Modeling the Thermodynamics of Biobutanol Extraction Using $scCO_2$ Solvent

A Major Qualifying Project Submitted to Faculty of Worcester
Polytechnic Institute in Partial Fulfillment of the Requirements for
The Degree of Bachelor of Science

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Abstract

This MQP attempts to model the separation of a proposed continuous liquid-liquid extraction process of n-butanol using an experimental strain of carbon dioxide tolerant bacteria. This water-scCO2-butanol ternary system model evaluation was simulated using Aspen Plus and the fugacity coefficients for two of the methods were calculated in MATLAB software. After some initial difficulties, this report determines that none of the mixing rules native to Aspen Plus v8.2 are adequate to model the ternary system and the standard Peng-Robinson method for a pure species fails to model the nuances of a ternary mixture. Future research groups would greatly benefit from assistance from someone experienced with Fortran to modify Aspen mixing rules or MATLAB when evaluating an equation of state's fugacity coefficients.

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1. Introduction

Since the Industrial Revolution, petroleum and fossil fuels have been the primary producers of power generation in the world, from steam engines fueled by coal fire to internal combustion engines fueled by gasoline. While the use of oil and natural gas has been dated back thousands of years to ancient China and coal use was prevalent in medieval England, they were not utilized on the same scale or for the same ends as today. Early engines and home heating relied on coal because of its cleaner burn than wood charcoal and its abundance near the surface in England and the rest of Europe. Natural gas was used for street lighting and home heating until the light bulb displaced the need for gas streetlamps. It was not until Edwin Drake successfully extracted petroleum from a well in the earth and the rise of the internal combustion engine over steam powered engines that oil saw widespread use outside of whale oil for lamps. As more infrastructure and industries grew around these fuel sources, more research time was spent optimizing fuel efficiency and innovating fuel usage. It is now to the point that in the United States in 2011, petroleum, natural gas, and coal account for 80% of the energy consumption and accounted for 67% of electrical energy production, 89% of industrial energy consumption, 93% of residential and commercial energy consumption, and 96% of the energy consumed for transportation needs. (U.S. Energy Information Administration 2012)

While these practices and infrastructure may have initially proven fairly sustainable, the modern world's projected energy consumption will greatly increase as developing countries continue to industrialize. Projections suggest countries outside of the Organization for Economic Cooperation and Development (OECD) could account for as much as 65% of the world energy consumption in 2040, up from 54% in 2010, while OECD countries will have relatively steady energy consumption rates. (U.S. Energy Information Administration 2013) Combined with the inherent scarcity of non-renewable fossil fuels, the commonly accepted correlation between global climate change and man-made carbon dioxide emissions, and estimations for peak oil production occurring between 2010 and 2030, the sustainability of oil production is questionable. (ASPO, 2007; Bartlett, 2000) Even increased utilization of natural gas from preexisting oil wells will experience diminishing production within a decade or two. In order to meet the growing modern energy requirements, the global energy profile will need to include more renewable energy sources if the status quo is to be maintained in the future.

One solution to combat fossil fuel scarcity is utilizing agricultural waste to create renewable biofuels. Research has expanded in recent years to producing ethanol from renewable feedstocks for use as a transportation fuel and additive. The Renewable Fuel Standard (RFS) was created by the United States government in 2005 as a part of the Energy Policy Act, setting yearly standards requiring the blending of renewable fuels with transportation fuels (Renewable Fuels: Regulations & Standards 2015). Since the initiation of the RFS, corn has been used as a feedstock to produce ethanol, leading to the incorporation of E-10, or fuel consisting of 10% ethanol, into daily use in the country. Figure 1 shows the recent increase in ethanol consumption and production in the United States due to its use in transportation fuels (U.S. Production, Consumption, and Trade of Ethanol 2014). Research efforts have also been focused on producing ethanol from lignocellulosic biomass, or feedstocks that do not affect the country's food supply, such as switchgrass and corn stover (Biomass Feedstocks n.d.).

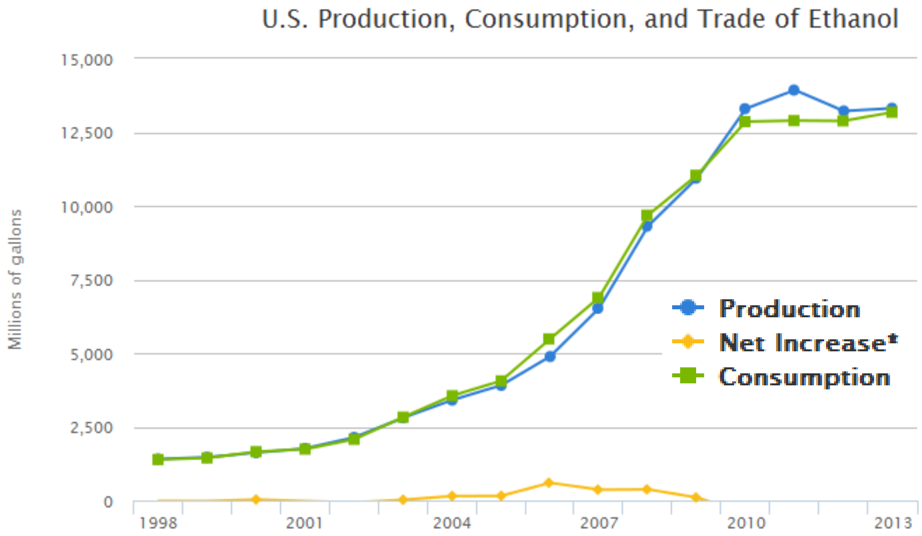

Figure 1: US Production and Consumption of Ethanol (US Department of Energy)

Butanol is an ideal gasoline additive or substitute for future fuel needs due to its lower volatility, higher viscosity, higher heat of combustion, and hydrocarbon intersolubility than ethanol among other desirable properties. (Jin, et al. 2011) A well-documented butanol production method is ABE (acetone-butanol-ethanol) fermentation. Enzyme strains like c. beijerinckii and c. acetobutylicum utilize starch and sugar from materials like corn and molasses to create acetone, butanol, and ethanol in a 3:6:1 ratio. (Qureshi and Blaschek 2001) (Bowles and Ellefson 1985) However, there are several problems which occur in ABE fermentation that prevent this process from becoming a fully continuous butanol production process at an economically feasible scale. One issue is that effect of butanol concentration on c. acetobutylicum, which reduces sugar uptake and ATP production in the enzyme. This effectively reduces yield as butanol concentration increases, making ABE fermentation better suited to a batch or semi-batch production schedule without further process considerations. ABE fermentation can also suffer production losses due to enzyme contamination, which could be costly in a continuous process without frequent concentration monitoring. Since butanol and the water of the fermentation broth form a heteroazeotrope, separation is a more difficult and expensive process than single column distillation. (Luyben 2008)

This study investigated the mass balance and thermodynamics of continuous in situ liquid-liquid extraction of butanol from fermentation broth using supercritical carbon dioxide as the extractant. The proposed system uses a genetically engineered, CO_2-phillic strain of *b. megaterium* to produce butanol from a starchy feed stock while $scCO_2$ removes the butanol from the broth and kills undesired microbes. AspenTech software was used to model the ternary system equilibrium and reactor performance for many operating conditions. The most accurate mixing rule was determined experimentally for relevant concentrations of butanol.

2. Literature Review

Butanol as a Biofuel

Ethanol has long been used as a biofuel, produced from corn feedstocks. Biofuels allow nonrenewable resources, such as oil and petroleum, used to produce transportation fuels to be replaced by renewable resources. Benefits of biofuels include reduced emission of greenhouse gases, the use of more environmentally benign chemicals, and their ability to be used indefinitely, unlike nonrenewable fossil fuels. The present use of ethanol in a mixture with gasoline reduces the negative effects of the use of fossil fuels for transportation fuels, but this positive impact can continue to be increased.

Butanol, like ethanol, is a chemical that has the potential to replace part or all of the oil-based fuels that are currently used. In addition, butanol has properties that make it preferable as a fuel to ethanol. These properties include a higher energy density, a lower volatility, and a lower hygroscopicity, or ability to absorb water from the atmosphere (Xue, et al., 2014). The lower volatility and hygroscopicity make butanol more similar to gasoline than ethanol, and the high energy density makes it more effective as a fuel. Butanol can be better blended with gasoline and used as a fuel additive within the current transportation fuel infrastructure. However, the toxicity of butanol causes it to cause negative effects on bacteria cells used in fermentation. Butanol recovery techniques are developed and used to reduce the effect of the toxicity of butanol, and have the potential to make butanol viable as a transportation fuel additive. (Xue, et al., 2014)

Ternary Mixture

One of the objectives of this project was to understand the interactions between the three components in a system of butanol, water, and supercritical carbon dioxide, as originally studied by Athanassios Panagiotopoulos and Robert Reid (Panagiotopoulos & Reid, 1986). The ternary plot generated as a part of this study is shown in Figure 2 below.

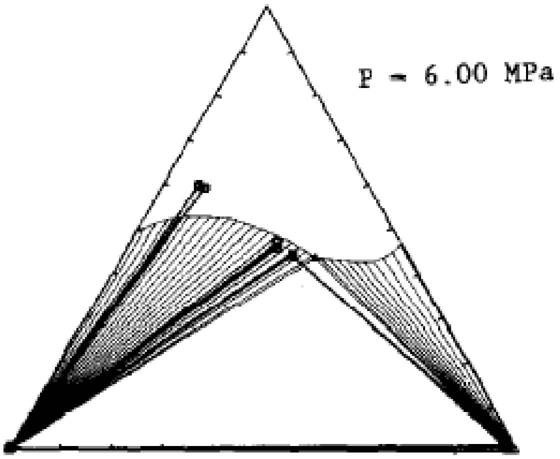

Figure 2: Ternary Diagram of Butanol, Water, and Carbon Dioxide (Panagiotopoulos & Reid)

An additional study in 2002 analyzed the same ternary mixture (Chen, Chang, & Chen, 2002). Data from this study was used for comparison to data obtained from all Aspen Plus models, and is summarized in Figure 3 below.

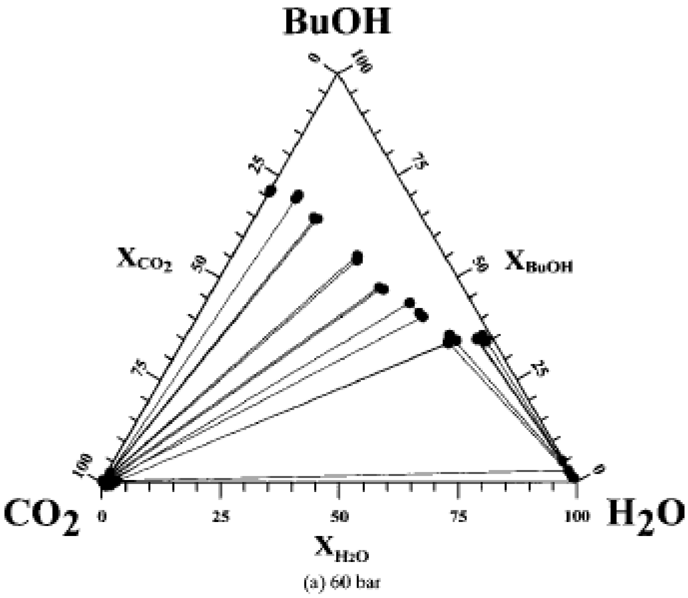

Figure 3: Ternary Diagram of Butanol, Water, and Supercritical Carbon Dioxide (Chen, Chang, & Chen)

MATLAB

We turned to an alternative method of modeling a non-standard equation of state after Aspen failed to adequately model the system with its native calculation methods. The project advisor, Prof. Michael Timko, presented a study of the water - supercritical carbon dioxide - butanol ternary system that modeled the experimental data with a high degree of accuracy. (Reid and Panagiotopoulos 1986) These researchers describe their own modified form of the Peng-Robinson (PR) cubic equation of state that not only accounts for binary interaction parameters between each of the species in the system, but also modifies the expression with a density-dependent term to account for "low density systems" based on a previous iteration of their mixture equation that lacked the density correction factor.

The MATLAB scripts used to model this process were originally based off of an example from a textbook for a Soave-Redlich-Kwong (SRK) cubic equation of state molar volume solver. (Mostoufi and Constantinides 1999) This initial script operated with user input variable amounts as a vector for operating pressure, the desired species' critical temperature and pressure, the desired operating temperature and pressure, and its acentric factor. The script is then run with a custom function (NRpoly) that solves for the compressibility factor using the cubic notation of the SRK equation over the pressure range. The main script then calculates the ideal molar volume of the species as one line on a log-log plot and the "real" molar volume of the species as another line on the same plot to ease visual comparison between the ideal and "real" volume.

Standard Equation of State Modeling

The first step was to modify the original MATLAB script to calculate molar volumes for the standard PR equation. This is a very simple procedure since SRK and PR can both we written with the same generic cubic equation of state formula:

$$P = \frac{RT}{V_m - b} - \frac{\alpha a}{{V_m}^2 + ubV_m + wb^2}$$

where P is pressure, R is the ideal gas constant, T is temperature, Vm is molar volume, a and b are equation-dependent formulas that account for the critical properties of a species, α is an equation-dependant formula originally made by Soave to account for the vapor pressure data of hydrocarbons and a species' acentric factor, and u and w are equation-dependant parameters. The variable values for SRK are:

$$\alpha = \left(1 + (0.48 + 1.57\omega - 0.176\omega^2)\left(1 - {T_r}^{0.5}\right)\right)^2$$

$$a = \frac{0.427\, R^2\, {T_c}^2}{P_c}$$

$$b = \frac{0.8664\, R\, T_c}{P_c}$$

u = 1; w = 0

And PR has similar equations with the values:

$$\alpha = 1 + \kappa\left(1 - {T_r}^{0.5}\right)^2$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

$$a = \frac{0.457235\, R^2\, {T_c}^2}{P_c}$$

$$b = \frac{0.077796\, R\, T_c}{P_c}$$

u = 2; w = -1

where ω is a species' acentric factor, Tc is a species' critical temperature, Pc is a species' critical pressure, and Tr is the reduced temperature, which is the operating temperature divided by the critical temperature.

3. Methodology

Aspen Plus Modeling

In order to model the extraction of butanol from a butanol-water mixture using supercritical carbon dioxide as a solvent, it is important to understand the interactions between the three components to model the system. Aspen Plus was used to model the ternary mixture of butanol, water, and carbon dioxide, with the goal of achieving a ternary plot that matches literature data for the ternary mixture and using this understanding of the mixture in a model of a butanol extraction system. The ternary feature within Aspen Plus was used to analyze the results of a ternary analysis. The results were then graphed and compared to the results of previous studies (Panagiotopoulos & Reid, 1986) (Chen, Chang, & Chen, 2002). The analysis was first performed using the Peng-Robinson equation of state, and was later expanded to other equations of state in an attempt to fit the generated curve to the literature data. These equations of state included the Soave-Redlich-Kwong (SRK) equation of state, SRK with Wong-Sandler mixing rules, Peng-Robinson with Wong-Sandler mixing rules, Peng-Robinson with Boston-Mathias mixing rules, and the Schwartzentruber-Renon equation of state. These equations of state and mixing rules were all chosen based on the recommendations of the Methods Assistant within Aspen Plus. The Aspen model was solved with all mixing rules, and the results were graphed on a ternary graph against the literature data (Chen, Chang, & Chen, 2002).

After finding difficulty in fitting ternary data generated from Aspen Plus to literature data, several other methods were explored. These included using a data regression to manually the fit the ternary plots to the literature data, as well as the use of the PC-SAFT equation of state to model the ternary system.

Additionally, a separation block was used to study the simple separation of butanol from a butanol-water mixture because of the difficulty in fitting an equation of state to the literature data. Figure 4 below shows the configuration that was studied in Aspen Plus.

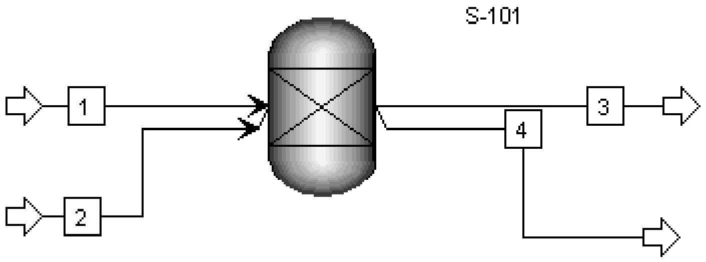

Figure 4: Configuration for Simple Separation Model in Aspen Plus

In Figure 3, a “Sep” block in Aspen Plus is shown, allowing simple split fractions to be set for the separation. In order to simulate the extraction of butanol from water, stream 1 entering the separation block was set to carry 0.02 mol/hr of butanol and 1 mol/hr of water. Stream 2 was set to carry 1 mol/hr of carbon dioxide into the system. Split fractions were then set, with 90% of the feed butanol, 99% of the feed carbon dioxide, and 1% of the feed water exiting the separation block in stream 3. Stream 4 contains the majority of the water in the system, a small amount of butanol, and trace amounts of carbon dioxide. Once this model was created, the ratio of carbon dioxide to water entering the separation unit was varied to test its effect on the water content of the butanol phase, stream 3.

MATLAB

Modifying the MATLAB Script

The modified form of the PR equation of state proposed by Panagiotopoulos and Reid uses similar parameters and can still be defined in the same cubic format the same as SRK and standard PR making this equation compatible with the NRPoly function, but is designed to accommodate a mixture of species based on the binary interactions between them:

$$P = \frac{RT}{V - b_m} - \frac{a_m}{V^2 + uVb_m + w{b_m}^2}$$

$$a_m^0 = \sum_i \sum_j x_i x_j \sqrt{a_i a_j}$$

$$a_m = a_m^0 + \frac{b_m}{VRT} \sum_i \sum_j x_i x_j \left(x_i \lambda_{ij} + x_j \lambda_{ji}\right)$$

$$b_m = \sum_i x_i b_i$$

The λ parameter values are described below in Table 1 in the units provided by Penagiotopoulos and Reid:

Table 1: Lambda Binary Interaction Pparameters Used by Panagiotopoulos and Reid

Binary System	λ_{12} [J^2 m^3 / mol^3]	λ_{21} [J^2 m^3 / mol^3]
CO_2 (1) - water (2)	-1715	1715
water (1) - n-butanol (2)	1595	-1595
CO_2 (1) - n-butanol (2)	1310	-1310

The λ binary interactions parameters were stored in a 3x3 element matrix in MATLAB and individual elements were referenced for summation using nested "for" loops and a variable to store the final sum. No literature was found for the value of λ for like species, so this value is assumed to be 0 in the matrix.

Modeling Species Fugacity Coefficients

To better understand the thermodynamics of the ternary system and verify a valid model equation, fugacity coefficients were included for scripts including PR equation of state and the modified PR equation for comparison. The equation used for the PR fugacity coefficient is based on the equation found for a pure species in *Engineering and Chemical Thermodynamics* by Milo D. Koretsky:

$$\ln\varphi = (Z-1) - \ln\frac{(V-b)P}{RT} - \frac{\alpha a}{2\sqrt{2}bRT}\ln\frac{\left(V+\left(1+\sqrt{2}\right)b\right)}{\left(V+\left(1-\sqrt{2}\right)b\right)}$$

where φ is the fugacity coefficient. Due to the manual variable input of the species properties accepting only one scalar value, the script is unable to plot standard PR fugacity coefficients within MATLAB. This was overcome by plotting the data from the individual plots generated by MATLAB in Microsoft Excel as shown in Figure 5 below.

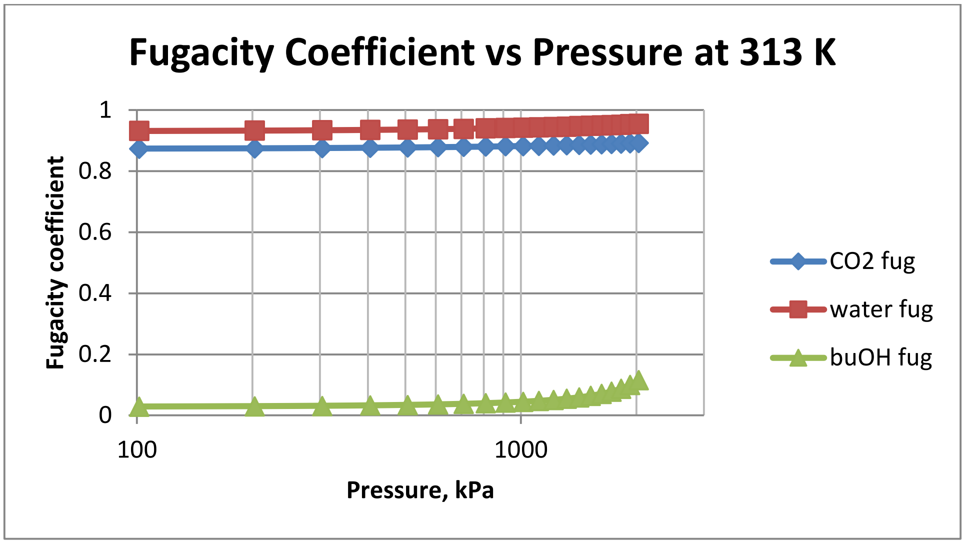

Figure 5: Semi-log plot of fugacity coefficients of CO2, water, and n-butanol at 313 K modeled by PR

The modified fugacity coefficient equation defined by Panagiotopoulos and Reid is significantly longer than the standard equation and uses summations of another binary interaction parameter, k, listed below for a specific species k. The value of u and w is that of the PR equation of state for the following equations:

$$\ln\varphi_k = \frac{b_k}{b_m}\left(\frac{PV}{RT}-1\right) - \ln\frac{P(V-b_m)}{RT} +$$

$$\frac{-a_m^0 b_k + 2b_m\Sigma_0^k + \frac{u}{2w}\left(\frac{2b_k}{b_m}\Sigma\Sigma - 2\Sigma_1^k - \Sigma_2^k\right)}{\sqrt{u^2-4w}\,{b_m}^2 RT}\ln\frac{2V + b_m\left(u-\sqrt{u^2-4w}\right)}{2V + b_m\left(u+\sqrt{u^2-4w}\right)}$$

$$\frac{\frac{2b_k}{b_m}\Sigma\Sigma - 2\Sigma_1^{\mathrm{k}} - \Sigma_2^{\mathrm{k}}}{2w{b_m}^2RT}\ln\frac{V^2}{V^2 + ub_mV + w{b_m}^2}$$

$$\Sigma\Sigma = \sum_i\sum_j \lambda_{ij}{x_i}^2x_j\sqrt{a_ia_j}$$

$$\Sigma_0^k = \sum_i x_i\,(1 - k_{ik})\sqrt{a_ia_k}$$

$$\Sigma_1^k = \sum_i x_ix_k\,\lambda_{ki}$$

$$\Sigma_2^k = \sum_i {x_i}^2\;\lambda_{ik}$$

The subscript i denotes that the specific species k is interacting with species i, summed together shows k interacting with all species excluding itself because k_{ij} is 1 when i = j. Table 2 below details the values used for unitless binary parameter k:

Table 2: Values of Binary Interaction Parameter k used by Panagiotopoulos and Reid

Binary System	k_{12}	k_{21}
CO_2 (1) - water (2)	0.0275	0.0275
water (1) - n-butanol (2)	-0.164	-0.164
CO_2 (1) - n-butanol (2)	0.125	0.125

Like the λ binary interaction parameters, the k binary interaction parameters were stored in a 3x3 matrix and elements were referenced in summation using nested "for" loops and a variable created to store the summed value.

4. Results

Aspen Plus Modeling

As discussed above, Aspen Plus was used to model the ternary system of butanol, water, and supercritical carbon dioxide. Initially, the Peng-Robinson equation of state was used to model the ternary data for the system. Figure 6 below shows a ternary diagram obtained, with the pressure varied from 2 to 10 MPa.

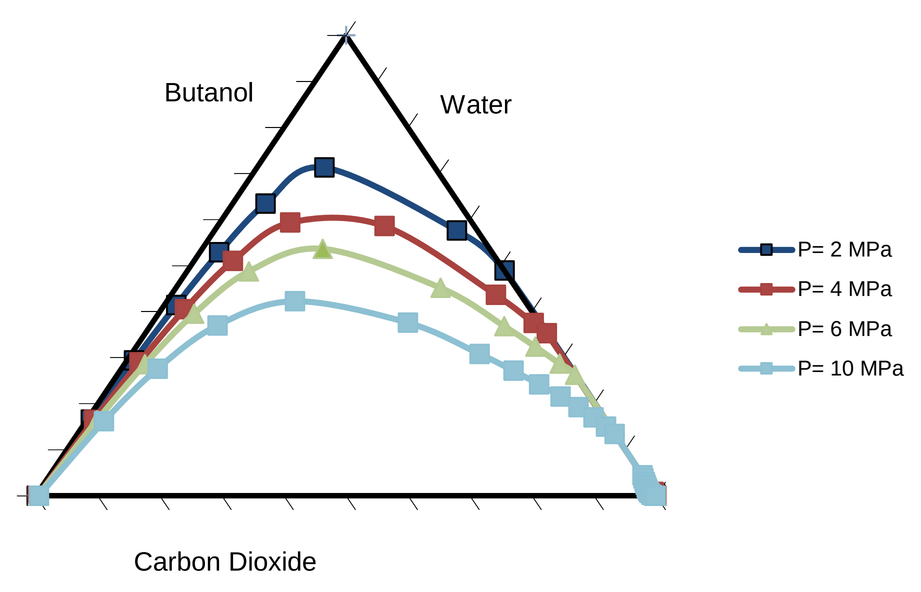

Figure 6: Ternary Diagram of Butanol-Water-Carbon Dioxide System at Varying Pressures

This figure shows the large amount of fluctuation in the ternary data that is caused by changes in pressure for this system. This fluctuation is due to the proximity of supercritical carbon dioxide to the critical point at high pressures, causing high dependence of the system on pressure and temperature.

Various equations of state and mixing rules were tested for comparison with literature results for the ternary mixture. Figure 5 shows the results of these tests.

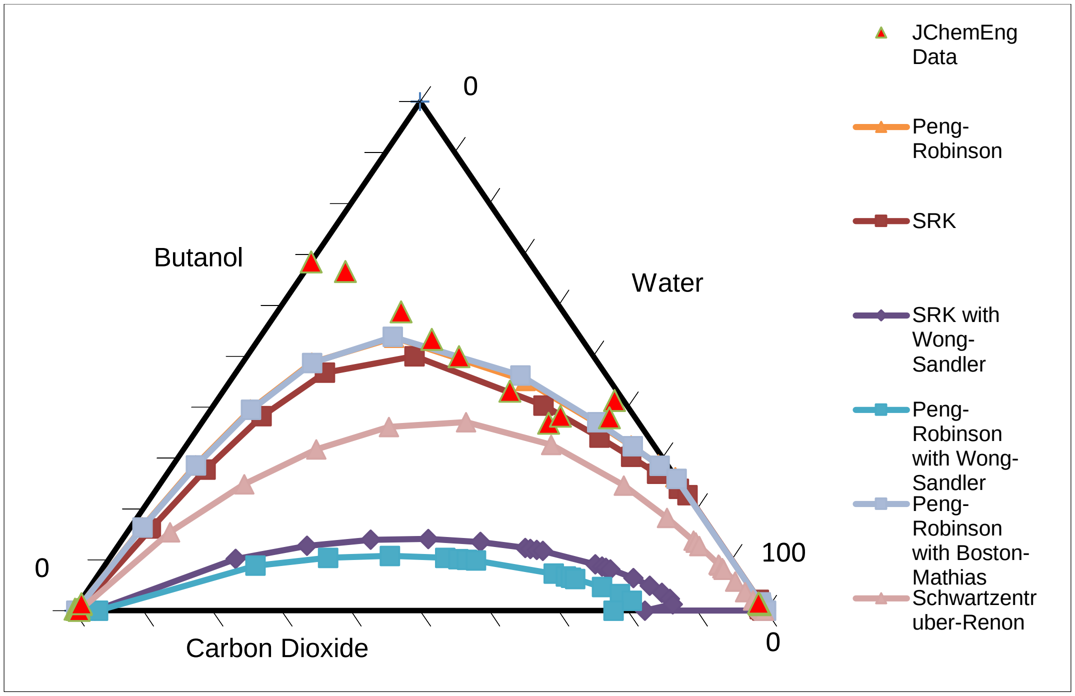

Figure 7: Ternary Diagram with Various Tested Equations of State

Figure 7 shows that the Peng-Robinson equation of state and Peng-Robinson with Boston-Mathias mixing rules generated nearly the same results. These two equations of state best fit the literature data. The results from these trials in Aspen fit the literature data fairly well at butanol concentrations of greater than 25%, but fit the data very poorly when butanol concentration is less than 5%, the region which is important for butanol extraction. From these tests, it was discovered that none of the mixing rules and equations of state built in to Aspen Plus were capable of generating ternary data that could match the literature data. This problem could potentially be solved by entering the mixing rule developed by Reid and Panagiotopoulos for the ternary system. It was determined that the difficulty of this exceeded the scope of the problem, and other approaches were taken to attempt to develop a model of the system.

A simple model of the extraction of butanol from water was created to better understand the system. In this model, described above, the ratio of carbon dioxide to water entering the separation unit was varied. The results of these trials are shown in Table 3 below.

Table 3: Results of Butanol Separation with Varying Feed CO2/Water Ratio

Inlet Molar Flow Rates (mol/hr)			**Carbon Dioxide/Water Ratio**	**Temperature (^{0}C)**	**Pressure (bar)**	**Butanol Recovery (mol/hr)**	**Water Content of Butanol Phase (mol/hr)**
Butanol	**Water**	**CO_2**					
0.02	1	1	1	60	60	0.018	0.01
0.02	1.33	0.67	0.504	60	60	0.018	0.0133
0.02	1.5	0.5	0.333	60	60	0.018	0.015
0.02	1.7	0.3	0.176	60	60	0.018	0.017
0.02	1.8	0.2	0.111	60	60	0.018	0.018
0.02	0.67	1.33	1.985	60	60	0.018	0.018
0.02	0.5	1.5	3	60	60	0.018	0.005
0.02	0.3	1.7	5.667	60	60	0.018	0.003
0.02	0.2	1.8	9	60	60	0.018	0.002

This table shows that as the ratio between the inlet molar amounts of carbon dioxide and water was increased, the water content of the butanol phase decreased. As a result, a high ratio of carbon dioxide to water fed to the system should be used to minimize the water content in the butanol phase, making the separation more effective. Additional data from the first trial in the table above as sample results from the simple separation can be found in Table 9 in the Appendix.

MATLAB Modeling

The MATLAB scripts developed for this project are able to plot the fugacity coefficients of the standard Peng-Robinson cubic equation of state. According to Figure 1 above as well as Figures 2 through 4 below, all values for φ are beneath 1. This was expected behavior since fugacity is a measurement of chemical energy in a system relative to the ideal energy expected without species interactions. The species in this ternary system do not actively repel each other and the presence of supercritical carbon dioxide affects the solubility of n-butanol in water. What was unexpected when modeling the fugacity coefficients was the low value of the fugacity for n-butanol as a pure species. While not mathematically impossible, it is a physically unrealistic value for the fugacity coefficient. This phenomena is believed to be caused by the calculation of φ in the script. The equation does not account for the n-butanol remaining in the liquid phase within the temperature range specified. As shown in Figures 8 through 10, the fugacity coefficient of n-butanol according to PR did not reach a value comparable with carbon dioxide and water until almost 2 megapascals at 425 K, which it overshoots as the vapor concentration of n-butanol increases proportionately with temperature.

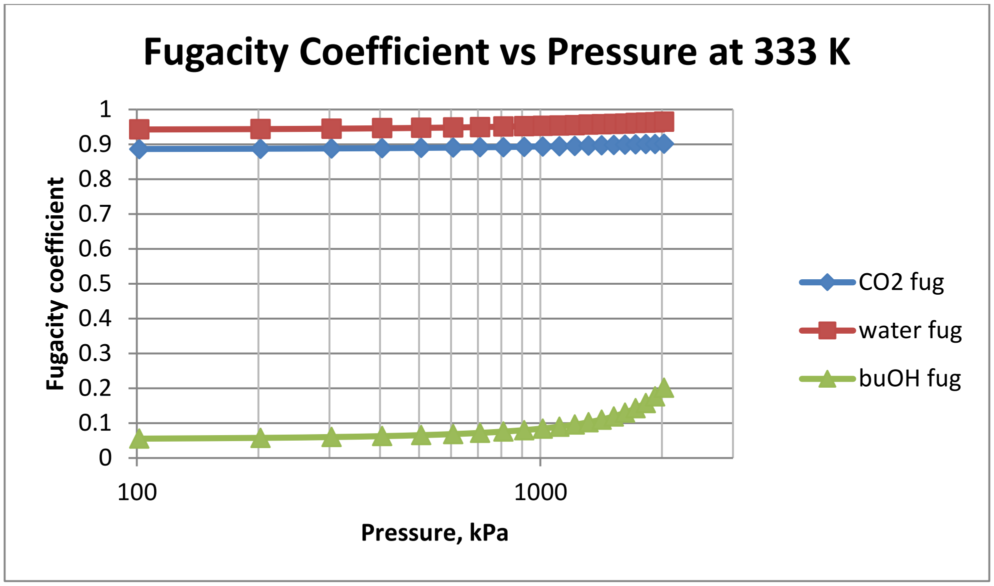

Figure 8: Semi-log plot of fugacity coefficients of CO2, water, and n-butanol at 333 K modeled by PR

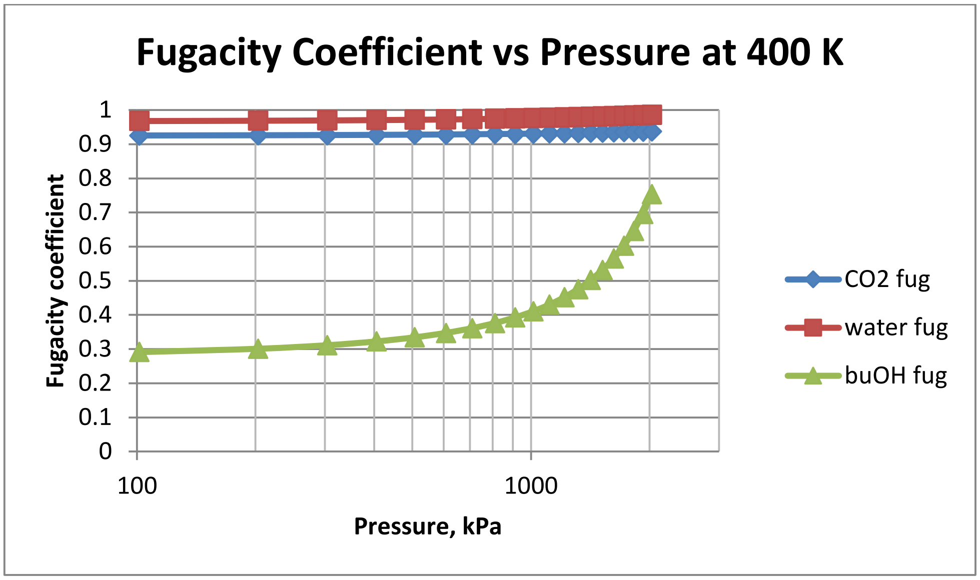

Figure 9: Semi-log plot of fugacity coefficients of CO2, water, and n-butanol at 400 K modeled by PR

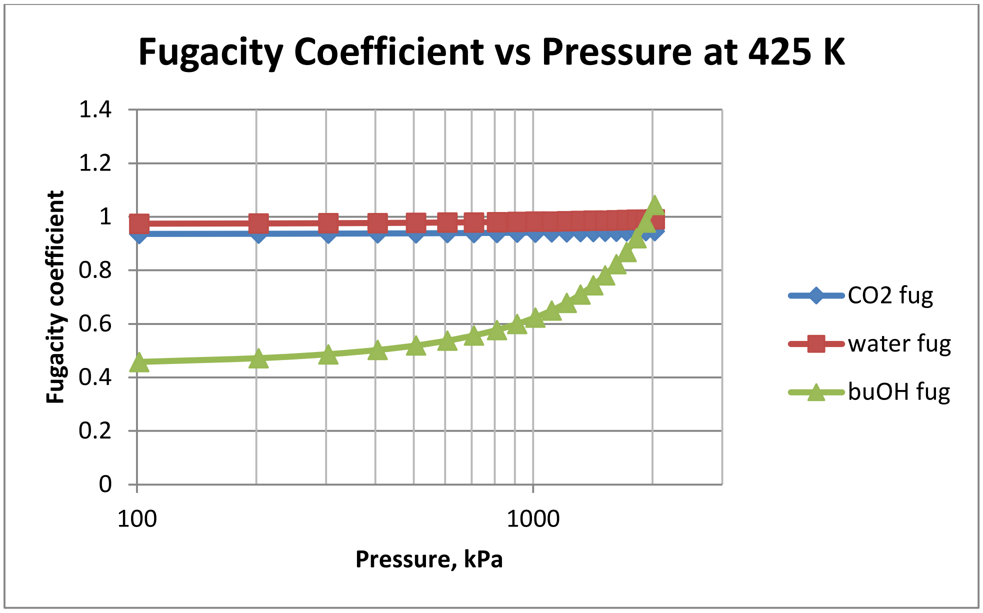

Figure 10: Semi-log plot of fugacity coefficients of CO2, water, and n-butanol at 425 K modeled by PR

Based on the rapid shift in the fugacity coefficient of n-butanol and its low value relative to the other two species, the standard Peng-Robinson cubic equation of state is an inadequate modeling equation for this system since it does not account for interactions between the species and the vapor concentration of n-butanol.

The MATLAB scripts developed to model the modified PR equation of state developed by Panagiotopoulos and Reid, while more complex and show a tighter clustering between the fugacity coefficients of each species since it accounts for phase interactions, the equation still encounters a logic error that plots all of the fugacity coefficients on the magnitude of 10 to the sixth or seventh power as shown in Figure 11.

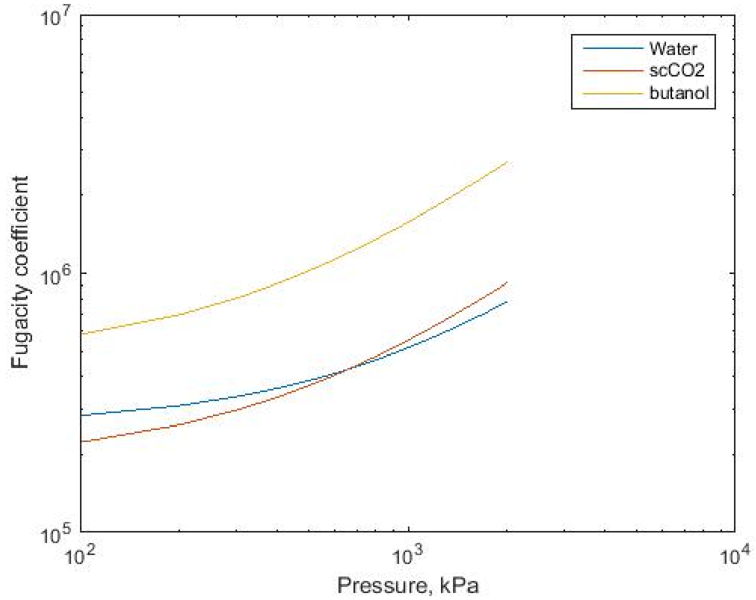

Figure 11: MATLAB loglog plot of fugacity coefficients for the water - scC02 - n-butanol system

The logic error that caused this miscalculation of the fugacity coefficients was not located exactly and debugged before project completion, but can be resolved given additional time. Manual calculator calculations suggest the location of the problem is most likely within the "phi" variable in the script Example1_2_nPRmixfinal.m.

5. Conclusions and Recommendations

The original scope of this project was to model the water-scCO2-butanol system in Aspen Plus to aid the reactor design, better inform the expectations of the bacteria design team, and better understand any potential problems with the process not encountered within other literature. Unfortunately, success using Aspen to accurately model anything more complex than the individual species or the binaries within this ternary system proved difficult, especially in the low butanol concentration range expected within a realistic fermentation broth. The project was then rescoped to simply discover the most reliable modeling equation for this process using Aspen and investigating the underlying thermodynamics of this system using a MATLAB script to compute the system's fugacity coefficient at various operating conditions and broth compositions.

This can be explained by the proximity of the carbon dioxide solvent to its critical point in this model. Many reports on this ternary system are within this expected temperature and pressure range with real experimental results, so the failing is most likely with Aspen's inability to accurately model the interactions within the binaries of this system, how the solvent may affect the solubility of butanol within the water, or includes invalid assumptions within its calculations that are not apparent within the user interface. It is recommended that further investigation of the existing models within the coding of Aspen be done or a custom mixing rule be coded in Fortran using a more accurate model of this system's nuances.

Initial attempts to fix the error found in the modified PR equation of state fugacity coefficient solver included accounting for the exponential value of the fugacity coefficient term, but MATLAB could not calculate numbers or plot them since the values were e to the 10 to the sixth and seventh power. Multiple attempts at rearranging the parentheses for more accurate grouping proved equally ineffective. Manual calculation of the variable values other than the term for "phi" matched the values generated by MATLAB, making them unlikely candidates for the source of the logic error. Experimental values by Panagiotopoulos and Reid in their 1986 paper show that this is an accurate model, making this the most accurate candidate for future modeling of this ternary system after the unknown logic error is resolved. It is recommended that someone who is more experienced with MATLAB review the syntax in the "phi" variable in script Example1_1_nPRmixfinal.m and consider any other alternatives for the miscalculation that have not already been considered.

6. References

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7. Appendix

Raw MATLAB Data:

Figure 3.1 Data:

butanol		water		CO_2	
P [kPa]	Phi	P [kPa]	Phi	P [kPa]	Phi
101.325	0.028709	101.325	0.931901	101.325	0.873777
202.65	0.029892	202.65	0.933096	202.65	0.874736
303.975	0.031176	303.975	0.934294	303.975	0.875698
405.3	0.032575	405.3	0.935496	405.3	0.876661
506.625	0.034106	506.625	0.9367	506.625	0.877626
607.95	0.035787	607.95	0.937908	607.95	0.878594
709.275	0.037643	709.275	0.939119	709.275	0.879563
810.6	0.039703	810.6	0.940332	810.6	0.880535
911.925	0.042	911.925	0.94155	911.925	0.881509
1013.25	0.04458	1013.25	0.94277	1013.25	0.882485
1114.575	0.047498	1114.575	0.943993	1114.575	0.883463
1215.9	0.050824	1215.9	0.94522	1215.9	0.884443
1317.225	0.054651	1317.225	0.946449	1317.225	0.885426
1418.55	0.059101	1418.55	0.947682	1418.55	0.886411
1519.875	0.064341	1519.875	0.948918	1519.875	0.887398
1621.2	0.070599	1621.2	0.950158	1621.2	0.888387
1722.525	0.078207	1722.525	0.9514	1722.525	0.889378
1823.85	0.087652	1823.85	0.952646	1823.85	0.890372
1925.175	0.099692	1925.175	0.953895	1925.175	0.891367
2026.5	0.115566	2026.5	0.955148	2026.5	0.892365

Figure 3.2 Data:

butanol		**water**		**CO_2**	
P [kPa]	**Phi**	**P [kPa]**	**Phi**	**P [kPa]**	**Phi**
101.325	0.055712	101.325	0.943321	101.325	0.886602
202.65	0.05792	202.65	0.944435	202.65	0.88742
303.975	0.06031	303.975	0.945552	303.975	0.88824
405.3	0.062905	405.3	0.946671	405.3	0.889061
506.625	0.065734	506.625	0.947794	506.625	0.889884
607.95	0.06883	607.95	0.948918	607.95	0.890709
709.275	0.072231	709.275	0.950046	709.275	0.891534
810.6	0.075986	810.6	0.951176	810.6	0.892362
911.925	0.080152	911.925	0.952309	911.925	0.893191
1013.25	0.084803	1013.25	0.953445	1013.25	0.894021
1114.575	0.090025	1114.575	0.954583	1114.575	0.894853
1215.9	0.095934	1215.9	0.955724	1215.9	0.895687
1317.225	0.102673	1317.225	0.956868	1317.225	0.896522
1418.55	0.110429	1418.55	0.958015	1418.55	0.897358
1519.875	0.119454	1519.875	0.959164	1519.875	0.898197
1621.2	0.130085	1621.2	0.960316	1621.2	0.899036
1722.525	0.142793	1722.525	0.961471	1722.525	0.899878
1823.85	0.158252	1823.85	0.962628	1823.85	0.900721
1925.175	0.177465	1925.175	0.963789	1925.175	0.901565
2026.5	0.201989	2026.5	0.964952	2026.5	0.902411

Figure 3.3 Data:

butanol		**water**		**C0$_2$**	
P [kPa]	**Phi**	**P [kPa]**	**Phi**	**P [kPa]**	**Phi**
101.325	0.291352	101.325	0.967981	101.325	0.92529
202.65	0.301076	202.65	0.968897	202.65	0.925903
303.975	0.311471	303.975	0.969815	303.975	0.926516
405.3	0.32261	405.3	0.970735	405.3	0.927131
506.625	0.334575	506.625	0.971657	506.625	0.927746
607.95	0.347462	607.95	0.97258	607.95	0.928362
709.275	0.361382	709.275	0.973505	709.275	0.928979
810.6	0.376463	810.6	0.974432	810.6	0.929597
911.925	0.392857	911.925	0.97536	911.925	0.930216
1013.25	0.410745	1013.25	0.97629	1013.25	0.930835
1114.575	0.43034	1114.575	0.977222	1114.575	0.931456
1215.9	0.451897	1215.9	0.978156	1215.9	0.932077
1317.225	0.475728	1317.225	0.979092	1317.225	0.932699
1418.55	0.502213	1418.55	0.980029	1418.55	0.933321
1519.875	0.53182	1519.875	0.980968	1519.875	0.933945
1621.2	0.565137	1621.2	0.981909	1621.2	0.934569
1722.525	0.602908	1722.525	0.982852	1722.525	0.935195
1823.85	0.646088	1823.85	0.983797	1823.85	0.935821
1925.175	0.695931	1925.175	0.984743	1925.175	0.936448
2026.5	0.754108	2026.5	0.985692	2026.5	0.937075

Figure 3.4 Data:

butanol		**water**		**$C0_2$**	
P [kPa]	**Phi**	**P [kPa]**	**Phi**	**P [kPa]**	**Phi**
101.325	0.457777	101.325	0.973774	101.325	0.935555
202.65	0.471724	202.65	0.974634	202.65	0.936123
303.975	0.486547	303.975	0.975497	303.975	0.936692
405.3	0.502332	405.3	0.976361	405.3	0.937261
506.625	0.519175	506.625	0.977226	506.625	0.93783
607.95	0.537187	607.95	0.978093	607.95	0.938401
709.275	0.556494	709.275	0.978961	709.275	0.938972
810.6	0.577241	810.6	0.979831	810.6	0.939544
911.925	0.599594	911.925	0.980703	911.925	0.940117
1013.25	0.623748	1013.25	0.981576	1013.25	0.94069
1114.575	0.64993	1114.575	0.982451	1114.575	0.941264
1215.9	0.678406	1215.9	0.983327	1215.9	0.941839
1317.225	0.709492	1317.225	0.984205	1317.225	0.942414
1418.55	0.743563	1418.55	0.985084	1418.55	0.94299
1519.875	0.781072	1519.875	0.985965	1519.875	0.943567
1621.2	0.822566	1621.2	0.986848	1621.2	0.944145
1722.525	0.868716	1722.525	0.987732	1722.525	0.944723
1823.85	0.920353	1823.85	0.988618	1823.85	0.945302
1925.175	0.978516	1925.175	0.989505	1925.175	0.945881
2026.5	1.044526	2026.5	0.990394	2026.5	0.946462

Aspen Plus Modeling Raw Data

Results of Ternary Mixture with Peng-Robinson Equation of State

Mole Fractions of Mixture Components		
Butanol	**Water**	**Carbon Dioxide**
0	0.003298	0.9967025
0.163819	0.016787	0.8193942
0.2856785	0.032909	0.6814128
0.3952012	0.057408	0.5473907
0.4875054	0.099777	0.4127176
0.5363515	0.194349	0.2692991
0.4515837	0.426634	0.1217822
0.368553	0.57067	0.0607772
0.3240841	0.642778	0.033138
0.2870241	0.700599	0.0123765
0.2624567	0.737543	0
0.0155522	0.984448	0
0.0124093	0.986349	0.00124143
0.00873951	0.988753	0.00250735
0.00557704	0.991109	0.00331357
0.00202335	0.994506	0.00347118
0.000157574	0.997886	0.00195663
2.17E-05	0.998811	0.0011672
5.35E-06	0.999163	0.000831207
1.76E-06	0.999347	0.000651603
6.65E-07	0.999455	0.000544344
0	0.999552	0.000447981

Results of Ternary Mixture with Soave-Redlich-Kwong (SRK) Equation of State

Mole Fractions of Mixture Components		
Butanol	**Water**	**Carbon Dioxide**
0	0.006289	0.9937109
0.1612501	0.030649	0.8081013
0.2775018	0.051618	0.6708804
0.3820231	0.08021	0.5377671
0.4677236	0.128737	0.4035391
0.5000548	0.24194	0.2580048
0.4030514	0.476843	0.1201052
0.3403196	0.588959	0.0707213
0.3020842	0.653865	0.0440508
0.2691007	0.707812	0.0230872
0.2396285	0.754005	0.00636665
0.2270633	0.772937	0
0.0215327	0.978467	0
0.0190962	0.979684	0.00121993
0.0143096	0.98214	0.00355056
0.0102462	0.984369	0.00538517
0.00679362	0.986494	0.00671234
3.12E-03	0.989355	0.00752558
2.90E-04	0.993788	0.00592175
3.37E-05	0.99567	0.00429669
7.59E-06	0.996488	0.00350457
2.37E-06	0.996955	0.00304235
8.80E-07	0.99725	0.00274908
0	0.997533	0.00246738

Results of Ternary Mixture with Soave-Redlich-Kwong (SRK) Equation of State with Wong-Sandler Mixing Rules

Mole Fractions of Mixture Components		
Butanol	**Water**	**Carbon Dioxide**
0	0.030567	0.9694329
0.1017317	0.18264	0.7156288
0.1273211	0.272987	0.5996914
0.139241	0.359268	0.5014913
0.1410966	0.441184	0.417719
0.1348866	0.519681	0.3454325
0.1233187	0.590496	0.2861848
0.1216327	0.598727	0.2796404
0.1191485	0.609806	0.2710457
0.117248	0.618581	0.2641713
0.0909793	0.707811	0.2012101
0.0871229	0.718723	0.1941538
0.0843904	0.726126	0.189484
0.081389	0.734336	0.1842746
0.0641981	0.775914	0.1598881
0.0489525	0.807437	0.1436107
0.0352356	0.831773	0.1329912
0.0231993	0.849056	0.1277448
0.0126400	0.858801	0.1285593
0	0.82488	0.1751198

Results of Ternary Mixture with Peng-Robinson Equation of State with Wong-Sandler Mixing Rules

Mole Fractions of Mixture Components		
Butanol	**Water**	**Carbon Dioxide**
0	0.035036	0.9649644
0.0886195	0.218098	0.6932824
0.1038065	0.315268	0.5809251
0.1075971	0.402861	0.4895417
0.1038377	0.484426	0.4117364
0.1015082	0.504818	0.3936739
0.1000425	0.518061	0.3818969
0.0985641	0.531297	0.3701388
0.072811	0.656558	0.2706313
0.0673279	0.6772	0.2554724
0.064725	0.685632	0.2496433
0.0622224	0.693059	0.2447185
0.0462251	0.739856	0.2139184
0.0323728	0.772469	0.1951584
0.0192233	0.796405	0.1843713
0	0.779626	0.2203737

Results of Ternary Mixture with Peng-Robinson Equation of State with Boston-Mathias Mixing Rules

Mole Fractions of Mixture Components		
Butanol	**Water**	**Carbon Dioxide**
0	0.003397	0.9966033
0.1637382	0.017253	0.8190092
0.2853513	0.03376	0.6808888
0.3945444	0.058646	0.5468096
0.4867096	0.100908	0.4123821
0.5380357	0.191496	0.2704687
0.462077	0.413965	0.123958
0.3702679	0.571051	0.0586806
0.3228952	0.645747	0.0313582
0.2845168	0.703818	0.0116654
0.2590018	0.740998	0
0.0161541	0.983846	0
0.012854	0.985997	0.00114951
0.00903055	0.988653	0.00231658
0.00567305	0.991244	0.00308266
0.00185777	0.99492	0.0032222
0.000154313	0.997933	0.00191268
0.0000233	0.998773	0.00120328
0.0000060	0.999119	0.000874598
0	0.999307	0.00069071
0.0000008	0.999421	0.000578001
0	0.999524	0.000475715

Results of Ternary Mixture with Schwartzentruber-Renon Equation of State

Mole Fractions of Mixture Components		
Butanol	**Water**	**Carbon Dioxide**
0	0.008118	0.9918816
0.1541597	0.061757	0.7840832
0.2485835	0.121785	0.6296314
0.317252	0.191563	0.4911847
0.3611948	0.274059	0.3647458
0.3708888	0.380642	0.2484688
0.326241	0.526332	0.1474268
0.2459815	0.671558	0.0824603
0.1825583	0.76549	0.0519521
0.1383689	0.825255	0.036376
0.1340891	0.830819	0.0350915
0.1342422	0.830676	0.0350817
0.1248744	0.842747	0.0323786
0.089047	0.887843	0.0231103
0.0893641	0.887412	0.0232239
0.0823574	0.896062	0.0215803
0.0795023	0.899568	0.0209295
0.0564917	0.927405	0.0161031
0.0361827	0.951745	0.0120725
0	0.971317	0.00866758
0.0112472	0.982303	0.00644995
0	0.987445	0.00524589
0.0052490	0.990202	0.00454901
0.00394143	0.991953	0.0041059
0.00295028	0.993243	0.00380702
0	0.996705	0.00329502

Literature Data Used for Comparison for Ternary Data for Mixture of Butanol, Water, and Carbon Dioxide (Chen, Chang, & Chen, 2002)

Mole Fractions of Mixture Components		
Butanol	**Water**	**Carbon Dioxide**
0.003	0.0001	0.9969
0.0022	0.0033	0.9945
0.0119	0.0047	0.9834
0.0058	0.005	0.9892
0.0006	0.0072	0.9922
0.0135	0.0041	0.9824
0.0198	0	0.9802
0.6854	0.0001	0.3145
0.6663	0.0591	0.2746
0.5875	0.1789	0.2336
0.5332	0.2504	0.2164
0.4992	0.3066	0.1942
0.4313	0.4143	0.1544
0.3682	0.5018	0.13
0.4131	0.5742	0.0127
0.3788	0.5839	0.0373
0.3822	0.5118	0.106
0.0119	0.9853	0.0028
0.0139	0.9828	0.0033
0.0124	0.9842	0.0034
0.0153	0.9814	0.0033

Sample Results from Simple Separation of Butanol from Water

	Stream 1	Stream 2	Stream 3
Substream: MIXED			
Mole Flow kmol/hr			
N-BUT-01	2.00E-05	1.80E-05	2.00E-06
HYDRO-01	0.001	1.00E-05	0.00099
CARBO-01	0.001	0.00099	1.00E-05
Total Flow kmol/hr	0.00202	0.001018	0.001002
Total Flow kg/hr	0.0795741	0.045245	0.034329
Total Flow l/min	0.0100943	0.005644	0.000834
Temperature C	60	60	60
Pressure bar	60	60	60
Vapor Frac	0.9584655	0.971998	0
Liquid Frac	0.0415345	0.028002	1
Solid Frac	0	0	0
Enthalpy cal/mol	-50166.79	-93056.5	-8937.31
Enthalpy cal/gm	-1273.491	-2093.76	-260.861
Enthalpy cal/sec	-28.14914	-26.3143	-2.48755
Entropy cal/mol-K	-3.166191	-9.53685	-5.84176
Entropy cal/gm-K	-0.0803741	-0.21458	-0.17051
Density mol/cc	0.00333521	0.003006	0.020016
Density gm/cc	0.1313845	0.133617	0.685767
Average MW	39.39314	44.44473	34.26088
Liq Vol 60F l/min	0.00181569	0.00092	0.000896