2.2. Then the electrolyte wizard can be used in order to add the chemistry and specify the property method, but it is recommended that this setup be completed manually to ensure nothing is added or set up differently.

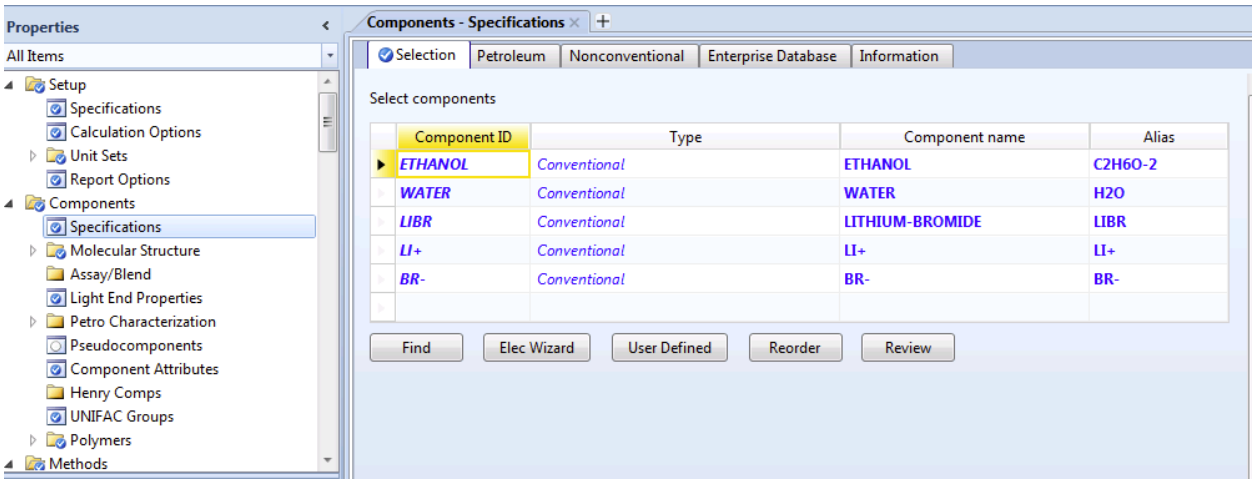


Figure 2.2: Component specifications required for the ternary system of water, ethanol and LiBr.

Next the specifications for the methods need to be set. The base method of ENRTL-RK, an unsymmetric model, is chosen and the "Use true components" box is checked as seen in Figure 2.3. The use of true or apparent components will be seen repeatedly and both will end up being used for the regression itself. The true component approach causes Aspen Plus to solve equations for the chemistry simultaneously with the unit operation. In addition the results will be reported in terms of the ions not the salt itself. Alternatively the apparent component approach means that Aspen Plus solves the chemistry equations as part of the physical property calculations and the ions and any salts present are not part of unit operation calculations. Once this is complete the run mode can be changed from "Analysis" to "Regression" in the top ribbon.

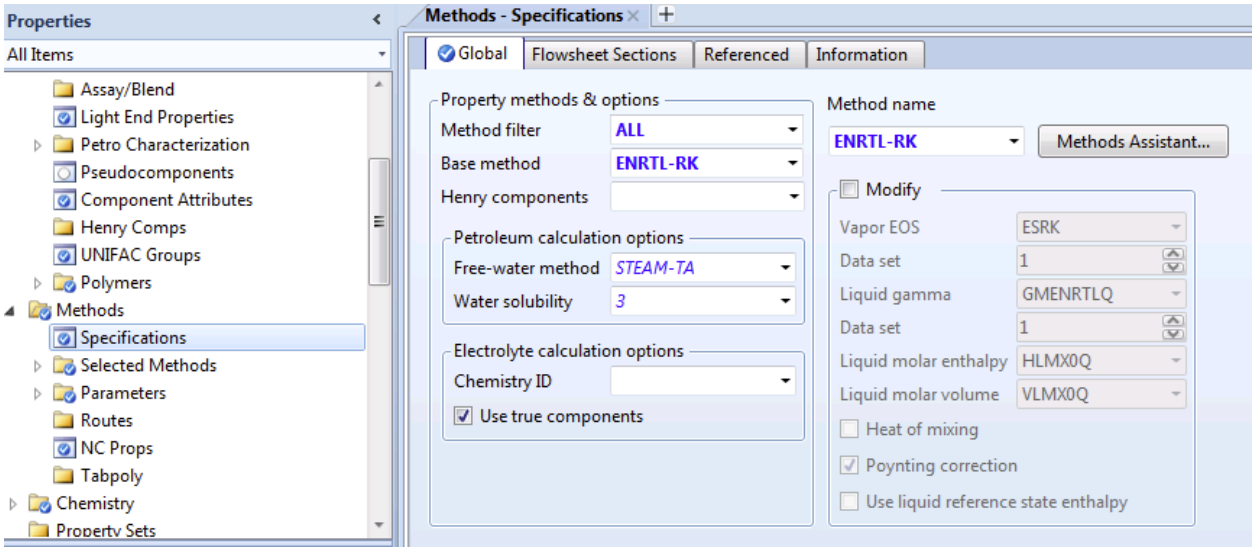


Figure 2.3: Method specifications for the ternary system of water, ethanol and lithium bromide.

Once the initial components are added the missing data for the components of interest need to be pulled from various Aspen databases. This can be done by clicking on retrieve parameters under the tools heading in the home ribbon. In the case of some electrolytes, in this case lithium bromide, the Aspen database does not contain all of the necessary properties to perform the regression using Redlich-Kwong as the EOS therefore they must be added in manually. The missing parameters are the critical pressure P_c, critical temperature T_c, critical volume v_c and z_c.

These four values were obtained by looking at similar salts that Aspen did have the missing data for, as summarized in Table 2.2. When looking at the critical values of these other electrolytes obtained it is easy to see that some values keep appearing specifically P_c as 50, T_C as 1726.85, V_C as 100 and Z_C as 0.2. These values were observed to be simplifying assumptions in the Aspen Plus database for electrolytes similar to lithium bromide. Since these values are only needed for the Redlich-Kwong EOS and lithium bromide is not present in the vapor phase the use of these values is a safe assumption to make. Therefore these values can be entered on the REVIEW-1 sheet under the Pure Components folder as can be seen in Figure 2.4.

Table 2.2: Comparison of Critical Values for Similar Electrolytes

	$CaCl_2$	HBr	LiI	NaBr	KBr	NaCl	KCl
P_c (bar)	50	85.5183	170	192.517	50	50	50
T_c (C)	1726.85	90.05	2096.85	4013.85	1726.85	1726.85	1726.85
V_c (cc/mol)	100	99.9271	-	398	100	100	100
Z_c	0.2	0.283	-	0.215	0.2	0.2	0.2

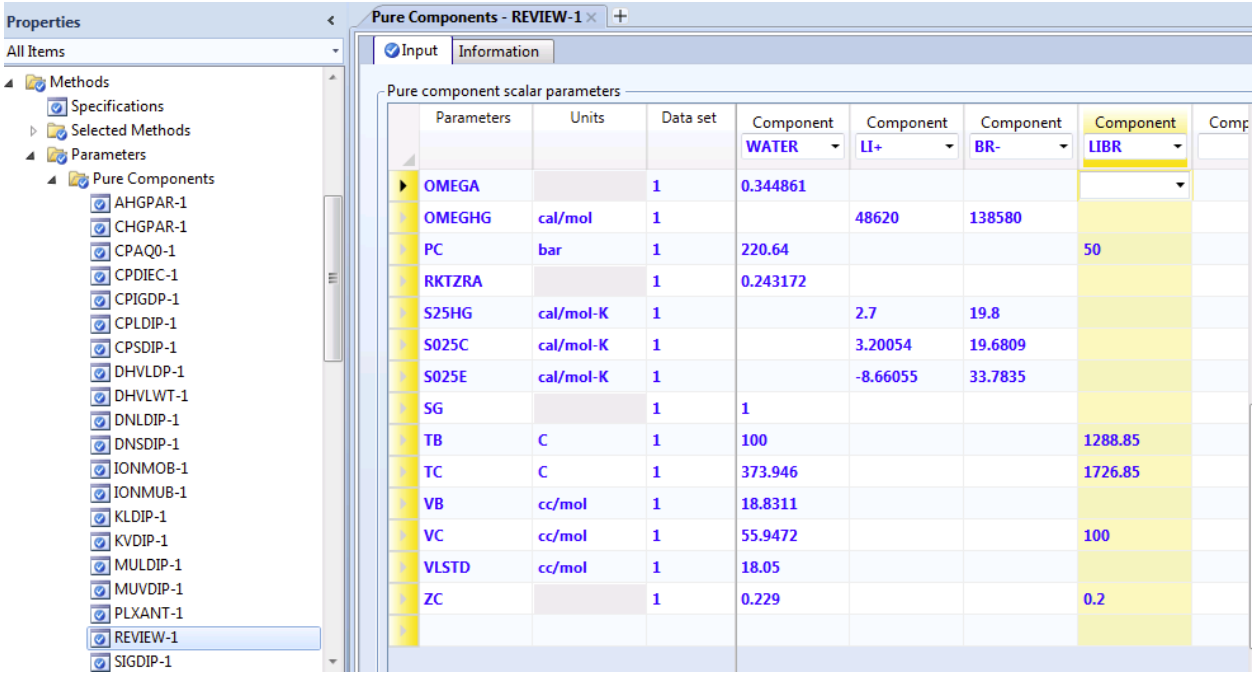


Figure 2.4: Input of critical properties for lithium bromide.

In addition to the missing information concerning the critical values of lithium bromide, there is also missing information required for the calculations of the heat of vaporization which is necessary for the vapor liquid equilibrium calculations. Aspen calculates the heat of vaporization for a given electrolyte using a specified equation or method, however, similarly to how the needed critical parameters for the Redlich-Kwong EOS the necessary coefficients are missing. Using the THRSWT-1 selection listed under pure components in the same way that REVIEW-1 was there is a list of eight rows where each one specifies the method used to calculate each of the eight pure component thermodynamic properties: 1-Solid Volume, 2-Liquid Volume, 3-Liquid Vapor Pressure, 4-Heat of Vaporization, 5-Solid Heat Capacity, 6-Liquid Heat Capacity, 7-Ideal Gas Heat Capacity, and 8-Second Virial Coefficient as can be seen in Figure 2.5. In the case of lithium bromide the model used to calculate heat of vaporization is listed as 0 which indicates the Watson equation is used, the necessary parameters are included in DHVLWT.

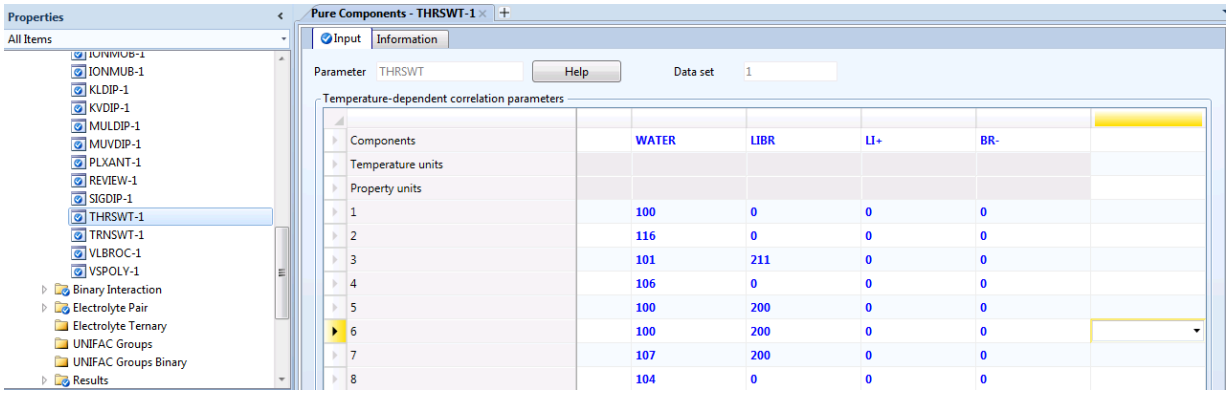


Figure 2.5: Specified methods used to calculate pure component thermodynamic properties.

Table 2.3: Equations and Parameters used to calculate Heat of Vaporization in Aspen Plus V8.8

If THRSWT/4 is	Then this equation is used	And this parameter is used
0	Watson	DHVLWT
106	DIPPR	DHVLDP
301	PPDS	DHVLDS
401	IK-CAPE	DHVLPO
505	NIST TDE Watson equation	DHVLTDEW

Therefore a new Pure Component Parameter needs to be added, in this case, DHVLWT, which can be done by selecting a new pure component property and then selecting T-dependent correlation and under Heat of vaporization selecting DHVLWT as seen in Figure 2.6. The corresponding equation for DHVLWT, the Watson Heat of Vaporization equation can be seen in Equation 2.24:

$$\Delta_{vap}H_i^*(T_i) = \Delta_{vap}H_i^*(T_1)\left(\frac{1-T/T_{ci}}{1-T_1/T_{ci}}\right)^{a_i+b_i(1-T/T_{ci})} \tag{2.24}$$

The parameters listed as 1 through 5 under DHVLWT correspond to variables in the equation. Specifically 1-$\Delta_{vap}H_i^*(T_1)$, 2-T_1, 3-a_i, 4-b_i and 5-T_{min}. For other similar salts only 1 and 2 need to be entered as 3 generally is set equal to 0.38 or left blank, 4 is either left blank or left as 0 and 5-T_{min} as 0K or -273.15°C. The values for 1 and 2 added for lithium bromide are 33150 and 1300 respectively.

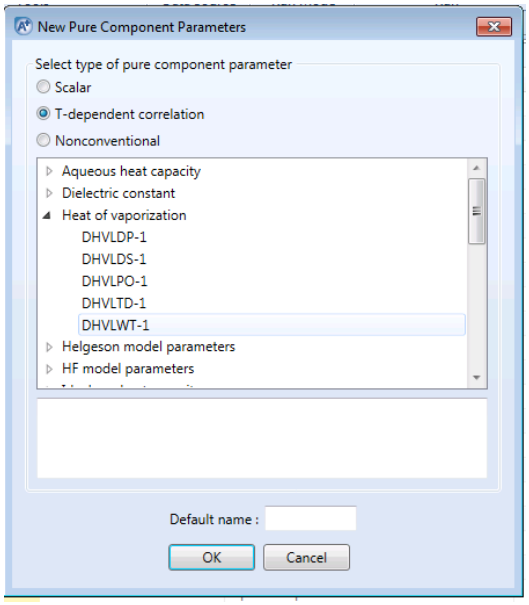


Figure 2.6: Creation of new pure component parameter: DHVLWT.

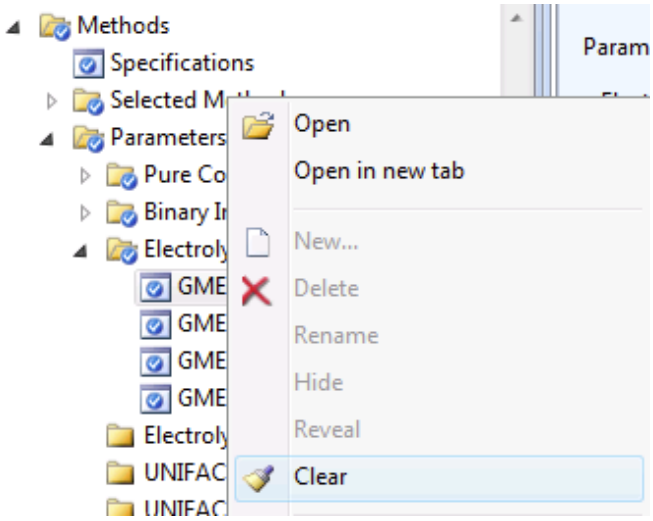


Figure 2.7: Clearing existing parameter values for GMENCD and GMENCE.

Next any existing values for the parameters that will be regressed should be removed. This is especially true in this instance because by default the binary electrolyte pair parameters for ELEC-RK for lithium bromide and water are temperature dependent. Therefore unless the the regression is done to include GMENCD and GMENCE then they need to be cleared by right clicking on their name in the property browser as is the case in Figure 2.7 so that Aspen will not automatically replace them during calculations. For GMENCN-1, the non randomness factor, the values were cleared and then Water-LiBr was added back in with a value of 0.2 which the commonly used for aqueous electrolyte relationships.[7]

The essential interaction between the solvent and the electrolyte is the dissociation that occurs and therefore the dissociation reaction that occurs must be added in. This is done by adding a new chemistry under the chemistry folder in the property browser. Once a new one is created the reaction can be added as a dissociation reaction of lithium bromide. From there the ions and their relative stoichiometry can be added resulting in the reaction listed as LIBR → LI+ + BR-. After this has been completed the experimental data can be added. The majority of experimental data used had vapor pressures calculated while holding the temperature constant for a variety of differing molalities. As Aspen does not permit the experimental data to be entered in the form of molalities the data must be converted to mole fractions. For convenience, the equation has been included as Equation 2.25.

$$x_{libr} = \frac{molality}{molality + \frac{1000}{MW_{solvent}}} \tag{2.25}$$

The experimental data used for this regression included data for each of the binary systems, that is, water and lithium bromide, ethanol and lithium bromide, and finally water and ethanol. Ternary data for the water, ethanol and lithium bromide system was included as well. The data used was all in the form of vapor pressures and the data type used was TPXY. For each set of data the components present needed to be selected however, in the case of the ethanol and lithium bromide data water still needs to be added as a component because an unsymmetric

method is being used. For each of the binary systems the temperature, pressure and mol fraction of each component in the liquid must be entered.

Generally, experimental data is reported as having held either the temperature, pressure or concentration of one of the components constant. The data should therefore be broken up into groups. For example if the vapor pressures are listed for various compositions at a in groups of constant temperature each groups should be a separate data set in order for the regression to perform better. This could easily result in two to five data sets for each binary pair being regressed. In the case of entering data for the ethanol and lithium bromide data the y values for lithium bromide and water can be set equal to zero while ethanol can be set equal to one. The most important item to change while entering data is that under the constraints tab lithium bromide must be removed as a component for the phases in equilibrium. In addition, special attention must be paid to the standard deviations entered for the data sets as they can have a profound impact on the results obtained.

Following the input of data the regression can be set up. First within the regression folder a new run can be created. Ultimately three different regressions will be created. For both the lithium bromide-ethanol and the lithium bromide-water mixtures the same setup can be used. On the setup form the chemistry ID of the dissociation reaction will need to be added and should be the only one available to select as an option. In addition the “Use true components” box must be unchecked. In the case of the water and ethanol mixture the chemistry box should remain empty and the “Use true components box” should remain checked.

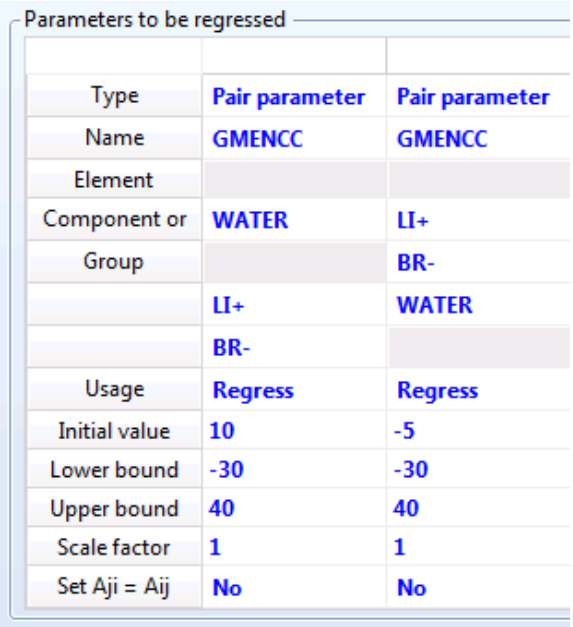
The data that corresponds to the two components under consideration can then be added as the data sets, the defaults of a weight of 1, neither consistency or reject data checked for the ethanol and lithium bromide data but consistency checked for the other two regressions. Area tests should be listed as the test method and an area tolerance of 10% can remain unchanged. In the case of the ethanol and water the ternary experimental data can be added with a reduced weight and consistency unchecked. The ternary experimental data should also be added to the ethanol and lithium bromide regression with a weight of 1.

Parameters to be regressed

Type	Pair parameter	Pair parameter	Pair parameter	Pair parameter
Name	GMENCC	GMENCC	GMENCN	GMENCN
Element				
Component or	ETHANOL	LI+	ETHANOL	LI+
Group		BR-		BR-
	LI+	ETHANOL	LI+	ETHANOL
	BR-		BR-	
Usage	Regress	Regress	Regress	Regress
Initial value	15	-10	0.01	0.01
Lower bound	-30	-30	0	0
Upper bound	40	40	0.3	0.3
Scale factor	1	1	1	1
Set Aji = Aij	No	No	No	No

Figure 2.8: Parameters to be regressed for the ethanol-LiBr binary pair

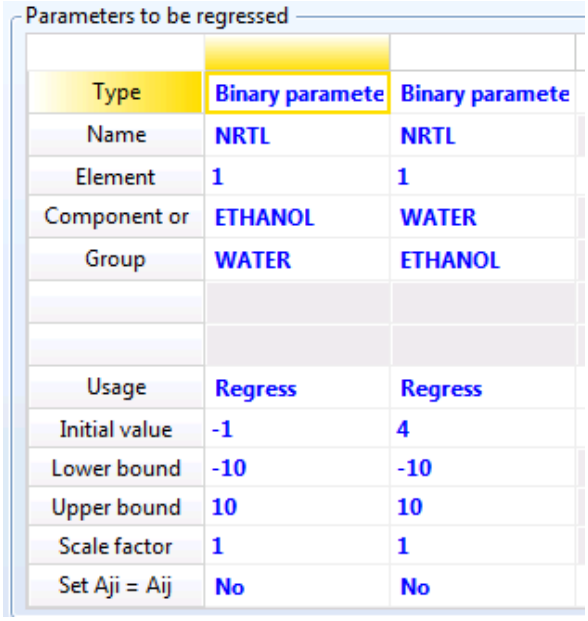
Then the parameters to regress must be entered in on the Parameters tab. In the case of the ethanol and lithium bromide system four parameters were entered for regression which are summarized in Figure 2.8 and are all the type known as “Pair parameter” where GMENCC corresponds to c_{ij} and c_{ji} in Equation 2.12 and GMENCN is the non randomness factor. In the case of lithium bromide and water the non randomness factor will not be adjusted but GMENCC will be regressed, similarly this is summarized in Figure 2.9. Finally the ethanol and water binary pair which is considered type “Binary parameter” NRTL 1 and 2, further details can be seen in Figures 2.8-2.10. At this point the regression can be run to achieve the parameters. Once the regression has been completed Aspen Plus will prompt to replace all of the parameters, and in most instances it is fine to replace them all.



Parameters to be regressed

Type	Pair parameter	Pair parameter
Name	GMENCC	GMENCC
Element		
Component or	WATER	LI+
Group		BR-
	LI+	WATER
	BR-	
Usage	Regress	Regress
Initial value	10	-5
Lower bound	-30	-30
Upper bound	40	40
Scale factor	1	1
Set Aji = Aij	No	No

Figure 2.9: Parameters to be regressed for the water-LiBr binary pair



Parameters to be regressed

Type	Binary paramete	Binary paramete
Name	NRTL	NRTL
Element	1	1
Component or	ETHANOL	WATER
Group	WATER	ETHANOL
Usage	Regress	Regress
Initial value	-1	4
Lower bound	-10	-10
Upper bound	10	10
Scale factor	1	1
Set Aji = Aij	No	No

Figure 2.10: Parameters to be regressed for the ethanol-water binary pair

2.2.2 Evaluation of Regressed Data

The accuracy of the regressed parameters and resulting model can be compared to the experimental data within the result tabs for each of the three regressions run to achieve information such as the percentage difference between the experimental data and the model resulting from the regressed parameters. In order to compare the ternary Aspen property model with the ternary experimental data there are multiple approaches. The first is using Aspen Plus to evaluate the information in a very similar method that was performed for each regression. The second is to manually get the data points of interest for comparison using an Aspen simulation Flash 2 block.

The first is the easier method that can be done by creating a new regression case but setting it to evaluation rather than regression. Following that the *chemistry* should be set to include the dissociation reaction and the *use true components* box should be unchecked. Then the ternary data set(s) can be added and run. It is important to note that when running this one should opt to not rerun the previous regressions. Once the results are calculated details concerning how well the experimental data and the model match are available and graphs can be created using

Aspen Plus though generally better comparisons and graphs are obtained using the second method explained.

The second method is done using excel in conjunction with the simulation environment of Aspen Plus. To setup the Aspen Plus part of it a Flash2 unit is created with one feed stream producing two product streams, one liquid, one vapor. To set up the Flash2 block the vapor fraction should be set to 0.0001. The purpose of this is so that the liquid phase composition can be controlled, the small amount that will be present in the vapor will have a negligible effect of the liquid composition but will enable the vapor fraction to be calculated. Next a constant pressure or temperature can be set depending on the available ternary experimental data. Then under the Block folder Block Options should be opened and the electrolyte calculation options should be changed to include the chemistry ID of the dissociation reaction as well as to change the simulation approach to apparent components. If this is not added and changed then the results will not properly take into account the relationship between the three components and the VLE curve will barely change regardless of the fraction of electrolyte added to the system.

Next the feed stream needs to be setup. The recommendation is to use a mass flow rate and have the ethanol and water components always add up to 100 kg/hr of flow, the pressure and temperature setting of the stream should not matter in this instance due to the nature of the Flash2 block which will adjust them to the block settings. It will affect the calculated duty but in this instance that is not a value of interest and therefore does not matter here. Once the ethanol and water flow rates are set the desired amount of salt can be added. A good range is between 0 and 50 kg/hr. This stream flow will be altered after each run in order to construct the x-y curves of interest. For example the ratio of water and ethanol can be adjusted while keeping the flow of lithium bromide constant. This can then be repeated at other values of lithium bromide flow in order to construct a series of VLE curves that illustrate the effect adding an electrolyte to a mixed solvent solution has on the VLE data.

For each run the vapor composition can be calculated by dividing the flow of the component of interest, in this case ethanol by the total flow of the vapor stream to obtain the y value which can then be plotted against the composition of the liquid phases which will correspond to the initial ratio of water to ethanol. Each of these values will need to be recording

in excel in order to construct the appropriate VLE curves which can then be compared to the experimental data. An example can be seen in the results and discussion section of this chapter. Although the VLE data are some of the most useful data, especially for comparison purposes they are not the only useful property. Unlike the vapor and liquid concentrations the Aspen Property environment can be used to directly calculated these values for a range of specifications. For example vapor pressure is one of the most common available pieces of experimental data and therefore can be a useful tool for comparison. In order to calculate the vapor pressure first a new property set needs to be added. The physical property that corresponds to vapor pressure is PBUB. Once the property set is created a new analysis needs to be created of the type "generic."

The input of the Analysis can be setup using Point(s) without flash and the box "use flash retention" can be unchecked. Any flow can be entered under component flow in this instance because the mole fraction is going to be varied under the Variable tab. In the variable tab the constant pressure or temperature can be set. In this case the pressure is set at atmospheric pressure and the temperature is varied by adding it as a variable as is the mole or mass fraction of lithium bromide. The range or list of values to calculate the vapor pressure can then be generated. It is important to keep in mind that the units of the variables cannot be changed. This is one of the few instances in Aspen where this is the case. The temperature used will be the default for the unit set that is in use. Under the tabulate tab the property set of interest needs to be selected and then the simulation can be run in order to calculate the vapor pressure at the temperatures and component fractions of interest. These calculated values can then be compared directly using the graphing capabilities of Aspen or copied and used in a program such as Excel.

2.3 Results and Discussion

The regression of the experimental data sets enabled the parameters to be determined for the ternary ethanol-water-lithium bromide system.[9-12] Ternary experimental data obtained from personal correspondence with Drystill Holdings Inc. was used to conduct an evaluation in Aspen Plus and calculate the accuracy of the data.[12] Further, the parameter fitting to model lithium

bromide demonstrates that the unsymmetric eNRTL model is completely valid for use in a mixed solvent system where one of the solvents is water. This result is also supported by the work completed by Weng et. al. 2016 whom modeled a mixed solvent ternary system of water ethanol and calcium chloride using the eNRTL-RK model. The parameters they found to represent the water-ethanol-$CaCl_2$ system were used to validate the parameters for water-ethanol-LiBr verifying that both sets were on the same order of magnitude as the ones found for the lithium bromide system as seen in Table 2.4 and Table 2.5 comparing the parameters found by Wang et. al. and those found for the ethanol water and lithium bromide system.

Table 2.4: eNRTL Parameters for Ternary Water-Ethanol-$CaCl_2$ System[5]

Species i	Species j	T_{ij}	α_{ij}
Water	Ethanol	1.688	0.3
Ethanol	Water	-0.059	0.3
Water	LiBr	10.518	0.2
LiBr	Water	-5.078	0.2
Ethanol	LiBr	23.733	0.0496
LiBr	Ethanol	-12.718	0.0496

Table 2.5: Regressed eNRTL Parameters of Ternary Ethanol-Water-LiBr System

Species i	Species j	T_{ij}	α_{ij}
Water	Ethanol	1.79862	0.3
Ethanol	Water	-0.0978	0.3
Water	LiBr	15.058	0.2
LiBr	Water	-5.946	0.2
Ethanol	LiBr	20.404	0.0784
LiBr	Ethanol	-9.952	0.0784

In addition, the regression results coupled with the graphical representation of the model seen in Figure 2.11 demonstrates that the model can reproduce experimental results within an acceptable margin of error. This means that the fundamental basis of the model is reasonably appropriate for the system and can be used in the modeling of the pass through distillation system.

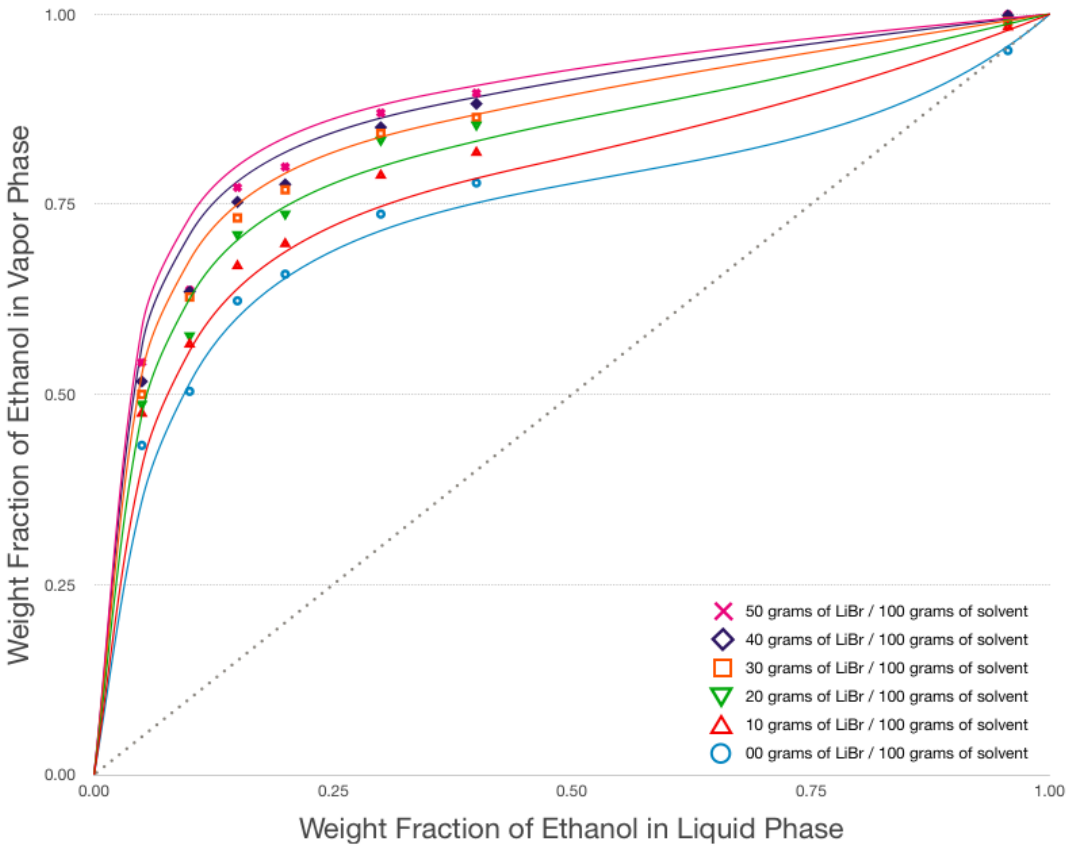


Figure 2.11: Comparison of experimental VLE data against the model developed using Aspen Plus for the ternary system ethanol-water-LiBr.[12]

The parameters determined are reasonably accurate for the temperatures they were regressed with however in future studies, along with the addition of more experimental data at a wider range of temperatures a temperature dependent model could conceivably be created. This would likely prove more accurate due to the range of temperatures and pressures used throughout the pass through distillation process. However, the parameters fit here work reasonably well for the majority of the temperatures encountered in the evaporation part of the process, as well as the temperatures within the absorber and evaporator.

2.4 Conclusion

The eNRTL-RK property method proved to be an appropriate property model to use to model the ternary ethanol-water-LiBr system by fitting binary parameters to experimental data. Using the experimentally found vapor pressures for each binary pair in conjunction with experimental data concerning the vapor pressures of the ternary system reasonably accurate parameters could be determined. This is exciting for multiple reasons, one being that the parameters found can be used in other applications based upon the ternary system of ethanol, water, and lithium bromide. The second reason is that it enables the simulation of Pass Through Distillation (PTD) as applied to bioethanol removal from a fermentation broth to be conducted with some level of accuracy. This is especially important due to the complexities associated with the effects varying levels of electrolytes have on the behavior of a solvent mixture.

3. Simulation of Bioethanol Purification using Pass-Through Distillation

The process of Pass-Through Distillation (PTD), through which temperature sensitive components can be separated without large energy requirements, has recently been developed by two companies: Fielding Chemical Technologies Inc. and Drystill Holdings Inc. One of the most promising applications for the technology is in the separation of bioethanol from a fermentation broth. This is achieved by separating the temperature sensitive materials, such as biomass, under a rough vacuum and absorbing the vapors, in this case bioethanol, into a brine which will enable the mixture to be condensed without the use of expensive refrigeration units. This is a process that has the potential for low energy separation of bioethanol through the use of electrolytes such as the lithium bromide as described in Chapter 2. Thus the ternary property model of ethanol, water, and lithium bromide can be implemented in order to further explore the PTD process specifically in the context of their process for the separation of bioethanol from a fermentation broth.

3.1 Background

One of the most prevalent applications for the PTD process concept is towards bioethanol and the separation of bioethanol from a fermentation broth. The two companies, Fielding Chemical Technologies as well as Drystill Holdings Inc. have developed such a system.[13-14] The process flow diagram for this system can be seen in Figure 3.1. Due to the applications extending beyond the biofuel fermentation area there is interest in accurately modeling the process in programs such as Aspen Plus. This will enable the testing and investigation of process variations,such as the addition of a recycle stream or the use of a salt other than lithium bromide, much easier and at a lower cost compared to real-world experimentations.

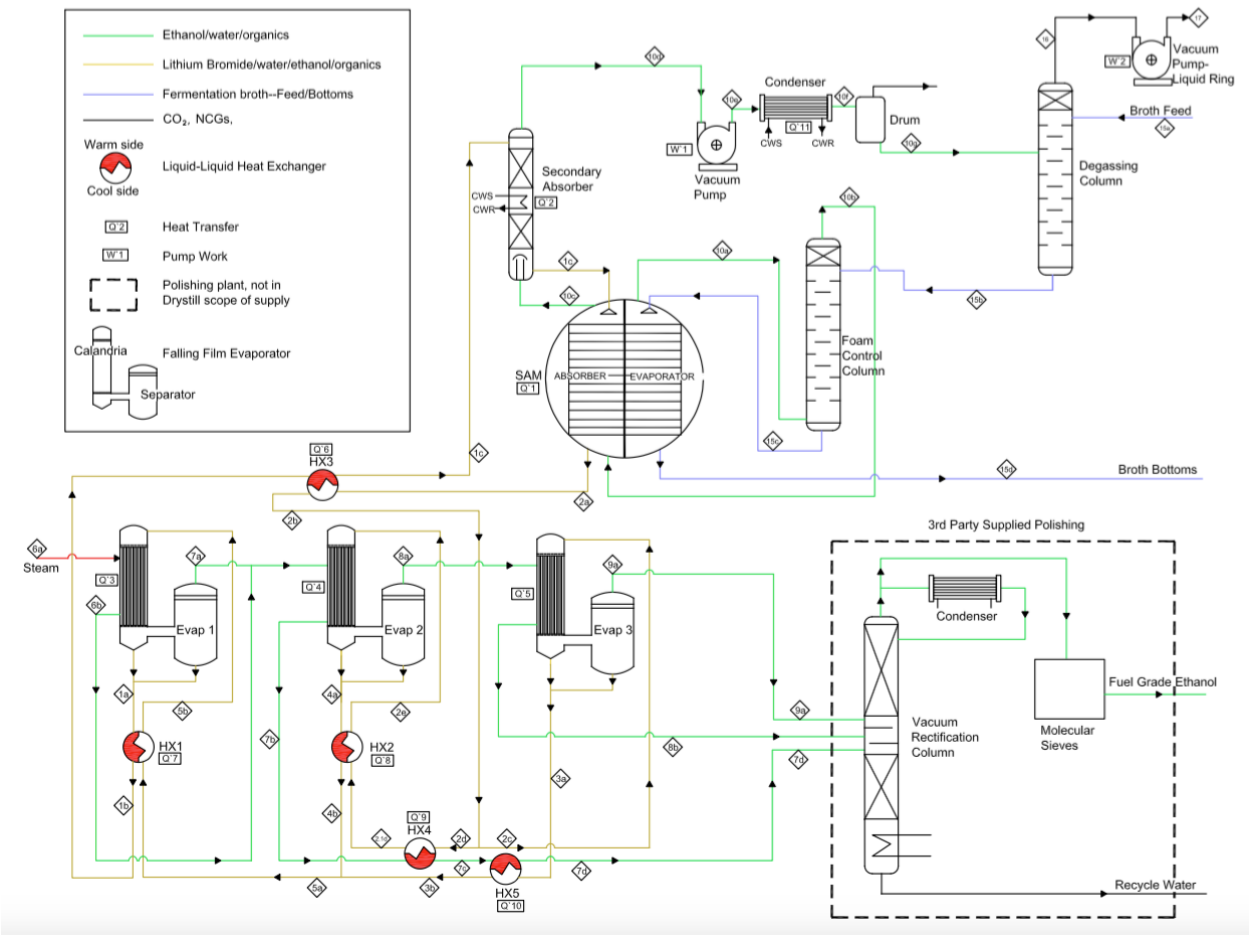


Figure 3.1: Process flow diagram for ethanol purification using pass-through distillation.[14]

The process itself begins with a fermentation broth that contains a mixture of materials such as water, ethanol, biomass, carbon dioxide, and various other compounds. This stream is first fed into a degassing column in order to separate out as much of the carbon dioxide and any other non-condensable gases that are present in the stream. The unit is operated at a pressure of approximately 300 torr which is maintained through the use of a vacuum pump. The remaining fluid in the column, primarily consisting of water, ethanol, biomass,trace amounts of CO_2 and other compounds is removed and fed into the Foam Control Tower. The purpose of this unit is to increase the concentration of ethanol that will be fed into the second half of the process where it will be absorbed into a brine. This is important as the ultimate goal of this system is to remove all ethanol from the fermentation broth for later re-use. The unit operates at a pressure slightly

below 30 torr. Both the vapor and liquid streams exiting the foam control tower are fed into a custom unit developed by Drystill Holdings Inc. known as a Stripper/Absorber Module (SAM).

The SAM unit is made up of two halves: an evaporator and an absorber. These two units are contained in the same housing and the heat generated by the mixing of the brine with the foam control column's vapor stream is transferred to the evaporation unit using heat pipes. The liquid stream received from the foam control column is fed to, and evaporated in, the SAM evaporator; the resulting vapor is then returned to the foam control column. This vapor primarily consists of ethanol, water and what remains of the carbon dioxide. The liquid stream of the SAM evaporator is removed from the process entirely and includes the biomass and other components from the broth thus removing the temperature sensitive portion of the feed stream. The SAM evaporator operates at a pressure of approximately 30 torr and an associated temperature of around 30°C ensuring that there is no damage or fouling.

The absorber half of the SAM unit is fed by the vapor stream from the foam control column and is tied directly to a secondary absorption column through a vapor stream leaving the SAM absorber and a liquid stream entering the unit from the secondary absorber. Much like the evaporator half of the SAM, the absorber operates at slightly below the pressure of the SAM evaporator. The purpose of both the SAM absorber, as well as the secondary absorber, is to mix a recycle stream of concentrated brine from the second half of the process with the remaining water and ethanol from the feed stream to create a dilute brine that is around 45 wt% lithium bromide. The secondary absorber is fed a liquid stream from the second half of the process that contains the concentrated brine that is around 70 wt% lithium bromide and 30 wt% water with some trace amounts of ethanol. The vapor from the secondary absorption column is reminiscent of the foam control column where, ideally, the rest of the carbon dioxide is pulled off along with some water and ethanol by the use of a second vacuum pump. This stream is then sent through a condenser at atmospheric pressure to condense out the water and ethanol present in the stream. The carbon dioxide is then separated from the liquid water and ethanol through the use of a flash drum as a byproduct stream. The liquid stream containing the water and ethanol is fed back into the system as a liquid stream to the top of the degassing column.

The liquid leaving the SAM absorber in the form of a dilute brine is then fed into the second half of the system in order to remove the ethanol from the system and reconcentrate the brine. To accomplish this the second half consists of three evaporators and multiple heat exchangers in a multi-effect evaporator scheme. The liquid stream leaving the SAM absorber is pressurized up from 30 torr to nearly atmospheric pressure. It is then fed through a heat exchanger (HX3) in order to raise it to nearly its bubble point. At this point the stream is split. 30% is sent to the feed stream of evaporator 3 and the remaining 70% is fed through two different heat exchangers: HX4 and HX2. The exchangers continue to heat the stream so that it is on the verge of flashing when it is fed into the feed stream for evaporator 2. The vapor from evaporator 2 is fed to the calandria of evaporator 3 in order to heat up the feed stream and cause evaporation to take place. The spent vapor is then removed from the process as a product stream as is the vapor from evaporator 3 accounting for two of the three product streams.

The liquid streams from evaporators 2 and 3 are then each fed through a heat exchanger, HX2 and HX4 respectively, before combining and passing through HX5 in order to raise the stream nearly to the flashing point prior to being fed into evaporator 1. Evaporator 1 is heated using an inlet steam feed of 200 psig saturated steam. Once the steam condenses in the calandria of the falling film evaporator the spent steam is mixed with the vapor from evaporator 1 and fed into the calandria to heat evaporator 2. After exiting evaporator 2 the stream will exit the process as the third product stream after passing through HX4 and HX5 to remove any remaining usable heat. The liquid stream from evaporator 1 passes through HX1 and HX3 before returning as a concentrated brine to the secondary absorber in the first half of the system.

3.2 Methodology

The simulation of the Pass-Through Distillation process in regards to the separation of bioethanol from a fermentation broth has been developed as a foundation for future work and to encourage further understanding of the processes involved. Aspen Plus V8.8 was used to simulate the system. Each unit of the system, as described in Chapter 3.1, was separately studied and considered in order to select and customize the Aspen block which would best mimic its operation while maintaining rigorous calculations. While some simplifying assumptions and

slight alterations were required for the Aspen simulation to properly converge, the resulting process model in Aspen resembles a real-world pilot plant based upon the PTD processes.

3.2.1 Modifications to Property Model

The previously defined and explored setup in Chapter 2 to model the ternary system of ethanol-water-lithium bromide is essential for the simulation of this system. However, with the addition of carbon dioxide slight alterations need to be made to properly account for the solubility of carbon dioxide in ethanol and water. The addition of carbon dioxide helps to properly simulate the feed the system traditionally deals with. Although the process of interest is the application of PTD to separate bioethanol from a fermentation broth many of the components were omitted from the simulation itself as they are quickly removed and are not present in large enough quantities to significantly affect the results. However the component carbon dioxide was added to the feed stream and therefore also needed to be added to the property model.

A couple changes were made to the property model. First, carbon dioxide was added to the list of specified components and as a Henry's component. This allows Aspen to account for the solubility of carbon dioxide in both water and ethanol. These parameters required to model this solubility can all be obtained from the Aspen database for both the ethanol and carbon dioxide binary pair as well as the water and carbon dioxide binary pair. Under the 'Henry Comps' folder within the 'Components' folder a new Henry's component can be added as seen in Figure 3.2. Second, with carbon dioxide added to the right hand column, Aspen should open a prompt asking if parameters should be added. These parameters will be visible in the Binary Interaction folder within the Methods and Parameters folders. Aspen will also, incorrectly, populate parameters for the lithium bromide and water system; therefore the values under GMENCD-1 and GMENCE-1 need to be manually cleared. It is import to note that this clearing of values will not overwrite the user inputted values obtained in the regression from Chapter 2.

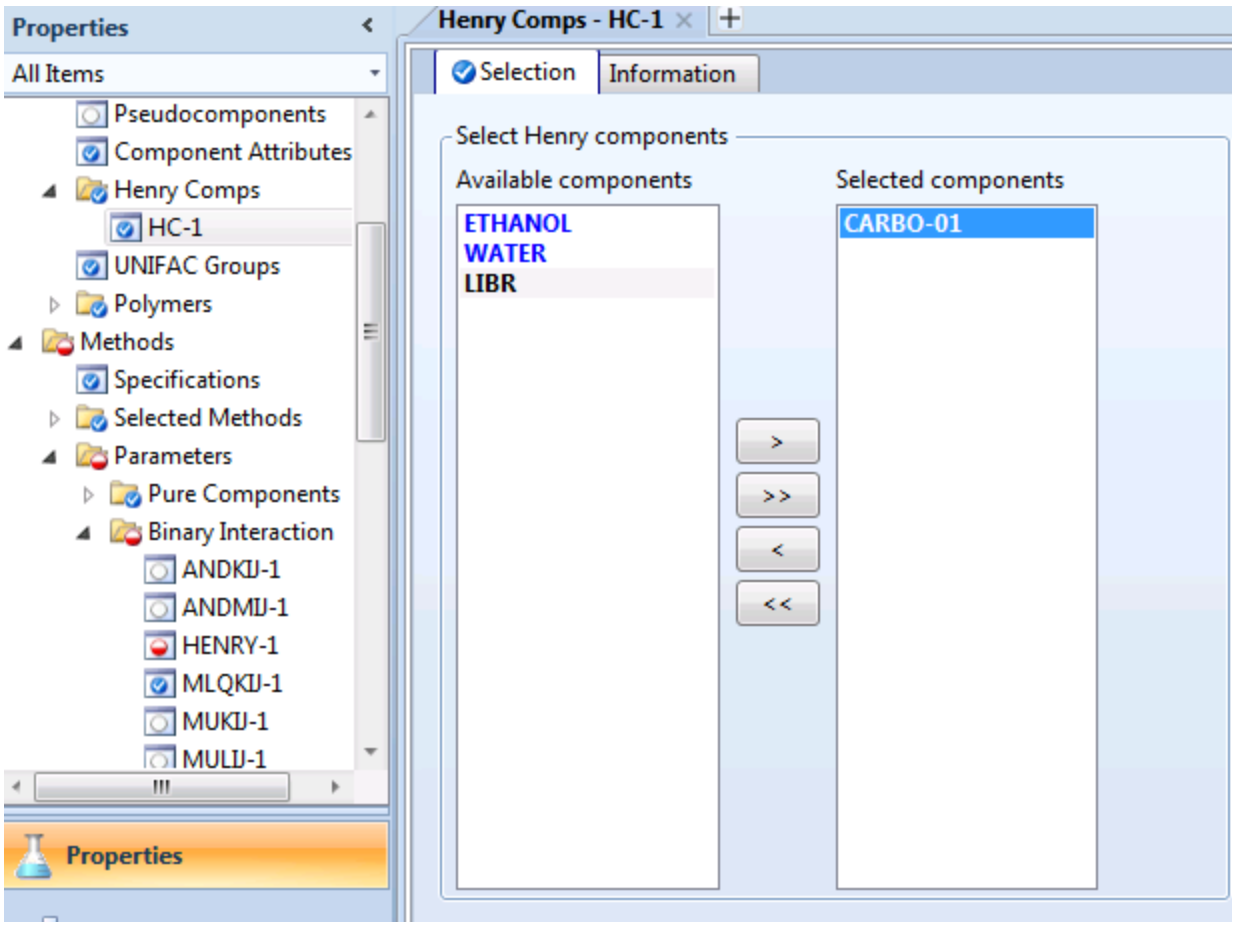


Figure 3.2: Selection of carbon dioxide as a Henry component.

3.2.2 Feed Streams

The input for the process feed streams highlighted in Figure 3.3 is critical for the accurate simulation of the Pass-Through Distillation process. Two of the three inlet streams specified are actual feed streams that can be controlled in the physical process. The third is a stream that has been added for the simulation to run with the purpose of adding the lithium bromide into the system in reality this feed stream does not exist but must be implemented here in order to account for the closed loop nature of the lithium bromide. This spliced stream, 1C-IN must ultimately equal stream 1C-OUT and therefore must be carefully adjusted. The feed stream, 15A in the original process contains a fermentation broth. For the purpose of the simulation the feed

stream has been reduced to three components: water, ethanol and carbon dioxide. This stream was fed to the process at 4 bar, 35°C and 100,000 kg/hr. The mass fraction of ethanol was set to 0.05, carbon dioxide was set to 0.001 and water made up the remainder of the stream at 0.949 mass fraction all which is summarized in Figure 3.4.

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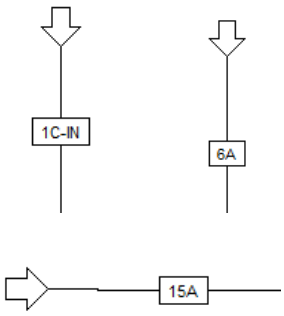

Figure 3.3: The streams in the simulation that required specification.

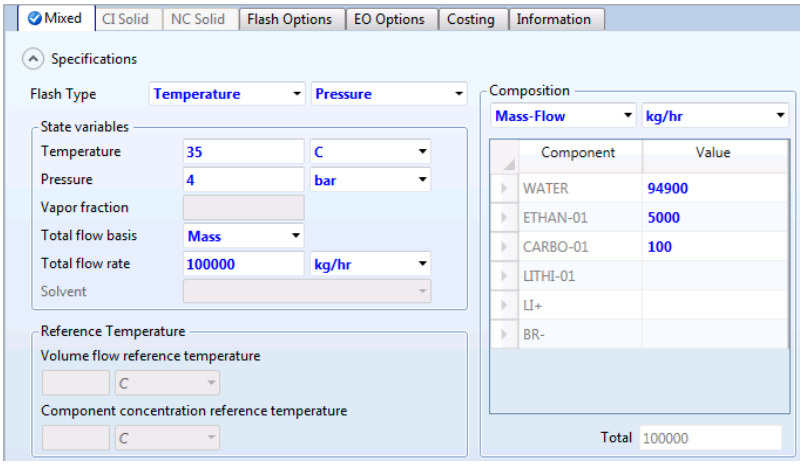

Figure 3.4: Specifications for stream 15A, the feed stream for the PTD process.

The pseudo feed stream of 1C-IN is the stream in the process that is the most heavily concentrated with brine. The desired weight fraction of lithium bromide between the entrance to the secondary absorber in stream 1C-IN and the exit of the dilute brine in the bottom of the SAM absorber was 0.7 wt fraction and approximately 0.45 wt fraction. Therefore the stream 1C-IN was set to the 0.7 lithium bromide wt fraction and the overall flow rate of the system was varied until a concentration of lithium bromide in stream 2A was about 0.45 wt fraction which ended up being around a flow rate of 25000 kg/hr as seen in Figure 3.6.

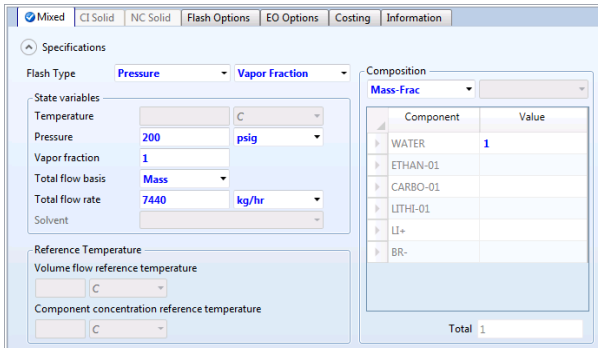

Figure 3.5: Specifications for stream 6A, the steam stream for the PTD process.

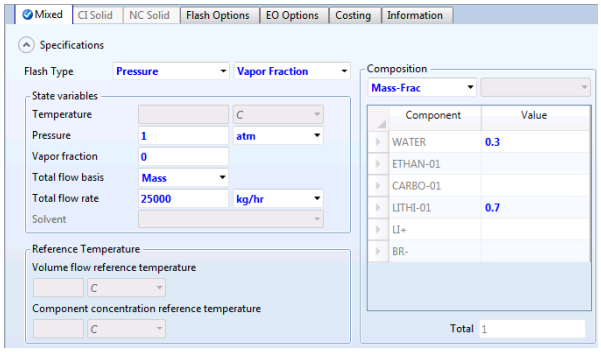

Figure 3.6: Specifications for stream 1C-OUT, the pseudo stream introducing the lithium bromide for the PTD process.

The stream 6A represents the steam being fed to the system. Although many steam pressures could be used, 200 psig saturated steam was chosen as it is commonly available in plants to use as a utility stream. The flow rate of stream 6A was adjusted in order to ensure that stream 1C-OUT was equal to 1C-IN as the liquid stream coming off of evaporator 1 is stream 1A has the same flow rate and composition as stream 1C-OUT. Ultimately it was found a flow rate of 7440 kg/hr would return the 25000 kg/hr of concentrated brine seen in stream 1C-IN back up to the secondary absorber as seen in Figure 3.5.

3.2.3 Degassing Column

The primary purpose of the degassing column is to remove as much of the carbon dioxide from the feed stream as possible since gases at low pressures take up a significant volume. The unit was modeled using a Flash2 block, visible in Figure 3.7, to take into consideration the flash of the feed stream as pressure decreases from 3000 torr (4 bar) to 300 torr. No heat is added to or removed from this block as it operates solely on the change in pressure occurring in order to free the carbon dioxide dissolved in the water and ethanol which can be seen in Figure 3.8. The vapor stream that ideally contains mostly carbon dioxide will then exit and enter one of the two vacuum pumps while the liquid stream will enter the foam control column.

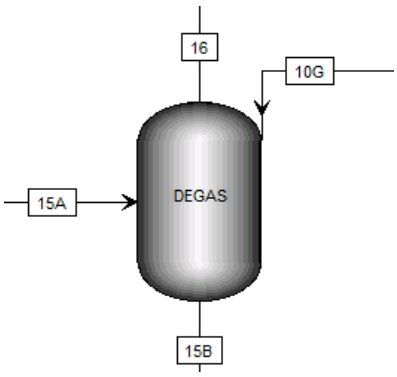

Figure 3.7: Degassing column unit and streams tied into it.

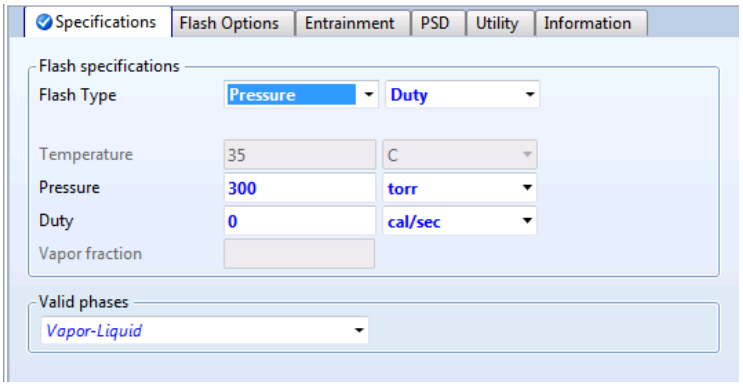

Figure 3.8: Setting used for the degassing column setup.

3.2.4 Vacuum Pumps

Once the vapor stream containing predominantly carbon dioxide leaves the degassing column it enters one of the two vacuum pumps. Here the stream is simulated to enter at the pressure of the degassing column, 30 torr, and exit at atmospheric pressure. When setting up this unit, visible in Figure 3.12, there are a couple important aspects related to the quality of the pump inlet stream that must be taken into consideration For example: generally pumps do not handle anything other than liquids and, by default, Aspen is set to produce a warning or error when a vapor is detected entering the pump. These error messages and any problems that accompany them can be avoided by changing the 'stream vapor fraction checking' option to *None* on the 'calculation options' tab and changing the 'valid phases' on the 'flash options' tab from *liquid only* to *Vapor-Liquid* as can be seen in Figures 3.9, 3.10 and 3.11 respectively.

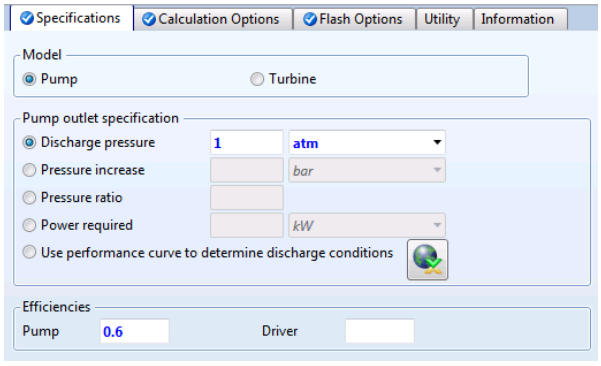

Figure 3.9: Setting for the vacuum pump on the specifications tab of the pump block setup.

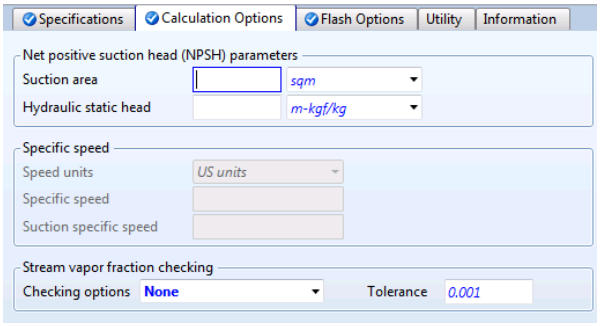

Figure 3.10: Setting for the vacuum pump on the Calculation Options tab of the pump block setup.

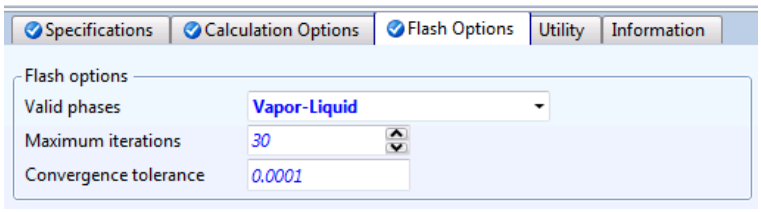

Figure 3.11: Setting for the vacuum pump on the Flash Options tab of the pump block setup.

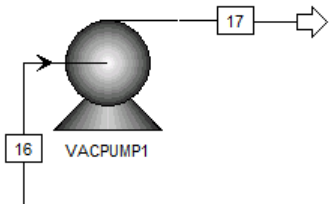

Figure 3.12: Vacuum Pump unit for the degassing column and streams tied into it.

3.2.5 Foam Control Column

The foam control column is in some regards an extension of the SAM-evaporation unit as, in reality, its pressure is dependent upon on the pressure of the SAM. In the simulation the pressures must be manually accounted for. The vapor coming off the top of the foam control column is ultimately the ethanol that will ideally be separated out as a product for future use. As previously mentioned the unit operates at around 30 torr and slightly under that of the SAM-evaporator therefore a pressure of 29 torr was assumed. As the block chosen to represent this unit is a RADFRAC column seen in Figure 3.14, which is rigorous by nature, correct setup is important to get accurate results or even results that converge at all. In addition, the RADFRAC column is often used for distillation column simulations and therefore must be adjusted to model a column absent of condenser and a reboiler. This can be done by changing the settings on the Configuration tab for the block setup so that both the option for the condenser and for the reboiler are changed to *None*. Also on this page, the 'convergence' value needs to be changed from *Standard* to *Custom* as see in Figure 3.13.

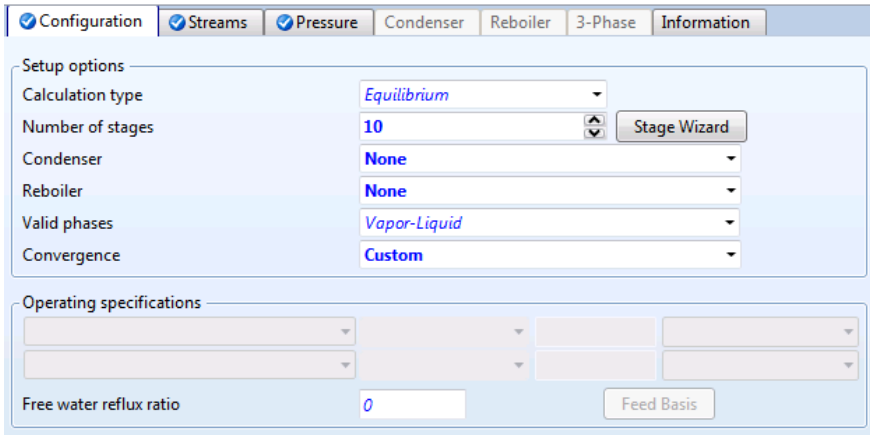

Figure 3.13: Settings for the Foam Control Column on the Configuration tab of setup for the column.

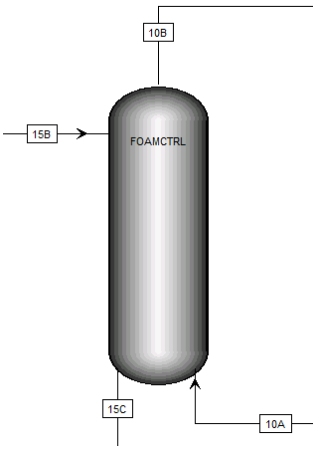

Figure 3.14: RADFRAC unit used to simulation the Foam Control Column.

The inlet streams of the RADFRAC block need to be identified by which stage they are entering the column on. Aspen labels its columns so that 1 is the top stage and in this instance 10 is the bottom stage. Stream 15B is the liquid stream from the degassing column and is set to enter on the top stage of the column. Stream 10A is returning from the SAM evaporator and is set to enter on the bottom stage, stage 10. In addition to specifying the stage the stream enters on the Convention option will need to be changed from *Above-Stage* to *On-Stage* as seen in Figure 3.15. For simplicity's sake, the pressure of the top column was set to 29 torr, which can be seen in Figure 3.16, as it is an approximation that will be close enough to get an initial operation model of the PTD process.

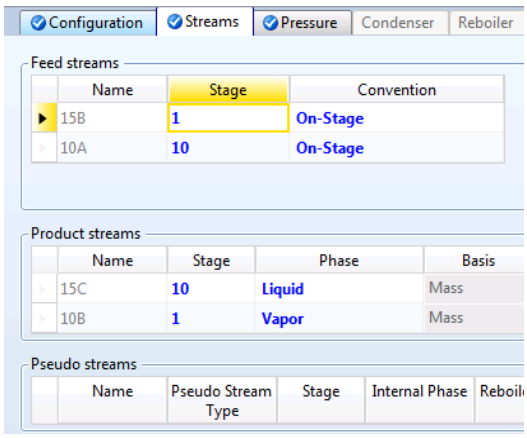

Figure 3.15: Stage settings for the inlet streams of the Foam Control Column.

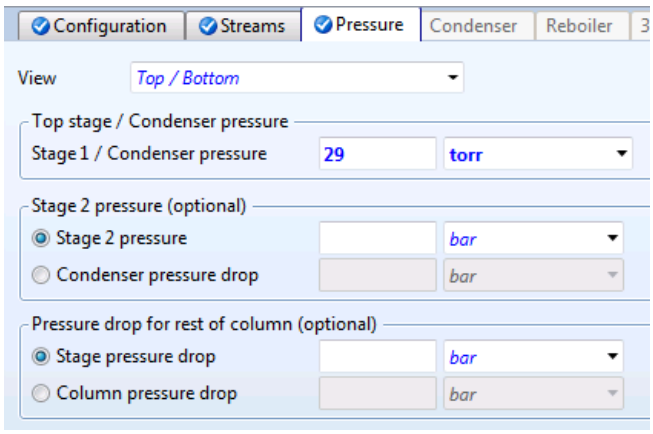

Figure 3.16: Pressure settings for the Foam Control Column.

Finally, to complete the setup of the foam control column the convergence of the unit needs to be changed as recommended by the Aspen help manual when modelling adsorption columns rather than distillation columns. Within the foam control block settings, the 'convergence' folder must be opened and the setting on the Convergence sheet must be altered. On this sheet on the *Basic* tab the Algorithm should be changed from *Standard* to *Sum-Rates* as illustrated in Figure 3.17. If there is no drop down menu for this option, it is likely that the convergence is set to something other than *custom* on the initial configuration sheet.

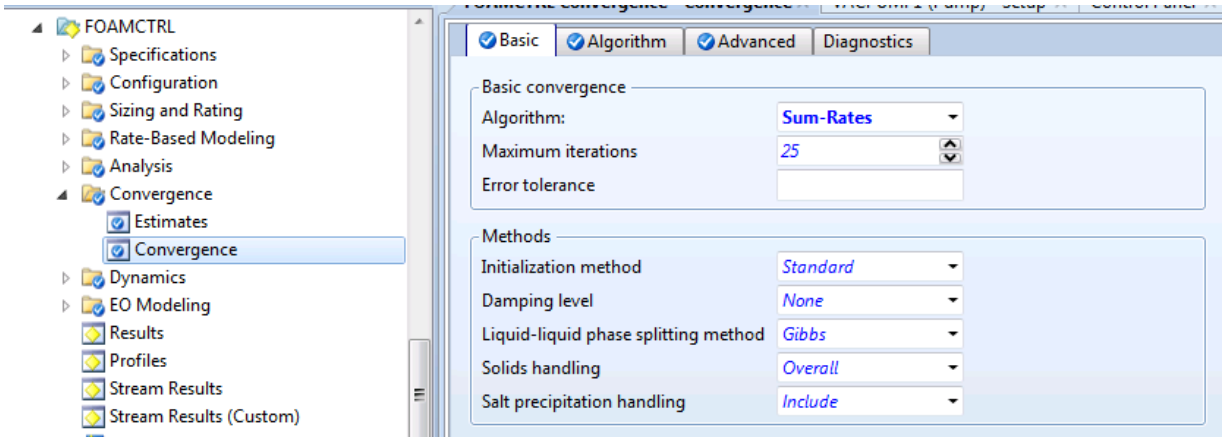

Figure 3.17: Location of the Convergence sheet for the block representing the foam control column as well as the settings for the basic convergence algorithm.

3.2.6 Stripper/Absorber Module (SAM)

The SAM unit represents what is in many ways the most complicated set of blocks in the system due to the fact that in reality the integral part of the unit is the transfer of heat from the absorption side of the unit to the evaporation side. Due to the complex interactions between the two interconnected units some simplifying assumption needed to be made which accurately duplicated the way these systems interact, but also remained within the simulation abilities of Aspen Plus. Both units were modeled using Flash2 blocks seen in Figure 3.20. In reality the excess heat generated from the heat of dilution in the absorption side of the unit is used to cause the evaporation in the evaporation side of the unit. However, that configuration leads to many convergence issues within Aspen, especially when small changes are made to the process elsewhere. Therefore a brief analysis was performed by comparing the amount of ethanol evaporated and the amount of energy required when the vapor fraction in the SAM evap was changed. Then an appropriate vapor fraction was chosen. A heat stream was added between the two halves of the SAM unit so that the SAM evaporator could take whatever the required energy was from the SAM-absorber. The SAM evaporator was set to an operational pressure of 30 torr as seen in Figure 3.18 and the SAM absorber set to 28 torr as seen in Figure 3.19.

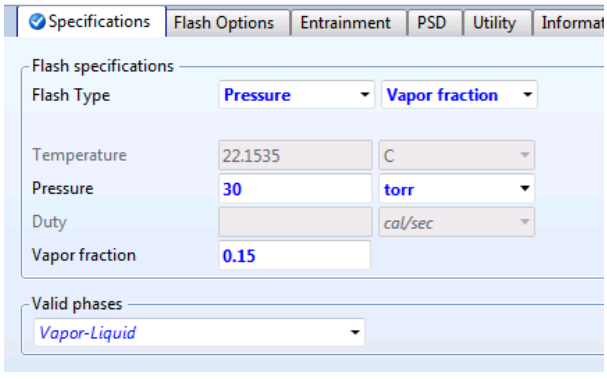

Figure 3.18: Block specifications for the SAM-evaporator unit.

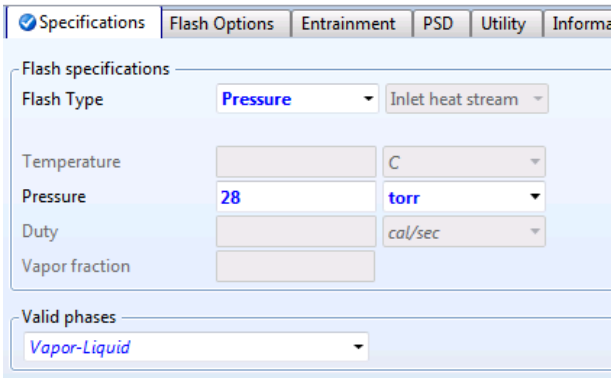

Figure 3.19: Setup for the SAM absorber unit.

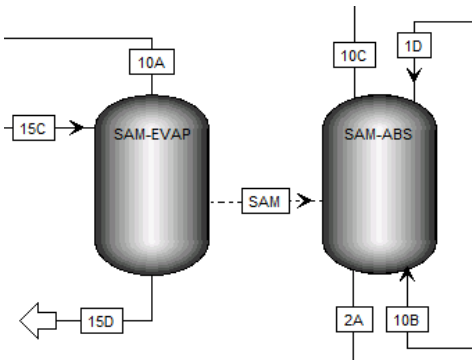

Figure 3.20: Illustration of SAM-evaporator and SAM-absorber setup including the addition of a heat stream.

3.2.7 Secondary Absorber

The secondary absorber can be considered an extension of the SAM absorber similar to the foam control column's relation to the SAM evaporator. Like the SAM evaporator and SAM absorber, the secondary absorber also operates at a pressure around 30 torr. A liquid stream of concentrated brine enters the secondary absorber on the top stage and a vapor stream is pulled off of the top that ideally contains the remainder of carbon dioxide in the system along with some ethanol and water. This tower is possibly the most complicated one to model; its operation was approximated using the RADFRAC block. Some complexity of the column stems from the heat generated during the dilution of the brine and therefore a cooler must be implemented in the column in part to reduce the vapor stream exiting the top of the column.

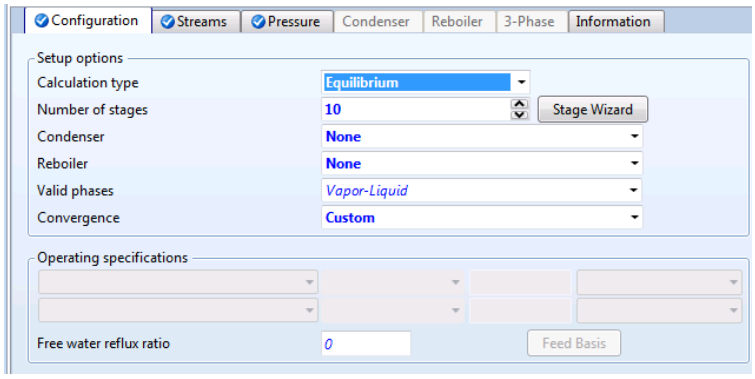

Figure 3.21: Setup of the configuration tab for the secondary absorber.

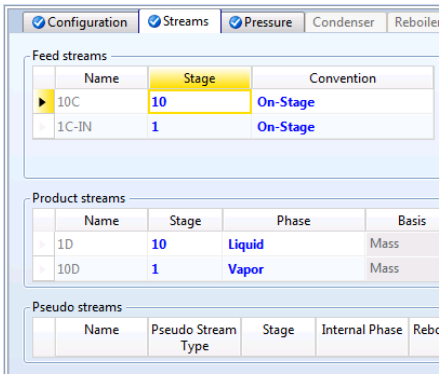

Figure 3.22: Setup of the streams tab for the secondary absorber.

Overall there are many similarities between the setup of the foam control column and the secondary absorber seen in Figure 3.26. For example, both use the equilibrium calculation type, are estimated to have approximately ten equilibrium stages and both the condenser and reboiler options are set to *None* as seen in Figure 3.21. In addition, as was with the foam control column, the convergence should be set to *convergence* so it can be changed. The streams should be set up so that the vapor stream leading to the second vacuum pump is coming off of stage 1 with the *On-Stage* convention as seen in Figure 3.22. The liquid stream entering the SAM-absorber should be set to stage 10 also with the *On-Stage* convention. Although the pressure is technically lower than that of the SAM-absorber it must be set to the same or higher to prevent calculation errors from occurring and therefore is set at 28 torr as illustrated in Figure 3.23.

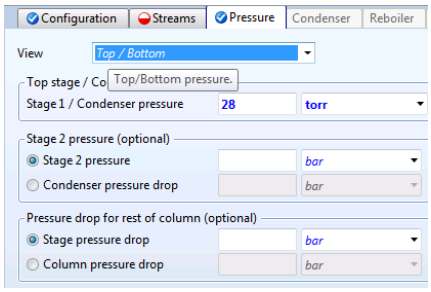

Figure 3.23: Setup of the Pressure tab for the secondary absorber

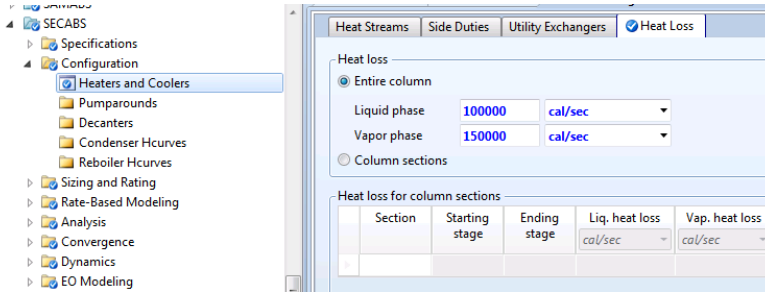

Figure 3.24: Setup of the column heat loss to simulate a cooling stream.

The part of the setup for the secondary absorber that differs significantly from the setup of the foam control column is the addition of a heat loss restriction on the column to simulate a cooler visible in Figure 3.24. Aspen Plus allows stage by stage heat removal but in this case it was decided that entire column heat loss would be better for the purpose of initial simulations. The heat loss amount was determined by attempting to minimize the ethanol lost in the vapor stream while permitting enough heat to enter the SAM absorber. This heat is then transferred to the SAM evaporator through the use of a heat stream. The final setting for the secondary absorber was the use of the Algorithm *Sum-Rates* for the convergence as seen in Figure 3.25.

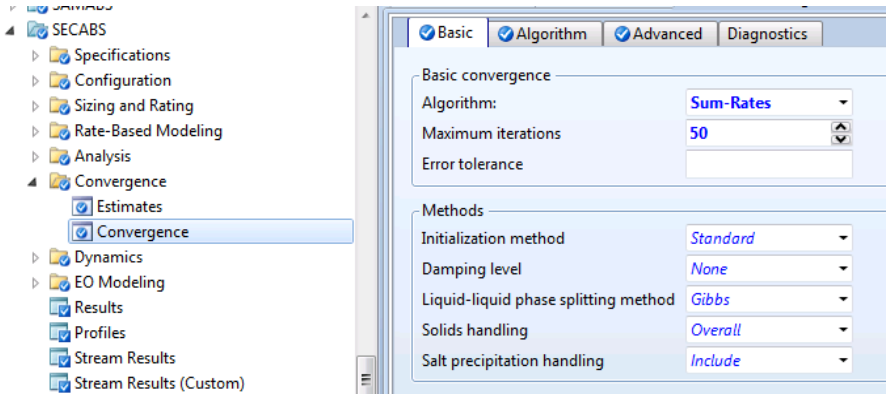

Figure 3.25: Convergence settings for the RADFRAC block representing the secondary absorber.

Figure 3.26: RADFRAC unit used to simulation the secondary absorber.

3.2.8 Condenser and Drum

The vapor stream coming off the top of the secondary condenser enters the second vacuum pump with specifications identical to the first vacuum pump. Following the pressurization of the stream to atmospheric pressure it passes through a condenser in order to condense all of the vapors from components such as ethanol and water to a liquid phase. This condenser unit was modeled using a Heater block, seen in Figure 3.28. The block specifications were set for a pressure equal to atmospheric pressure and a vapor fraction equal to the mass fraction of carbon dioxide in the inlet stream as seen in Figure 3.27. If the vapor fraction was set to zero it would calculate the cooling needed to also condense the carbon dioxide to a liquid state.

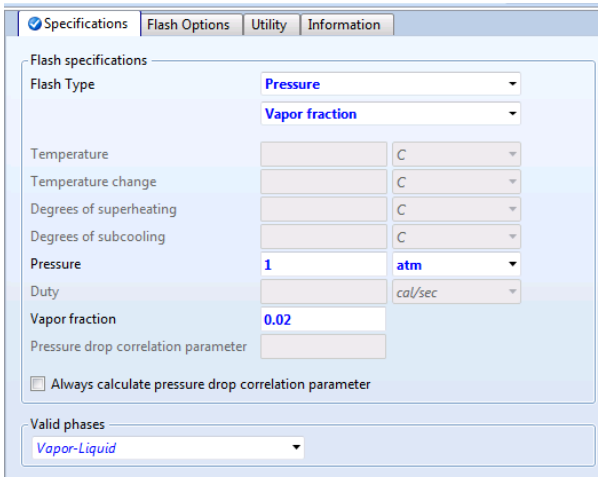

Figure 3.27: Specifications for the HEATER block representing the condenser.

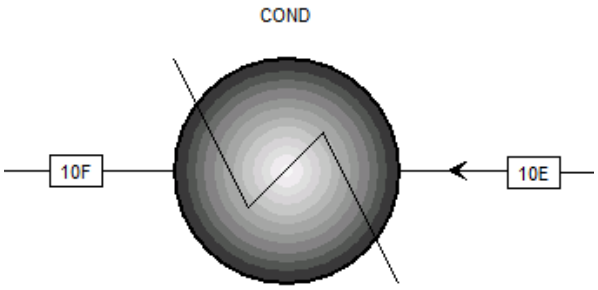

Figure 3.28: Illustration of the HEATER block and streams for the condenser.

After the stream passes through the condenser it enters a flash drum seen in figure 3.30, where the carbon dioxide and any other non-condensable gases exit as a byproduct stream and the remaining liquid phase is recycled to the top of the degassing unit. This unit was modeled using the SEP block. This block allows the manually specified distribution of components. It was used to ensure only carbon dioxide exited the vapor stream leaving the remaining water and ethanol to be returned into the degassing column. Therefore, the only settings required were those specifying that all carbon dioxide would be removed in the vapor stream as seen in Figure 3.29.

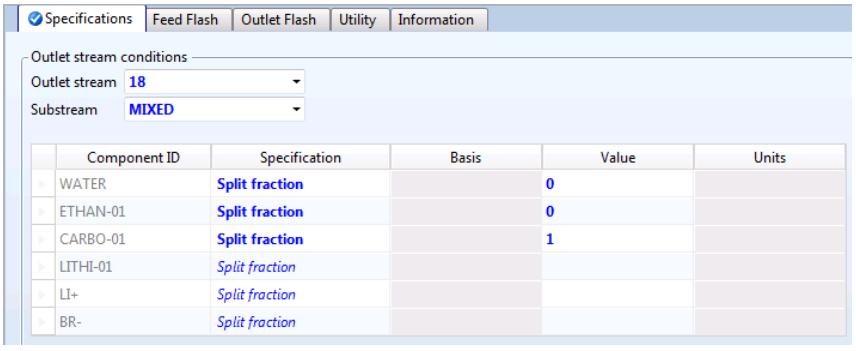

Figure 3.29: Specifications used to set up the SEP block in order to model the Drum.

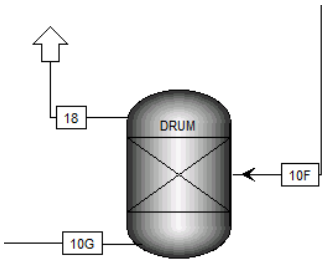

Figure 3.30: Illustration of the SEP block used to represent the Drum.

3.2.9 Evaporators

The three evaporators in the system were all built in using a Heater Block in conjunction with a Flash 2 unit. The heater block served as the approximation for the behavior of the calandria. For each of the evaporators it was assumed that the heat generated was from the phase change of the stream entering the calandria. In each of the three cases the stream entering the heater block was either a saturated vapor or partial vapor stream and left the heater block as a saturated liquid. This energy generated was then transferred to the Flash 2 unit which would result in partial flashing of the feed stream to the evaporator.

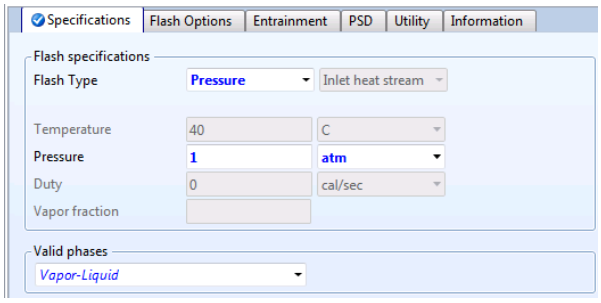

Figure 3.31: Specifications set for Evaporator 1.

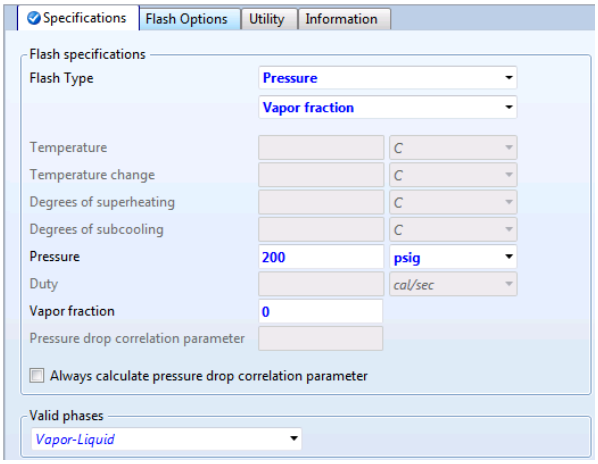

Figure 3.32: Specifications for Calandria 1.

Evaporators 1 and 2 were both set up in similar ways which can be easily seen in Figures 3.31-3.34. In both cases the calandra was set to have a vapor fraction of zero so that all of the energy generated from that phase change could be used in the flashing of the feed to both of the evaporator units. The separation portion of evaporator 1 was set at atmospheric pressure and the calandria side was set to the stream pressure of 200 psig. For the second evaporator system both the calandria side as well as the evaporator were set to slightly below atmospheric pressure at 730 torr but the remainder of the settings remained identical.

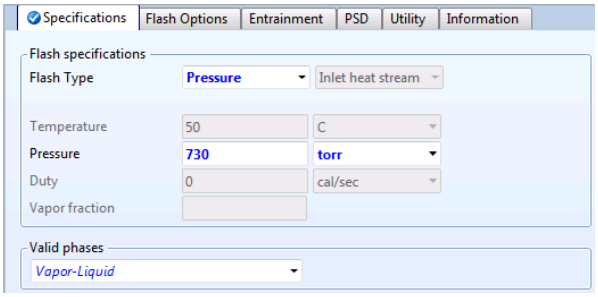

Figure 3.33: Specifications set for Evaporator 2.

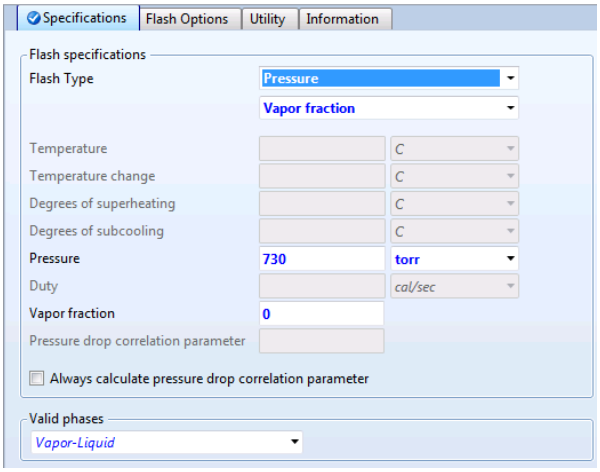

Figure 3.34: Specifications for Calandria 2.

The third evaporation system was set up a bit differently, as seen in Figures 3.35 and 3.36, as it was observed that an extremely large amount of energy was being transferred to the unit causing the majority of the evaporator feed to be flashed. This was remedied by having this particular unit operate backwards. The desired vapor fraction of the evaporator unit was set to 0.25 wt fraction and the pressure of both the evaporator and the calandria were set to 700 torr. The heat required for this separation was then taken from the stream passing through calandria thus only taking the energy required to separate the feed as desired and not all the energy available for the separation.

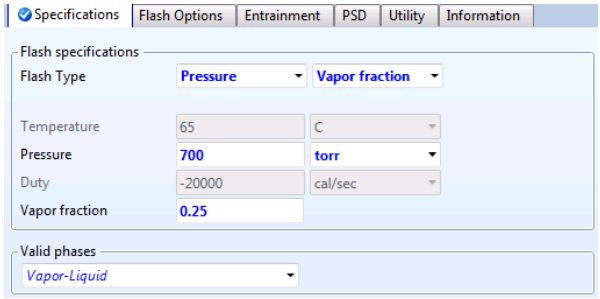

Figure 3.35: Specifications set for Evaporator 3

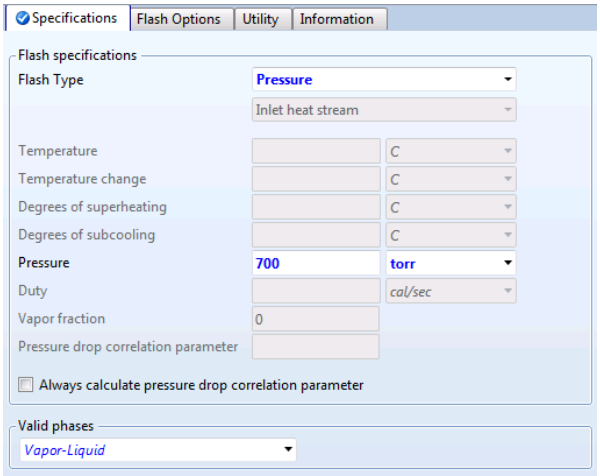

Figure 3.36: Specifications for Calandria 3

3.2.10 Heat Exchangers

For the modeling of this system the heat exchangers used the *Design* calculation mode rather than the *Simulation* calculation mode. This meant that Aspen would run adjusting the geometry of the unit to match the specs rather than calculating the results based upon the design of the heat exchanger. Initially the heat exchangers were set to have a LMTD of approximately 5°C but the resulting simulation had many errors and even caused streams to register a temperature akin to absolute zero. Therefore, the various heat exchangers were modified so that the two outlets would have a temperature difference of 5°C.

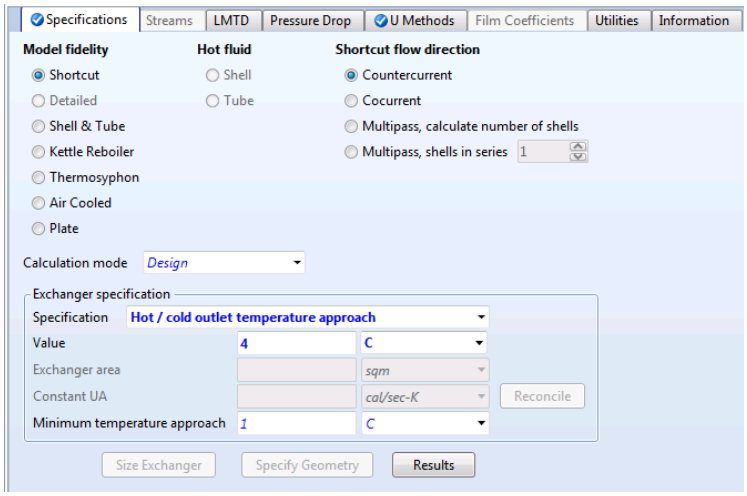

Figure 3.37: Set up of heat exchanger units

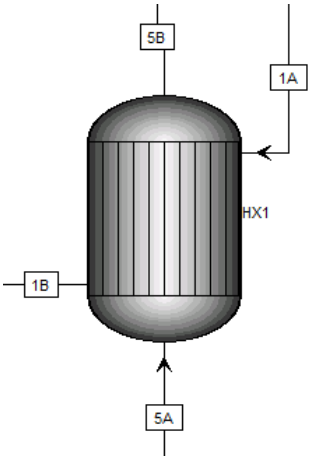

Figure 3.38: Illustration of the HeatX blocks used to model HX1-HX5.

3.2.11 Overall Considerations

Much of the system is relatively straightforward to configure such as the feed streams and pumps. Other parts of the system lend themselves as a more open ended problem where there is plenty of opportunity for tweaking and adjusting how a specific unit is calculated. Some examples include: how the various HeatX and Heater units function together as a system and the plethora of customization tweaks, such as tray sizes, for the RADFRAC blocks used in the secondary absorber and foam control column. For these reasons the setup details above should not be considered the "right" way to model this system but merely a framework moving forward to assist in the demonstration and a set towards the accurate simulation of this complex system.

3.3 Results and Discussion

The results of this Aspen Plus simulation overall show that the model built can be used as a framework for further development of the simulation of the PTD process applied to bioethanol extraction from a fermentation broth. There are areas where improvements could be made but they would require additional information about details such as the viscosity of an ethanol-water-lithium bromide mixture or the use of fortran code added to the operation of the various unit blocks. Thus overall the below results support the development of this simulation as a framework for further improvements on the modeling of the PTD system.

3.3.1 Feed Streams

As the streams being fed into the system are completely user configured and not calculated via Aspen there is little to comment on concerning results. However, it is important to note that for both stream 6A as well as stream 1C-OUT the compositions were set but the flow rates were chosen using trial and error. Specifically in the case of the 1C-OUT stream, the flow rate was adjusted until a composition of approximately 0.45 weight fraction lithium bromide was leaving the SAM-absorber is stream 2A. Therefore when changes were made to the secondary absorber, especially in regards to the heat loss of the entire column the amount of vapor leaving the top of the column increased requiring an increased flow rate. Similarly the cooler the secondary absorber was the less of the flow into the column was vaporized and the lower the stream 1C-OUT flow rate needed to be. Ultimately the flow rate of 25000 kg/hr was chosen based upon the operating conditions and results of the secondary absorber.

As previously mentioned the stream 6A, the 200 psig saturated steam entering the calandria of evaporator 1 had a flow rate entirely based off the fraction of liquid that needed to be removed in order to achieve the flow rate and approximate composition present in the concentrated brine stream of 1C-OUT and was done via trial and error. Although the trial and error method was ultimately effective in determining the necessary flow rates for streams 1C-OUT and 6A it could prove useful to expand the model through the addition of manipulator

blocks that would allow those values to be calculated automatically using the addition of some Fortran in conjunction with the Aspen blocks and the addition of a calculator block or two.

3.3.2 Degassing Column

The purpose of the degassing column is to simply remove the carbon dioxide from the feed stream. The feed stream entered the system at 4 bar and 35°C with a flow rate of 100,000 kg/hr. The mass fraction of carbon dioxide in that stream was equivalent to 0.001 indicating a flow rate of 100 kg/hr of carbon dioxide. Ideally only that carbon dioxide leaves through the vapor stream coming off the top of the degassing column. In the simulation 57.3028 kg/hr of the carbon dioxide is pulled off the top in addition to 2.12919 kg/hr of water and 1.56771 kg/hr of ethanol. The remainder of the carbon dioxide water and ethanol then are free to exit in the liquid stream to the foam control column but overall this unit appears to be accurately modeled using the Flash2 block. The set pressure for the unit of 300 torr could be altered and varied though to see how it affect the amounts of ethanol, water and lithium bromide to be pulled off the in the vapor stream leaving the column.

3.3.3 Vacuum Pumps

In regards to the two vacuum pumps in the system, both performed as predicted especially once the blocks were set to accept a vapor inlet. In both instances the vacuum pump raised the pressure from either 30 torr or 300 torr to atmospheric pressure. In the specific instance of the vacuum pump pulling vapor off of the degassing column the temperature was raised from an inlet of approximately 36°C to approximately 196°C. The concern though is with the second vacuum pump. In the second pump the pressure behaves as expected but the temperature increases from approximately 95°C to nearly 2250°C. The problem here does not appear to stem from the function of the pump block but from the large flow rate of the stream containing a significant amount of ethanol and water. In the case of the first pump only 2.12919 kg/hr of water and 1.56771 kg/hr of ethanol were in the stream. For the second vacuum pump though the stream contains 2061.43 kg/hr of water and 952.632 kg/hr of ethanol along with 40.18 kg/hr of carbon dioxide. This large flow rate is where the problem stems from and the best way to adjust it is through variations in how the RADFRAC block simulates the secondary absorber.

3.3.4 Foam Control Column

The foam control column has a primary function of removing as much ethanol in the vapor stream leaving the top stage of the column as possible, and allowing as much water as possible to be removed through the liquid stream at the base of the column. There are no heating or cooling streams associated with this column which simplifies the modeling of the unit considerably. The resulting flow rates for this column indicate that the unit is operating as it is expected to operate. For example, the vapor stream leaving the column for the SAM-absorber contains 14216.6 kg/hr of water, 5019.5 kg/hr of ethanol and 42.7 kg/hr of carbon dioxide, a mass fraction of about 0.26 ethanol. A significant amount of the water present in the feed stream is also removed and enters the SAM-evaporator, 97005.1 kg/hr of water, 1957 kg/hr of ethanol and essentially no carbon dioxide which is all within reason. The pressure for this column is set in the neighborhood of 30 torr. It could prove useful to have the pressure for this block calculated based off of the SAM-evaporator using one of the manipulator blocks present rather than setting a hard value for the column.

3.3.5 Stripper/Absorber Module (SAM)

The SAM provided a unique simulation challenge as it represented a piece of custom equipment that Aspen Plus had no designated or suggested block for. However, a few simplifying assumptions were made that enabled the pair of units to operate in a manner similar to what was expected. Vapor was removed from the top of the SAM-absorber to enter the secondary absorber, a flow rate of approximately 3477.16 kg/hr made up of 40.28 kg/hr of carbon dioxide and 3477.16 kg/hr of ethanol. Ideally the ethanol is completely absorbed by the concentrated lithium bromide brine. The ethanol and water absorbed by the brine exits the bottom of the SAM-absorber unit in stream 2A consisting of 19655.2 kg/hr of water, 4066.89 kg/hr of ethanol and 2.52 kg/hr of carbon dioxide. The amount of liquid removed from the system by the SAM-evaporator was equal to a total mass flow of 83,672.3 kg/hr with 82,740.7 kg/hr of that being water, and in the real system would also include the biomass. More ethanol could be recovered from the feed into the evaporator by increasing the amount of energy

removed from the SAM-absorber which ultimately is one of the most important pieces of the SAM unit that needed to be incorporated into the simulation

The transfer of heat from the absorber side of the unit to the evaporation side of the unit was accomplished through the use of a heat stream calculated by setting the SAM evaporator to take the energy required to keep a consistent vapor fraction in the unit which would allow a substantial amount of ethanol to be removed while minimizing the amount of energy required. However, one of the drawbacks of setting the vapor fraction within the SAM-evaporator was that the required amount of energy was pulled off of the SAM-absorber at all times. This lead to a temperature discrepancy where the temperature of the evaporator was greater than the temperature of the absorber. One could argue that a smaller vapor fraction should be maintained in the SAM-evaporator but it is much more likely that, as with the vacuum pump, the problem stems from the operation of the secondary absorption column.

3.3.6 Secondary Absorber

The secondary absorber in many ways proved to be one of the most problematic units to model. There were a number of reasons for this including the fact that it is one of the units where the first half of the process meets the second half of the process. The column needed a cooler to be implemented as to reduce the temperature from the exothermic reaction occurring during the addition of the ethanol and water from the foam control column to the concentrated brine from stream 1C-OUT. Also the RADFRAC column, although the best choice to simulate this unit, by default uses an equilibrium calculation which leads to an assumption of close to constant molar overflow. This results in excess vapor coming off the top of the column leading to the problems encountered with the second vacuum pump. In the simulation process the amount of vapor exiting the column was minimized by increasing the cooling of the tower. This lead to the problems encountered in the SAM-absorber where the temperature was lower than theoretically possible to provide the desired separation in the SAM-evaporator.

In order to fix some of these problems tied to the operation of the secondary absorber different calculation methods need to be implemented such as switching it from an equilibrium based calculation to a rate based calculation. Unfortunately, this too leads to issues as parameters required for these calculations do not exist in the Aspen databases. For example: the calculation

of the viscosity of the water, ethanol, lithium bromide and carbon dioxide mixture. Another reason that the rate based calculation method was not implemented was due to the fact that it can be very sensitive to small changes and is not realistic in the initial formulation of a simulation especially because some design parameters are needed such as the tray height and diameter which would need to be adjusted with any change in inlet streams to the column. Future studies should further investigate the implementation of this block here possibly coupled with design spec and calculator blocks so it can appropriately adjust settings when changes are made elsewhere in the model.

3.3.7 Condenser and Drum

The condenser and the flash drum are used in order to condense the vapors from the secondary vacuum pump and then return components such as the ethanol and water back into the system via the degassing column and remove the carbon dioxide from the system as a byproduct. In the case of the condenser it was initially set to cool the stream so that the vapor fraction was zero. This causes an issue where Aspen cools the stream to condense not only the water and ethanol present in the stream but also the carbon dioxide. Therefore the vapor fraction needs to be set at least equal to the mass fraction of carbon dioxide in the stream or alternative to a specified temperature. Due to the large amount of vapor requiring cooling and the large temperatures calculated by the vacuum pumps the energy calculation for the condenser will be incorrect until the issues with the secondary absorber can be resolved. In the case of the drum a "dummy" block of sorts was used to make sure accurate results could be obtained when the recycle stream was reintroduced to the degassing column. In addition it ensured that the carbon dioxide present in the stream was completely removed in order to help account for some of the errors stemming from the secondary absorber.

3.3.8 Evaporators

Several different arrangements were considered before deciding to model the multieffect evaporator system using a series of heaters tied to flash 2 units using an energy stream. This setup allowed the hot stream causing the evaporation taking place to be accurate. As previously mentioned the calandria, modeled using the heater block, was set up so that the incoming vapor

stream exited as a saturated liquid stream and the energy released could be used to cause the separation in the corresponding evaporation unit. All in all this setup worked reasonably well but there were some concerns with the results of the third evaporation unit where an extremely large amount of energy was added to the system. For this reason the evaporator was set up to only take enough energy to result in a vapor fraction equal to what was occurring in the second evaporator. One area of concern with this setup is reminiscent of problems encountered with the condenser. When the heater blocks were set to have a saturated liquid output any carbon dioxide remaining in the stream will need to be condensed as well resulting in an increase in energy supplied to the flash 2 block. This can ultimately be further traced back to the secondary absorber and the inability to get all of the carbon dioxide pulled off the top of the column along with minimal amounts of water and ethanol. Therefore there are two ways to address this issue either change the vapor fraction in the calandrias to the wt fraction of carbon dioxide present or set a specific temperature for the streams to be cooled down to.

3.3.9 Heat Exchangers

The heat exchangers were set up as rigorously calculated HEATX blocks. These were appropriate blocks for their function but some issues associated with them were the fact that, unlike reality, Aspen streams experience no pressure drop or change in temperature in between units and therefore the necessity of some of the heat exchangers was not as crucial in the simulation as they are in reality. In addition, the way that HEATX blocks operate either a simulation mode is used where the area of the heat exchanger or the overall energy transferred needs to be specified. As the area would change with any variance in the feed flow the simulation option was not desired. That meant the design calculation mode needed to be used so a property of the hot or cold stream had to be specified. The use of a LMTD of 5 resulted in many problems for the simulation and therefore the heat transfer occurring in each of the heat exchangers was considerably reduced and leaving room for further refining in future work.

3.3.10 Conclusion

The simulation of Pass-Through Distillation (PTD) using Aspen Plus V8.8 was overall successful. Custom units such as the stripper/absorber module were represented with reasonable

accuracy as were a series of multi-effect evaporators using a combination of HEATER blocks and FLASH2 blocks. Some simulation units such as the secondary absorber were reasonably modeled but left room for future work to explore more accurate methods that in turn would cause other nearby units to perform more accurate simulations. Overall this simulation of PTD provides a foundation for future work on the process and works as a learning tool to further understand how the separation of bioethanol from a fermentation broth can be effectively completed using the pass-through distillation process.

4 Conclusion

Aspen Plus V8.8 was used for the determination of parameters to use with the eNRTL-RK property method to accurately model the mixed solvent electrolyte system of ethanol, water and lithium bromide. These parameters can be implemented for a variety of applications especially the pass-through distillation application considered here. The accurate modeling of the ternary system was critical to the development of a foundation for the modeling of pass-through distillation with the specific application of separating bioethanol from a fermentation broth using a combination of evaporation, absorption, stripping and condensing to provide a low pressure, low temperature separation that does not damage temperature sensitive components present in a fermentation broth while at the same time minimizing energy required to achieve the separation. The simulation developed in Aspen Plus V8.8 to model this system will prove useful for future studies, as a teaching tool for how the process works, as well as a platform to test out variations in the system quickly with little associated risk.

References

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Appendix A: Property Data

Aspen Input File - Ternary System Data Regression[9-12]

```
;
;Input Summary created by Aspen Plus Rel. 34.0
;
;


DRS

DYNAMICS
   DYNAMICS RESULTS=ON

IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
       INVERSE-PRES='1/bar'

DATABANKS 'APV88 PURE32' / 'APV88 AQUEOUS' / 'APV88 SOLIDS' /  &
       'APV88 INORGANIC' / 'APEOSV88 AP-EOS' / NOASPENPCD

PROP-SOURCES 'APV88 PURE32' / 'APV88 AQUEOUS' / 'APV88 SOLIDS' &
        / 'APV88 INORGANIC' / 'APEOSV88 AP-EOS'

COMPONENTS
   ETHANOL C2H6O-2 /
   WATER H2O /
   LIBR LIBR /
   LI+ LI+ /
   BR- BR- /

CHEMISTRY C-1
   PARAM
   DISS LIBR LI+ 1. / BR- 1.

PROPERTIES ENRTL-RK
```

```
PROP-DATA REVIEW-1
   IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
      INVERSE-PRES='1/bar'
   PROP-LIST PC / TC / VC / ZC
   PVAL LIBR 50 / 1726.85 / 100 / .2

PROP-DATA DHVLWT-1
   IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
      INVERSE-PRES='1/bar'
   PROP-LIST DHVLWT
   PVAL LIBR 33150 1300 .3800000 0.0 -273.15

PROP-DATA NRTL-1
   IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
      INVERSE-PRES='1/bar'
   PROP-LIST NRTL
   BPVAL ETHANOL WATER -.0978487894 0.0 .3000000000 0.0 0.0  &
      0.0 -273.1500000 726.8500000
   BPVAL WATER ETHANOL 1.798621130 0.0 .3000000000 0.0 0.0  &
      0.0 -273.1500000 726.8500000
   BPVAL WATER CARBO-01 10.06400000 -3268.135000 .2000000000  &
      0.0 0.0 0.0 0.0 200.0000000
   BPVAL CARBO-01 WATER 10.06400000 -3268.135000 .2000000000  &
      0.0 0.0 0.0 0.0 200.0000000

PROP-DATA GMENCC-1
   IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
      INVERSE-PRES='1/bar'
   PROP-LIST GMENCC
   PPVAL ETHANOL ( LI+ BR- ) 20.40402870
   PPVAL ( LI+ BR- ) ETHANOL -9.952394090
   PPVAL WATER ( LI+ BR- ) 15.05825870
   PPVAL ( LI+ BR- ) WATER -5.945849820

PROP-DATA GMENCN-1
   IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
      INVERSE-PRES='1/bar'
   PROP-LIST GMENCN
   PPVAL ETHANOL ( LI+ BR- ) .0783888377
```

```
   PPVAL ( LI+ BR- ) ETHANOL .0783888377
   PPVAL WATER ( LI+ BR- ) .2

PARAMETERS
   BIPARAMETER 1 NRTL ETHANOL WATER 1 -1.00000000E+00  &
      -1.00000000E+01 1.00000000E+01 1.00000000E+00
   BIPARAMETER 2 NRTL WATER ETHANOL 1 4.00000000E+00  &
      -1.00000000E+01 1.00000000E+01 1.00000000E+00
   PAIRPARAM 3 GMENCC ETHANOL (LI+ BR-) 1 2.30000000E+01  &
      -3.00000000E+01 4.00000000E+01 1.00000000E+00
   PAIRPARAM 4 GMENCC (LI+ BR-) ETHANOL 1 -1.20000000E+01  &
      -3.00000000E+01 4.00000000E+01 1.00000000E+00
   PAIRPARAM 5 GMENCN ETHANOL (LI+ BR-) 1 1.00000000E-02  &
      0.E0 3.00000000E-01 1.00000000E+00
   PAIRPARAM 6 GMENCN (LI+ BR-) ETHANOL 1 1.00000000E-02  &
      0.E0 3.00000000E-01 1.00000000E+00
   PAIRPARAM 7 GMENCC WATER (LI+ BR-) 1 8.00000000E+00  &
      -3.00000000E+01 4.00000000E+01 1.00000000E+00
   PAIRPARAM 8 GMENCC (LI+ BR-) WATER 1 -4.00000000E+00  &
      -3.00000000E+01 4.00000000E+01 1.00000000E+00

CASE ETH-H2O
   PROPERTIES ENRTL-RK TRUE-COMPS=YES
   DATA-GROUPS BVLE310 CONSISTENCY=YES / BVLE311  &
      CONSISTENCY=YES / BVLE312 CONSISTENCY=YES / D-1  &
      WEIGHT=0.0001 / D-2 WEIGHT=0.0001 / D-4 WEIGHT=0.0001 /  &
      D-6 WEIGHT=0.0001 CONSISTENCY=NO
   PARAMETERS BINARY=1 2

CASE ETH-LIBR
   PROPERTIES ENRTL-RK CHEMISTRY=C-1 TRUE-COMPS=NO
   DATA-GROUPS SAF318EL / SAF323EL / D-3 / D-2 / D-4 /  &
      D-5 / D-6
   PARAMETERS PAIR=3 4 5 6

CASE H2O-LI
   PROPERTIES ENRTL-RK CHEMISTRY=C-1 TRUE-COMPS=NO
   DATA-GROUPS PAT333WL CONSISTENCY=YES / PAT323WL  &
      CONSISTENCY=YES / PAT343WL CONSISTENCY=YES
```

```
   PARAMETERS PAIR=7 8

CASE TERNARY
   PROPERTIES ENRTL-RK CHEMISTRY=C-1 TRUE-COMPS=NO
   DATA-GROUPS D-1 / D-2 / D-3 / D-4 / D-5 / D-6
   PARAMETERS PAIR=7 8
   CASE-OPTION REGRESSION=NO

DATA-GROUP BVLE047
   IN-UNITS SI
   SYSTEM-DEF TPXY ETHANOL WATER
   PHASE-EQ VL ETHANOL WATER
   DATA 1 335.12 25330 0.016 0.146 /
      2 333.12 25330 0.037 0.2755 /
      3 330.32 25330 0.065 0.365 /
      4 328.43 25330 0.09 0.4125 /
      5 325.33 25330 0.158 0.5015 /
      6 326.13 25330 0.209 0.5455 /
      7 325.53 25330 0.2385 0.565 /
      8 323.23 25330 0.3535 0.6045 /
      9 322.93 25330 0.4705 0.6445 /
      10 322.03 25330 0.497 0.654 /
      11 323.63 25330 0.5805 0.6925 /
      12 321.63 25330 0.6525 0.726 /
      13 322.93 25330 0.7 0.755 /
      14 321.83 25330 0.72 0.7685 /
      15 323.33 25330 0.7895 0.8152 /
      16 322.23 25330 0.8416 0.8502 /
      17 322.13 25330 0.8735 0.879 /
      18 322.93 25330 0.897 0.899 /
      19 322.63 25330 0.9485 0.9466 /
      20 320.73 25330 0.96 0.958 /
      21 323.43 25330 0.9719 0.97 /
      22 321.73 25330 0.9812 0.9798
   STD-DEV 1 0.1 -0.1 -0.1 -1

DATA-GROUP BVLE310
   IN-UNITS SI
   SYSTEM-DEF TPXY ETHANOL WATER
```

```
    PHASE-EQ VL ETHANOL WATER
    DATA 1 313.71 13150 0.117 0.461 /
        2 310.7 13150 0.241 0.567 /
        3 309.53 13150 0.383 0.632 /
        4 308.82 13150 0.492 0.668 /
        5 308.36 13150 0.59 0.714 /
        6 308.1 13150 0.656 0.737 /
        7 307.7 13150 0.771 0.812 /
        8 307.54 13150 0.84 0.855 /
        9 307.56 13150 0.864 0.874 /
        10 307.51 13150 0.897 0.904 /
        11 307.46 13150 0.908 0.91 /
        12 307.5 13150 0.911 0.914 /
        13 307.48 13150 0.934 0.934 /
        14 307.45 13150 0.947 0.947 /
        15 307.44 13150 0.971 0.969
    STD-DEV 1 0.1 0 -0.1 -1

DATA-GROUP BVLE311
    IN-UNITS SI
    SYSTEM-DEF TPXY ETHANOL WATER
    PHASE-EQ VL ETHANOL WATER
    DATA 1 323.53 19710 0.076 0.407 /
        2 320.52 19710 0.141 0.51 /
        3 318.05 19710 0.26 0.592 /
        4 317.04 19710 0.39 0.632 /
        5 316.35 19710 0.499 0.679 /
        6 315.9 19710 0.599 0.706 /
        7 315.55 19710 0.688 0.76 /
        8 315.29 19710 0.799 0.826 /
        9 315.26 19710 0.805 0.828 /
        10 315.19 19710 0.841 0.854 /
        11 315.15 19710 0.883 0.888 /
        12 315.16 19710 0.913 0.915 /
        13 315.13 19710 0.931 0.932 /
        14 315.13 19710 0.945 0.945 /
        15 315.14 19710 0.96 0.957 /
        16 315.14 19710 0.964 0.964
    STD-DEV 1 0.1 0 -0.1 -1
```

```
DATA-GROUP BVLE312
   IN-UNITS SI
   SYSTEM-DEF TPXY ETHANOL WATER
   PHASE-EQ VL ETHANOL WATER
   DATA 1 335.16 32860 0.063 0.356 /
        2 332.54 32860 0.104 0.463 /
        3 330.96 32860 0.15 0.494 /
        4 329.26 32860 0.248 0.556 /
        5 326.77 32860 0.454 0.662 /
        6 326.1 32860 0.581 0.696 /
        7 325.89 32860 0.657 0.732 /
        8 325.67 32860 0.76 0.792 /
        9 325.53 32860 0.839 0.85 /
        10 325.51 32860 0.854 0.868 /
        11 325.46 32860 0.913 0.913 /
        12 325.43 32860 0.931 0.931 /
        13 325.42 32860 0.932 0.934 /
        14 325.45 32860 0.965 0.963
   STD-DEV 1 0.1 0 -0.1 -1

DATA-GROUP D-1
   IN-UNITS SI
   SYSTEM-DEF TPXY ETHANOL WATER COMPOSITION=MASS-FRAC
   PHASE-EQ VL ETHANOL WATER
   DATA
Omitted by request
   STD-DEV 1 0.1 0.1 -0.01 -0.01

DATA-GROUP D-2
   IN-UNITS MET PRESSURE=Pa TEMPERATURE=K DELTA-T=C PDROP=bar  &
      INVERSE-PRES='1/bar'
   SYSTEM-DEF TPXY ETHANOL WATER LIBR COMPOSITION=MASS-FRAC
   PHASE-EQ VL ETHANOL WATER
   DATA
Omitted by request
   STD-DEV 1 0.1 -0.1 -0.01 -0.01 -0.1 -0.1

DATA-GROUP D-3
```

```
   IN-UNITS MET PRESSURE=Pa TEMPERATURE=K DELTA-T=C PDROP=bar  &
      INVERSE-PRES='1/bar'
   SYSTEM-DEF TPXY ETHANOL WATER LIBR COMPOSITION=MASS-FRAC
   PHASE-EQ VL ETHANOL WATER
   DATA
Omitted by request
   STD-DEV 1 0.1 -0.1 -0.01 -0.01 -0.1 -0.1

DATA-GROUP D-4
   IN-UNITS MET PRESSURE=Pa TEMPERATURE=K DELTA-T=C PDROP=bar  &
      INVERSE-PRES='1/bar'
   SYSTEM-DEF TPXY ETHANOL WATER LIBR COMPOSITION=MASS-FRAC
   PHASE-EQ VL ETHANOL WATER
   DATA
Omitted by request
   STD-DEV 1 0.1 -0.1 -0.01 -0.01 -0.1 -0.1

DATA-GROUP D-5
   IN-UNITS MET PRESSURE=Pa TEMPERATURE=K DELTA-T=C PDROP=bar  &
      INVERSE-PRES='1/bar'
   SYSTEM-DEF TPXY ETHANOL WATER LIBR COMPOSITION=MASS-FRAC
   PHASE-EQ VL ETHANOL WATER
   DATA
Omitted by request
   STD-DEV 1 0.1 -0.1 -0.01 -0.01 -0.1 -0.1

DATA-GROUP D-6
   IN-UNITS MET PRESSURE=Pa TEMPERATURE=K DELTA-T=C PDROP=bar  &
      INVERSE-PRES='1/bar'
   SYSTEM-DEF TPXY ETHANOL WATER LIBR COMPOSITION=MASS-FRAC
   PHASE-EQ VL ETHANOL WATER
   DATA
Omitted by request
   STD-DEV 1 0.1 -0.1 -0.01 -0.01 -0.1 -0.1

DATA-GROUP PAT323WL
   IN-UNITS SI
   SYSTEM-DEF TPXY WATER LIBR
   PHASE-EQ VL WATER
```

```
   DATA 1 323.15 11210 0.965222493 * /
      2 323.15 10220 0.940782105 * /
      3 323.15 8820 0.915974201 * /
      4 323.15 7200 0.887645903 * /
      5 323.15 5270 0.857929858 * /
      6 323.15 3640 0.830635885 * /
      7 323.15 2260 0.8011559 * /
      8 323.15 1330 0.776565106 *
   STD-DEV 1 0 -0.1 -0.1 -1

DATA-GROUP PAT333WL
   IN-UNITS SI
   SYSTEM-DEF TPXY WATER LIBR
   PHASE-EQ VL WATER
   DATA 1 333.15 18270 0.965222493 * /
      2 333.15 16580 0.940782105 * /
      3 333.15 14400 0.915974201 * /
      4 333.15 11750 0.887645903 * /
      5 333.15 8660 0.857929858 * /
      6 333.15 6020 0.830635885 * /
      7 333.15 3820 0.8011559 * /
      8 333.15 2310 0.776565106 *
   STD-DEV 1 0.1 -0.1 -0.1 -1

DATA-GROUP PAT343WL
   IN-UNITS SI
   SYSTEM-DEF TPXY WATER LIBR
   PHASE-EQ VL WATER
   DATA 1 343.15 28840 0.965222493 * /
      2 343.15 26140 0.940782105 * /
      3 343.15 22720 0.915974201 * /
      4 343.15 18550 0.887645903 * /
      5 343.15 13750 0.857929858 * /
      6 343.15 9660 0.830635885 * /
      7 343.15 6250 0.8011559 * /
      8 343.15 3880 0.776565106 *
   STD-DEV 1 0 -0.1 -0.1 -1

DATA-GROUP SAF318EL
```

```
   IN-UNITS SI
   SYSTEM-DEF TPXY ETHANOL LIBR WATER
   PHASE-EQ VL ETHANOL WATER
   DATA 1 318.15 22799 0.992241016 0.007758984 1 0 /
      2 318.15 22523 0.983837958 0.016162042 1 0 /
      3 318.15 22310 0.977685609 0.022314391 1 0 /
      4 318.15 21693 0.962905648 0.037094352 1 0 /
      5 318.15 20628 0.943182254 0.056817746 1 0 /
      6 318.15 20377 0.939120864 0.060879136 1 0 /
      7 318.15 20139 0.935725146 0.064274854 1 0 /
      8 318.15 19285 0.92477867 0.07522133 1 0 /
      9 318.15 18319 0.91433677 0.08566323 1 0 /
      10 318.15 16823 0.900586626 0.099413374 1 0 /
      11 318.15 14881 0.885258498 0.114741502 1 0
   STD-DEV 1 0 -5 -0.1 -0.1 0 0

DATA-GROUP SAF323EL
   IN-UNITS SI
   SYSTEM-DEF TPXY ETHANOL LIBR WATER
   PHASE-EQ VL ETHANOL WATER
   DATA 1 323.15 29125 0.992241016 0.007758984 1 0 /
      2 323.15 28775 0.983837958 0.016162042 1 0 /
      3 323.15 28506 0.977685609 0.022314391 1 0 /
      4 323.15 27723 0.962905648 0.037094352 1 0 /
      5 323.15 26373 0.943182254 0.056817746 1 0 /
      6 323.15 26049 0.939120864 0.060879136 1 0 /
      7 323.15 25751 0.935725146 0.064274854 1 0 /
      8 323.15 24662 0.92477867 0.07522133 1 0 /
      9 323.15 23439 0.91433677 0.08566323 1 0 /
      10 323.15 21551 0.900586626 0.099413374 1 0 /
      11 323.15 19104 0.885258498 0.114741502 1 0
   STD-DEV 1 0 -5 -0.1 -0.1 0 0

PROPERTY-REP NOPCES PROP-DATA DFMS NOPARAM-PLUS
;
;
;
;
;
```

Appendix B: Simulation

Aspen Input File - Pass-Through Distillation Simulation

```
;
;Input Summary created by Aspen Plus Rel. 34.0
;


DYNAMICS
   DYNAMICS RESULTS=ON

IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
       INVERSE-PRES='1/bar'

DEF-STREAMS CONVEN ALL

SIM-OPTIONS MASS-BAL-CHE=YES RESTART=NO

MODEL-OPTION

DATABANKS 'APV88 PURE32' / 'APV88 AQUEOUS' / 'APV88 SOLIDS' /  &
       'APV88 INORGANIC' / 'APEOSV88 AP-EOS' / NOASPENPCD

PROP-SOURCES 'APV88 PURE32' / 'APV88 AQUEOUS' / 'APV88 SOLIDS' &
       / 'APV88 INORGANIC' / 'APEOSV88 AP-EOS'

COMPONENTS
   WATER H2O /
   ETHAN-01 C2H6O-2 /
   CARBO-01 CO2 /
   LITHI-01 LIBR /
   LI+ LI+ /
   BR- BR-

HENRY-COMPS HC-1 CARBO-01

SOLVE
```

```
   RUN-MODE MODE=SIM

CHEMISTRY C-1
   DISS LITHI-01 LI+ 1. / BR- 1.

FLOWSHEET
   BLOCK DEGAS IN=15A 10G OUT=16 15B
   BLOCK VACPUMP1 IN=16 OUT=17
   BLOCK FOAMCTRL IN=15B 10A OUT=10B 15C
   BLOCK SAM-EVAP IN=15C OUT=10A 15D SAM
   BLOCK SECABS IN=10C 1C-IN OUT=10D 1D
   BLOCK VACPUMP2 IN=10D OUT=10E
   BLOCK COND IN=10E OUT=10F
   BLOCK HX3 IN=1B 2A-1 OUT=1C-OUT 2B
   BLOCK EVAP1 IN=5B S1 OUT=7A 1A
   BLOCK EVAP2 IN=2E S2 OUT=8A 4A
   BLOCK EVAP3 IN=2C OUT=9A 3A S3
   BLOCK HX5 IN=7C 3A OUT=7D 3B
   BLOCK HX4 IN=7B 2D OUT=7C 2-1D
   BLOCK HX1 IN=1A 5A OUT=1B 5B
   BLOCK HX2 IN=4A 2-1D OUT=4B 2E
   BLOCK MIX7 IN=7A 6B OUT=71-A
   BLOCK MIX5 IN=4B 3B OUT=5A
   BLOCK SPLIT1 IN=2B OUT=2D 2C
   BLOCK SAMABS IN=10B 1D SAM OUT=10C 2A
   BLOCK DRUM IN=10F OUT=10G 18
   BLOCK CAL1 IN=6A OUT=6B S1
   BLOCK CAL2 IN=71-A OUT=7B S2
   BLOCK CAL3 IN=8A S3 OUT=8B
   BLOCK PUMP IN=2A OUT=2A-1

PROPERTIES ENRTL-RK HENRY-COMPS=HC-1 CHEMISTRY=C-1 TRUE-COMPS=NO
   PROPERTIES NRTL

PROP-DATA REVIEW-1
   IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
      INVERSE-PRES='1/bar'
   PROP-LIST PC / TC / VC / ZC
   PVAL LITHI-01 50 / 1726.28 / 100 / .2
```

```
PROP-DATA DHVLWT-1
   IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
      INVERSE-PRES='1/bar'
   PROP-LIST DHVLWT
   PVAL LITHI-01 33150 1300 0 0 -273.15

PROP-DATA HENRY-1
   IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
      INVERSE-PRES='1/bar'
   PROP-LIST HENRY
   BPVAL CARBO-01 WATER 159.8650745 -8741.550000 -21.66900000  &
      1.10259000E-3 -.1500000000 79.85000000 0.0
   BPVAL CARBO-01 ETHAN-01 89.58307554 -5018.799805  &
      -11.89100000 0.0 10.00000000 40.00000000 0.0

PROP-DATA NRTL-1
   IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
      INVERSE-PRES='1/bar'
   PROP-LIST NRTL
   BPVAL WATER ETHAN-01 -0.0978488 0.0 .3000000 0.0 0.0 0.0  &
      0.0 1000.000
   BPVAL ETHAN-01 WATER 1.79862 0.0 .3000000 0.0 0.0 0.0  &
      0.0 1000.000

PROP-DATA GMENCC-1
   IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
      INVERSE-PRES='1/bar'
   PROP-LIST GMENCC
   PPVAL ETHAN-01 ( LI+ BR- ) 20.404
   PPVAL ( LI+ BR- ) ETHAN-01 -9.95239
   PPVAL WATER ( LI+ BR- ) 15.0583
   PPVAL ( LI+ BR- ) WATER -5.94585

PROP-DATA GMENCN-1
   IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
      INVERSE-PRES='1/bar'
   PROP-LIST GMENCN
   PPVAL ETHAN-01 ( LI+ BR- ) .0783888
```

```
   PPVAL ( LI+ BR- ) ETHAN-01 .0783888
   PPVAL WATER ( LI+ BR- ) .2
   PPVAL ( LI+ BR- ) WATER .2

DEF-STREAMS CONVEN 2A

DEF-STREAMS LOAD

STREAM 1C-IN
   SUBSTREAM MIXED PRES=1. <atm> VFRAC=0. MASS-FLOW=25000.
   MASS-FRAC WATER 0.3 / LITHI-01 0.7

STREAM 6A
   SUBSTREAM MIXED PRES=200. <psig> VFRAC=1. MASS-FLOW=7440.
   MASS-FRAC WATER 1.

STREAM 10A
   SUBSTREAM MIXED PRES=30. <torr> VFRAC=1. MASS-FLOW=10000.
   MASS-FRAC WATER 0.4 / ETHAN-01 0.6

STREAM 15A
   SUBSTREAM MIXED TEMP=35. PRES=4. MASS-FLOW=100000.
   MASS-FLOW WATER 94900. / ETHAN-01 5000. / CARBO-01 100.

DEF-STREAMS HEAT S1

DEF-STREAMS HEAT S2

DEF-STREAMS HEAT S3

DEF-STREAMS HEAT SAM

BLOCK MIX5 MIXER
   PARAM

BLOCK MIX7 MIXER
   PARAM

BLOCK SPLIT1 FSPLIT
```

```
   FRAC 2C 0.3

BLOCK DRUM SEP
   PARAM
   FRAC STREAM=18 SUBSTREAM=MIXED COMPS=WATER ETHAN-01  &
      CARBO-01 FRACS=0. 0. 1.

BLOCK CAL1 HEATER
   PARAM PRES=200. <psig> VFRAC=0. DPPARMOPT=NO

BLOCK CAL2 HEATER
   PARAM PRES=730. <torr> VFRAC=0. DPPARMOPT=NO

BLOCK CAL3 HEATER
   PARAM PRES=700. <torr> DPPARMOPT=NO

BLOCK COND HEATER
   PARAM PRES=1. <atm> VFRAC=0.02 DPPARMOPT=NO
   PROPERTIES NRTL HENRY-COMPS=HC-1 FREE-WATER=STEAM-TA  &
      SOLU-WATER=3 TRUE-COMPS=YES

BLOCK DEGAS FLASH2
   PARAM PRES=300. <torr> DUTY=0.

BLOCK EVAP1 FLASH2
   PARAM PRES=1. <atm>
   PROPERTIES ENRTL-RK CHEMISTRY=C-1 FREE-WATER=STEAM-TA  &
      SOLU-WATER=3 TRUE-COMPS=NO

BLOCK EVAP2 FLASH2
   PARAM PRES=730. <torr>

BLOCK EVAP3 FLASH2
   PARAM PRES=700. <torr> VFRAC=0.25

BLOCK SAM-EVAP FLASH2
   PARAM PRES=30. <torr> VFRAC=0.15

BLOCK SAMABS FLASH2
```

```
   PARAM PRES=28. <torr>

BLOCK HX1 HEATX
   PARAM MIN-OUT-TAPP=5. CALC-TYPE=DESIGN MIN-TAPP=5.  &
      U-OPTION=PHASE F-OPTION=CONSTANT CALC-METHOD=SHORTCUT  &
      ALLOW-TCROSS=YES BYPASS=NO
   FEEDS HOT=1A COLD=5A
   OUTLETS-HOT 1B
   OUTLETS-COLD 5B
   HOT-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO
   COLD-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO
   TQ-PARAM CURVE=YES

BLOCK HX2 HEATX
   PARAM MIN-OUT-TAPP=4. CALC-TYPE=DESIGN MAXIT=50  &
      U-OPTION=PHASE F-OPTION=CONSTANT CALC-METHOD=SHORTCUT  &
      ALLOW-TCROSS=YES BYPASS=NO
   FEEDS HOT=4A COLD=2-1D
   OUTLETS-HOT 4B
   OUTLETS-COLD 2E
   HOT-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO
   COLD-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO
   TQ-PARAM CURVE=YES

BLOCK HX3 HEATX
   PARAM MIN-OUT-TAPP=5. CALC-TYPE=DESIGN U-OPTION=PHASE  &
      F-OPTION=CONSTANT CALC-METHOD=SHORTCUT ALLOW-TCROSS=YES  &
      BYPASS=NO
   FEEDS HOT=1B COLD=2A-1
   OUTLETS-HOT 1C-OUT
   OUTLETS-COLD 2B
   HOT-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO
   COLD-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO
   TQ-PARAM CURVE=YES

BLOCK HX4 HEATX
   PARAM MIN-OUT-TAPP=5. CALC-TYPE=DESIGN U-OPTION=PHASE  &
      F-OPTION=CONSTANT CALC-METHOD=SHORTCUT ALLOW-TCROSS=YES  &
      BYPASS=NO
```

```
   FEEDS HOT=7B COLD=2D
   OUTLETS-HOT 7C
   OUTLETS-COLD 2-1D
   HOT-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO
   COLD-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO
   TQ-PARAM CURVE=YES

BLOCK HX5 HEATX
   PARAM MIN-OUT-TAPP=5. CALC-TYPE=DESIGN U-OPTION=PHASE  &
      F-OPTION=CONSTANT CALC-METHOD=SHORTCUT ALLOW-TCROSS=YES  &
      BYPASS=YES
   FEEDS HOT=7C COLD=3A
   OUTLETS-HOT 7D
   OUTLETS-COLD 3B
   HOT-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO
   COLD-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO
   TQ-PARAM CURVE=YES

BLOCK FOAMCTRL RADFRAC
   PARAM NSTAGE=10 ALGORITHM=SUM-RATES ABSORBER=NO MAXOL=25  &
      DAMPING=NONE
   COL-CONFIG CONDENSER=NONE REBOILER=NONE
   FEEDS 15B 1 ON-STAGE / 10A 10 ON-STAGE
   PRODUCTS 15C 10 L / 10B 1 V
   P-SPEC 1 29. <torr>
   COL-SPECS

BLOCK SECABS RADFRAC
   PARAM NSTAGE=10 NPA=0 ALGORITHM=SUM-RATES MAXOL=50  &
      DAMPING=NONE
   COL-CONFIG CONDENSER=NONE REBOILER=NONE
   RATESEP-ENAB CALC-MODE=EQUILIBRIUM
   HTLOSS HTLOSS-VAP=150000. HTLOSS-LIQ=100000.
   FEEDS 10C 10 ON-STAGE / 1C-IN 1 ON-STAGE
   PRODUCTS 1D 10 L / 10D 1 V
   P-SPEC 1 28. <torr>
   COL-SPECS
   PROPERTIES ENRTL-RK HENRY-COMPS=HC-1 CHEMISTRY=C-1  &
      FREE-WATER=STEAM-TA SOLU-WATER=3 TRUE-COMPS=NO
```

```
BLOCK PUMP PUMP
   PARAM PRES=0.9

BLOCK VACPUMP1 PUMP
   PARAM PRES=1. <atm> EFF=0.6 NPHASE=2 VFRAC-CHK=NONE
   PROPERTIES NRTL HENRY-COMPS=HC-1 CHEMISTRY=C-1  &
      FREE-WATER=STEAM-TA SOLU-WATER=3 TRUE-COMPS=YES
   BLOCK-OPTION FREE-WATER=NO

BLOCK VACPUMP2 PUMP
   PARAM PRES=1. <atm> EFF=0.6 NPHASE=2 VFRAC-CHK=NONE
   BLOCK-OPTION FREE-WATER=NO

EO-CONV-OPTI

CONV-OPTIONS
   WEGSTEIN MAXIT=200

STREAM-REPOR MOLEFLOW MASSFLOW MASSFRAC

PROPERTY-REP NOPARAM-PLUS
;
;
;
;
;
```