Energy Analysis of Butanol Extraction Using Supercritical Carbon Dioxide

A Major Qualifying Project Report submitted to the Faculty of

WORCESTER POLYTECHNIC INSTITUTE

in partial fulfillment of the requirements for the Degree of Bachelor of Science in

Chemical Engineering

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Abstract

This project analyzes a butanol fermentation and separation process using supercritical carbon dioxide and the bacterial strain recently discovered by the Massachusetts Institute of Technology (MIT). Butanol is a biofuel that has superior properties to ethanol, but current butanol production processes are not energy efficient with the industry standard between 8 and 12 MJ/kg. The goal of our project was to investigate the energy efficiency of a butanol extraction using supercritical carbon dioxide. We did this by finding an equation of state that models the behavior of the ternary system carbon dioxide-water-butanol, modeling the extraction process in Aspen Plus, running sensitivity analysis on different process parameters, heat integrating the process, and then analyzing four different process designs.

We determined that an altered version of the equation of state Soave-Redlich-Kwong (SRK) would accurately model the ternary system carbon dioxide-water-butanol at critical conditions. From our sensitivity analysis, we chose a 3:1 mass ratio of carbon dioxide to butanol in the reactor, a pressure of 65 bar for the first separator, and a carbon dioxide recycle ratio of 0.71. Our most efficient process design was a total recycle model that recycles the carbon dioxide produced by the fermentation reaction to be used to extract the butanol. The Total Recycle design had an energy requirement of 1.2 MJ/kg product, plus the energy requirement of the reactor, which was unknown. This is a very promising energy requirement, but we recommend further research be conducting on the cost and startup procedure of this process.

Acknowledgements

We would like to thank Michael Timko for guiding this project and showing his support throughout its completion. In addition, we would like to thank the Department Of Energy for funding the project and the Massachusetts Institute of Technology for collaborating with us.

Table of Contents

Table of Figures

Table of Tables

1.0 Introduction

When renewable energy and climate change are discussed, the conversation often focuses on electricity production; wind, solar, geothermal etc, but a large portion of the emissions and pollution comes from transportation. A green and sustainable replacement for burning fossil fuels in our planes, trains and automobiles would greatly reduce emissions and help provide energy security. Biofuel has great potential for use in the transportation industry because it is the only renewable and potentially green option for liquid fuel. It even has the potential to have net zero carbon emissions, because crops used as biomass to create biofuel take carbon dioxide (CO_2) from the atmosphere (Brown & Brown, 2014). Ethanol is a biofuel that has been implemented the most in the United States, however, butanol has the potential to be a superior biofuel.

Butanol can be mixed with gasoline up to 20% without any need to alter current automobile engines, as opposed to 10% for ethanol (Balat, 2011) (Ranjan & Moholkar, 2012). This is partially because it's energy density is 30MJ/kg which is much closer to gasolines 33MJ/kg than ethanols 20MJ/kg (Bioalcohols, 2010). Like ethanol, butanol is fermented, which means it requires glucose to feed microorganisms that produce alcohols. However, separating butanol from the water mixture requires a large amount of energy, especially because the microorganisms that create butanol can't survive at a certain percentage of butanol composition.

There has been research conducted on the potential of using supercritical carbon dioxide ($scCO_2$) to extract and separate butanol from water, as opposed to the typical liquid-liquid extraction method (Laitinen, A., & Kaunisto, J. 1999). Extraction using $scCO_2$ has been found to be a simpler and more energy efficient process of water/alcohol separation. However, until recently, there has been no butanol producing microorganism able to survive at supercritical conditions. Researchers at the Massachusetts Institute of Technology (MIT) recently discovered and are genetically engineering a bacteria that has many of the biological pathways to ferment butanol and can also survive at extremely high pressures in CO_2. Our project is to investigate the energy requirement of the process to continuously extract butanol using $scCO_2$ produced by the recently discovered bacteria at MIT.

2.0 Background

2.1 Bioenergy

Transportation today is mostly reliant on fossil fuels, which are limited resources that contribute to climate change and air pollution. Fossil fuel resources have been predicted to run out in the next 50 years, depending on a variety of factors. One renewable substitute for fossil fuels is bioenergy. Bioenergy includes biofuels, which are either liquid or gaseous fuels made from biomass and generally used as liquid fuels for transportation (Biomass Energy and Cellulosic Ethanol, n.d.). Today, bioenergy makes up about half of the renewable energy produced in the US, translating to about 5% of all US energy Consumption (Biomass - IER, 2015).

Biofuel has great potential for use in the transportation industry because it is the only renewable option available for liquid fuel. Biofuel is typically produced through fermentation, which implements yeast or bacteria to convert sugars to alcohols that can be used as fuel. The sugar used in this process generally comes from biomass; an organic material of biological origin. The complete process of producing and using biofuel is a renewable process that has the potential to have net zero carbon emissions (Brown & Brown, 2014). This is because crops used as biomass take carbon dioxide (CO_2) from the atmosphere. When the fuel is burned, the CO_2 is released back into the atmosphere in a cyclic process. As long as processing and production is green and zero emission, this system is a closed loop and won't add to the growing problem of climate change like fossil fuels does.

2.1.1 Corn Ethanol

In the United States, bioenergy is mainly from corn to make ethanol, an additive in gasoline. Bioethanol is one of the most commonly used biofuels for transportation because all modern vehicles can utilize a fuel of gasoline with up to 10% ethanol (Balat, 2011). Ethanol from corn is an expensive, inefficient process that is environmentally damaging. Due to land competition between energy and food crops, corn ethanol causes rising food prices. Corn agriculture causes environmental problems such as land degradation and habitat destruction. It also requires a substantial amount of water, which is a problem because of the increasing presence of drought and depletion of reservoirs in the US.

Economically, corn ethanol is a detriment to the US, even though the US is a world leader in ethanol production. This is because Brazil produces ethanol cheaper and more efficiency than the US, due to their use of sugarcane crop instead of corn. Sugarcane crop has more sugar per acre than corn and requires less processing power. An added benefit is that it reduces greenhouse gases by 90% if it is replacing gasoline, as opposed to 18% with corn (Balat, 2011). To make US corn ethanol competitive on the market, a 45 cent per gallon subsidy had to be set in place until 2011, as well as a 54 cent per gallon tariff. The Renewable Fuels Standard requires the production of 36 billion gallons of biofuels by 2022. This standard keeps the corn ethanol industry in business, even though economically and environmentally, the corn-ethanol industry in the United states is damaging (Biomass - IER, 2015).

2.1.2 Sustainable Biomass

There are two main sustainable sources of biomass; the waste products of agricultural processes and the harvest of a dedicated energy crop (Brown & Brown, 2014). It has been estimated that, by 2030, 680 dry tonnes of sustainable biomass resources could be made available. This translates to 54 billion gallons of ethanol, which is four times the amount of corn ethanol the US produced in 2010 (Biomass Resources in the United States, 2012).

The categories of waste materials include: agricultural waste, yard waste, municipal solid waste (MSW), food processing waste, manure, and invasive plant species (Brown & Brown, 2014). An example of a waste product from agricultural processes is the corn stalks from a corn harvest. Normally, these stalks would be a waste stream in the agricultural process. Using then as a source of biomass makes them a coproduct, and corn agriculture becomes more economical and environmentally friendly. However, corn stalks are difficult to break down to produce bioenergy, so further research is necessary to make this sustainable practice a reality.

Another benefit of using waste streams as a source of biomass is that the price for obtaining this biomass is generally only the cost of transit. In fact, it is even possible that biomass waste producers will pay for the disposal of their biomass waste. This is generally due to increasing cost of solid waste disposal and sewer discharges, as well as restrictions on landfilling. On the other hand, processing biomass waste materials into bioenergy has its challenges. The main difficulties include inconsistency in supply composition and the presence of various complex organic compounds that require different methods of processing (Brown & Brown, 2014).

Energy crops are crops grown specifically as an energy source, as opposed to a food source. Research is ongoing in developing ways to acquire energy from crops other than food crops, such as switchgrass (Biomass Energy and Cellulosic Ethanol, n.d.). Energy crops produce energy more efficiently than traditional biomass sources and require less fertilizer and pesticides to grow. In addition, land used to grow energy crops can be land not suitable for food-crops, so there is no competition for land against food (Biomass Energy and Cellulosic Ethanol, n.d.).

There are different types of energy crops, generally categorized into three categories: those high in lignocellulose, short rotation woody crops, and lipid based crops. Lignocellulose is indigestible to humans but energy crops lignocellulose generally return a higher energy yield. Grasses in particular have a high yield of lignocellulose, including corn, sugarcane and switchgrass (Brown & Brown, 2014) . This type of energy crop is harvested for its sugars that can then be fermented into an alcohol and used as a liquid fuel. In this report, we are most interested in this type of energy crop and its potential.

2.1.3 Butanols Potential as a Liquid Fuel

Butanol has the potential to be a better renewable liquid fuel option than ethanol because of its superior energy density. Butanol has an energy density of 30 MJ/L which is superior than ethanol's energy density of 20 MJ/L and closer to that of gasoline at 33 MJ/L (Bioalcohols, 2010). With existing technologies, butanol can be substituted into gasoline at 20%. Mixtures with higher butanol content are possible with small changes to car engines (Ranjan & Moholkar, 2012). In addition, butanol has a lower vapor pressure than ethanol, making it less volatile and able to have evaporative emissions. The potential drawback of butanol is that it is a toxic substance and verified that it will not cause issues with public health (Biobutanol, 2016).

The energy return on investment (EROI) is a number that compares the energy required to produce and distribute the energy source and the energy output. The EROI for oil and gasoline is about 20:1, meaning for every 1 unit of energy put into production and delivery of oil and gas, 20 units of energy are available for use. On the other hand, ethanol is a 5:1 EROI, but has been used because of its benefit to the environment (Hall, Lambert & Balogh, 2013). To be competitive to oil and gasoline, the EROI for butanol would ideally be close to that of oil and gasoline. Currently, the industry standard for producing butanol is in the range of 8 to 12 MJ/kg butanol. Because butanol has an energy density of 36 MJ/kg, to be as energy competitive as gasoline, butanol would need to be produced and processed on 1.8 MJ/kg of energy.

2.2 Supercritical Extraction

The process of separating alcohols from water traditionally requires a lot of energy. Various methods of liquid-liquid extraction have been tried before, but are not energy or logistically efficient. This lead to the investigation of supercritical solvents as a solvent extraction process in 1979 (Filippi and Moses, 1982). Supercritical extraction is the use of a supercritical fluid as a solvent to extract various components. This type of extraction has recently become more popular, especially in the form of countercurrent and continuous extraction, because supercritical extraction is simpler and more cost-effective than liquid-liquid extraction. This is especially true if CO_2 is the solvent, mostly because it is relatively easy to separate CO_2 from the solute post-extraction (Laitinen and Kaunisto, March 1999).

A supercritical fluid is a component at a temperature and pressure higher than its critical value. Generally these components are gases at standard temperature and pressure, and a liquid with gas-like properties at supercritical conditions. Special properties of a supercritical fluid include its ability to diffuse like a gas and act as a liquid solvent (Laitinen and Kaunisto, 1999). Supercritical carbon dioxide ($scCO_2$) has these properties, and is also environmentally safe, nontoxic, nonflammable, and exceptionally inexpensive. In addition, $scCO_2$ leaves little trace in the solute because at atmospheric conditions it is a gas, and has a technically ideal critical pressure and temperature (73.8 bar and 31.1 degrees Celsius) (Laitinen and Kaunisto, 1999).

The use of $scCO_2$ has been tested in various extraction columns. Generally, the packed columns have been very efficient, but costly because of their capacity limits. Spray columns on the other hand have high capacity, but are lacking the benefits of the packed column that a small diameter introduce. The idea of a mechanically agitated extraction column has been tested and determined to combine the beneficial properties of a high-efficiency packed column and a high-capacity spray column (Laitinen and Kaunisto, 1999).

2.2.1 Butanol Extraction Using Supercritical Carbon Dioxide

One use of supercritical fluid extraction is in separating organic compounds from solutions, especially low molecular weight alcohols with $scCO_2$. Phase equilibrium has been explored for different alcohols such as ethanol, methanol, isopropanol, and 1-butanol (Panagiotopoulos and Ried). However, low molecular weight alcohols have some issues in supercritical extraction due to their affinity for water and relatively high vapor pressure, which makes it difficult to separate from the $scCO_2$ solvent. On the other hand, higher molecular weight alcohols are generally less hydrophilic and volatile than low molecular weight alcohols, and would be more ideal for supercritical extraction. An example of a high molecular weight alcohol is Butanol (Laitinen and Kaunisto, March 1999).

The fermentation of sugars by bacteria to create butanol happens with the following chemical reaction. Glucose breaks down into two carbon dioxide molecules, one water molecule and one butanol molecule.

$$C_6H_{12}O_6 \rightarrow 2CO_2 + H_2O + C_4H_9OH$$

Butanol was not able to be extracted using supercritical carbon dioxide because the bacteria commonly used to produce butanol could not survive in $scCO_2$. However, the discovery of a bacteria *B. megaterium* that can produce butanol and survive in $scCO_2$ has recently been made by the Massachusetts Institute of Technology (MIT). With butanol extraction using supercritical CO_2 now a possibility, butanol production has the potential to be energy efficient. Butanol is a higher alcohol with similar energy density to gasoline. If an energy efficient process to create butanol is discovered, there is the potential to replace the use of gasoline with butanol.

3.0 Methods

For this project, we analyzed the possibility of producing fuel grade butanol at a lower energy requirement than the current standard, and less energy input then butanol provides as a fuel. At 100 bar, carbon dioxide ($CO_{2,}$) and water exist in two separate liquid phases. Butanol is soluble in supercritical CO_2, so it can be used to extract the butanol from the fermentation stage, where composition is mainly water. Once the butanol is extracted, a flash can be used to separate the CO_2 and butanol without using a distillation column. To analyze this process, the Aspen Plus Process Modeling System was used.

To analyse this extraction process we needed to model the ternary interactions between carbon dioxide, water and butanol. To do this, we determined an altered equation of state that would accurately model the system. The we were able to begin modeling the process in Aspen Plus. We took the idea for the general layout from the previous Major Qualifying Project (MQP) and made it more plausible. After designing the basic process, we tested various parameters to determine their effect on the process energy requirement. The next step was then to optimize the process using heat integration and analyse the energy requirements of different plausible scenarios. In analysing the scenarios, we could determine whether or not the process was feasible in terms of energy.

The project was done a cyclical process. We went through all the steps under set of assumptions and then when we got to the end, made some adjustments and started over. The results in this paper are from the last, most accurate cycle.

3.1 Setting up the Model

3.1.1 Choosing an Equation of State

The first step in this process was finding an equation of state that would accurately model the ternary behavior of the CO_2, water, butanol system. With the help of fellow student Luke Jackson, we tested all 94 preloaded equations of state in Aspen to see how well they predicted the ternary systems composition. To do this, we used composition data at the desired temperature and pressure, and ran a separator in Aspen with the same specifications. We then compared the results from the process model in Aspen to the literature data and calculated error.

Once we had all ninety-four results we reviewed them, none of them were accurate (see Appendix X for the spreadsheet and error). We chose three equations of state that we thought would be the most likely to accurately represent the mixture if we regressed data to adjust parameters. We then used literature data (Chen et al, 2002) to regress new parameters for these equations of state.

We ran six different temperature and pressure combinations with the new parameters. We plotted a graph with the literature data on one axis and the calculated values from the simulation on the other. We then added a line with an intercept of zero and a slope of one, a unity line, to see how the answers compared. We calculated the absolute average deviation and absolute average relative deviation values for the line to see how closely they fit. The closer the points were to the line the better the trend for the points and the more accurate the model was. We used this strategy to determine which of the three equations of state was the most accurate and the one we would use to build our model.

3.1.2 Building the Model

The next step was building the process. The previous MQP team had an outline for what was needed for the process. However they weren't using the regressed data so we rebuilt the simulation with the improved equation of state.

3.2 Sensitivity Analysis

We ran several sensitivity analysis to examine how different parameters of the process affect the energy requirement. We looked at three different parameters of the process. The carbon dioxide to butanol ratio in the stream leaving the reactor, how much carbon dioxide we recycle and the pressures of the separators.

3.2.1 Carbon Dioxide to Butanol Ratio

The first thing we tested was the CO_2 to ButOH ration in the stream leaving the fermenter. According to research (Laitinen, A., & Kaunisto, J. 1999) a ratio of 3:1 insures 99% of the BuOH will go into the carbon dioxide phase (Liquid 1 phase). In the event that a higher ratio was needed we tested how sensitive the energy requirement of the process is to the amount of CO_2 put into the system. We ran the simulation several times with different mass flow rates of carbon dioxide. As we increased the mass flow rate we increase the ratio of CO_2 and butanol. We ran the simulations with and without a recycle stream. We plotted the data on a graph with the ratio on the x axis and energy requirement in MJ/kg on the y axis to see the trend.

3.2.2 Recycle Ratio

Once we saw how the amount of carbon dioxide affects the energy requirement we decided to look at the recycle stream. We used a splitter to split the stream into recycle and purge streams. For this test we kept the ratio of carbon dioxide to butanol constant. We ran the simulation altering the inlet carbon dioxide and the split fraction in the splitter. We ran simulations beginning with no recycle and ending with total recycle (running the process completely on the carbon dioxide generated by the organisms in the reactor). We graphed the results to see what the trend and impact of the recycle ratio.

3.2.3 First Separation Pressure

There are two separators in the process. The last parameter we looked at was the pressure of the first flash separator. This is three phase separator. We wanted to see what happens when the first flash happens at different intermediate pressures. We looked at energy requirement, purity and recovery. We ran the simulations ranging from 35 bar to 65 bar at several butanol ratios. We plotted all of these on graphs to see the trends in all of these parameters, and determine what the best pressure to run the middle flash.

3.3 Heat Integration

In the last part of the project we looked at the results from the sensitivity analysis and came up with four potential designs that we could then heat integrate, to make as energy efficient as possible. In order to do this we looked at the energy requirement of each unit operation, and the temperature and pressure of the streams flowing in and out. Then, we looked to see if any of the hot streams could be used to heat cold streams and vise versa, to decrease the amount of energy we need to add to the system. Once we put the heat integration changes into the simulation we ran it again, added up the duties of the unit operations, and excluded the duties that were being done by streams already in the system, to get the final energy requirement for the system.

4.0 Results and Discussion

4.1 Equation of State

After testing all of the different equations of state in Aspen Plus and discovering that none of them accurately represented our data, we chose to explore three equations of state (EOS) that we predicted would best model the ternary system CO_2-water-butanol at our desired temperature and pressure. We did this by altering the parameters of the three EOS using composition data from the literature (Chen et al, 2002) for the three phase system in the temperature and pressure region the process was going to take place in. For this ternary system, there were three phases at the temperature and pressure we were investigating: liquid 1, liquid 2, and gas. Each of these phases has different compositions of CO_2, water, and butanol and needed to be predicted with the altered EOS.

To compare the EOS predicted compositions and the literature data, we calculated the absolute average relative deviation and the absolute relative deviation between the two sets of data. The equations used can be seen in Equations 1 and 2. In addition, we graphed the calculated compositions versus the experimentally determined compositions from the literature. If the two sets of data were the same, they would make a line with the equation x=y, called the unity line. Therefore, we compared the data in these graphs to the unity line. An example graph can be seen below in Graph 1, and all of these graphs can be seen in Appendix X.

Absolute Average Relative Deviation (%) = (abs($\bar{x}_{calc} - \bar{x}_{exp}$)/$\bar{x}_{exp}$) * 100% **Equation 1**

Absolute Average Deviation = abs($\bar{x}_{calc} - \bar{x}_{exp}$) **Equation 2**

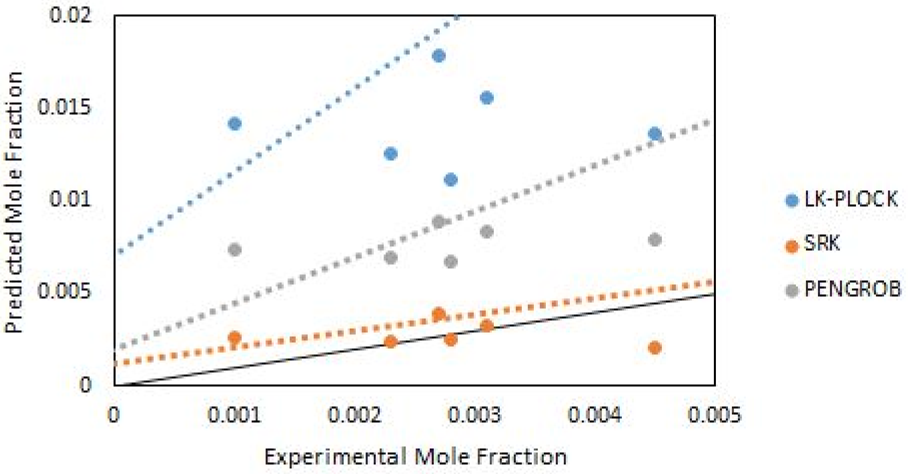

Figure 1: Comparison of experimentally found compositions versus calculated compositions for the Liquid 2 phase of CO_2 with a unity line

Analyzing the tables of absolute average relative deviation (AARD) and absolute relative deviation (ARD), we first looked at the the AARD percentage. If the AARD was high, we then looked at the ARD, and if the ARD was large enough to impact the prediction significantly, the altered EOS was deemed less likely to accurately represent the ternary system. However, if the number ARD was small, we deemed the prediction method accurate. For example, in Table 1, the gas phase of Butanol has an AARD of 272%, which is concerning. However, the ARD is 0.006, which is a small enough value that the inaccuracy in the AARD can be ignored and the prediction method is assumed accurate. The reason the AARD percentage is so high for that example is because the composition of Butanol in the gas phase at the corresponding temperature and pressure is so low.

Compound	**PENGROB Absolute Average Relative Deviation (%)**	**PENGROB Absolute Relative Deviation**
Gas		
CO2	1.05%	0.010
Butanol	272%	0.006
Water	43%	0.010
Liquid 1		
CO2	34%	0.041
Butanol	14%	0.052
Water	97%	0.475
Liquid 2		
CO2	241%	0.005
Butanol	33%	0.005
Water	7%	0.073

Table 1: PENGROB comparison to experimental results from the literature

The altered EOS PENGROB only has one point that is not accurate enough, and that is the liquid 1 phase of water, colored in red in Table 1.

Compound	**LK-Plock Absolute Average Relative Deviation (%)**	**LK-PLock Absolute Average Deviation**
Gas		
CO2	0.76%	0.007
Butanol	619%	0.010
Water	44%	0.010
Liquid 1		
CO2	15%	0.026
Butanol	84%	0.302
Water	57%	0.284
Liquid 2		
CO2	537%	0.011
Butanol	90%	0.011
Water	2%	0.022

Table 2: LK-Plock comparison to experimental results from the literature

The altered EOS LK-Plock has two points that were not deemed accurate enough, and that is the liquid 1 phase of both water and butanol, colored in red in Table 2.

Compound	**SRK Absolute Average Relative Deviation (%)**	**SRK Absolute Average Deviation**
Gas		
CO2	0.92%	0.009
Butanol	98%	0.007
Water	42%	0.010
Liquid 1		
CO2	14%	0.020
Butanol	8%	0.018
Water	7%	0.031
Liquid 2		
CO2	46%	0.001
Butanol	15%	0.005
Water	0%	0.003

Table 3: SRK comparison to experimental results from the literature

The altered EOS SRK doesn't have any points that are glaringly inaccurate and generally the points have small error. Therefore, we chose the altered SRK EOS to represent the data.

4.2 Simulation Results

After we determined how to predict phase composition for the CO_2-water-butanol ternary system with the altered SRK EOS, we built a basic process model using industry heuristics. We determined that pressurizing the CO_2 should be completed in four stages. In addition, three heat exchangers were needed to insure the carbon dioxide would not overheat and that the temperature would be at 40°C when entering the reactor where fermentation occurs. To model a reactor that could separate two phases a dummy separator was added to the simulation after the reactor. The previous MQP team used literature data to determine that 99% of the butanol generated would shift from the water phase to the CO_2 phase (Laitinen, A., & Kaunisto, J. 1999) - when there is a mass ratio of CO_2 to butanol around 3:1 and the butanol is more soluble. We used this information as well as binary information (King, M. B. et al) at 100 bar and 40^{o} C to set split fractions and ensure accurate data.

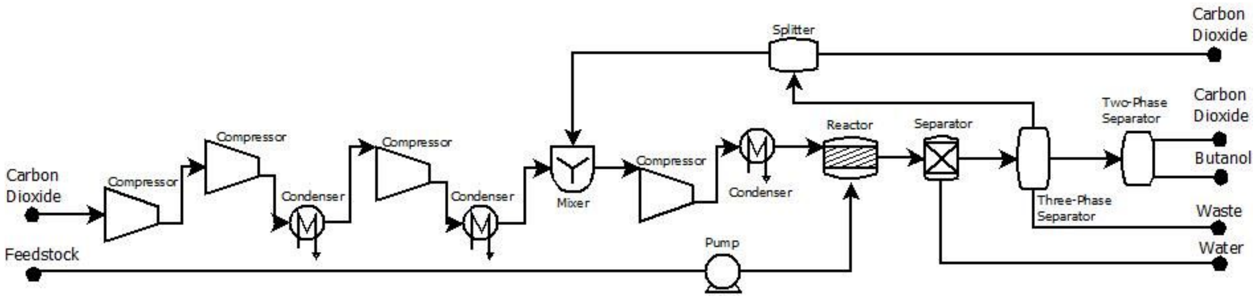

Figure 2: Basic Process Model

These split fractions were implemented in the separator after the reactor. In industry, these two blocks in Aspen would be one unit; a reactor with a mass transfer unit. However, Aspen Plus doesn't have a block representing this unit, so a dummy separator was used instead. Most of the water in the process drops out in this separation, as seen in Figure 1. A three phase flash separator was added to drop the pressure and separate some of the CO_2 and remaining water from the butanol. Finally, the simulation data showed that a distillation column was not necessary to get the purity desired, which is important because distillation columns require a lot of energy. Instead, a second flash with temperature and pressure for only two phases brings the product stream down to 1 bar and separates the butanol to a desired purity. The basic process model is shown in Figure 1.

4.3 Sensitivity Analyses

We completed several sensitivity analyses to determine how different parameters impact the energy requirement of the process. The factors we tested were: CO_2 to butanol mass ratio in the reactor, CO_2 recycle ratio, and pressure of the three phase separator. The following sections detail the results of those analyses.

4.3.1 Carbon Dioxide to Butanol Mass Ratio and Pressure Variations

The first parameters that were investigated are the pressure of the three phase separator, and the CO_2 to butanol mass ratio in the reactor. Graph 2 shows the correlation between the CO_2 to butanol mass ratio in the reactor and the energy required per kilogram of product for different pressures of the three phase separator. This data was used to determine the pressure of the three phase separator and the CO_2 to butanol mass ratio in the reactor that returned the lowest energy per kilogram of product. The simulation was run with a fixed 50% carbon dioxide recycle stream.

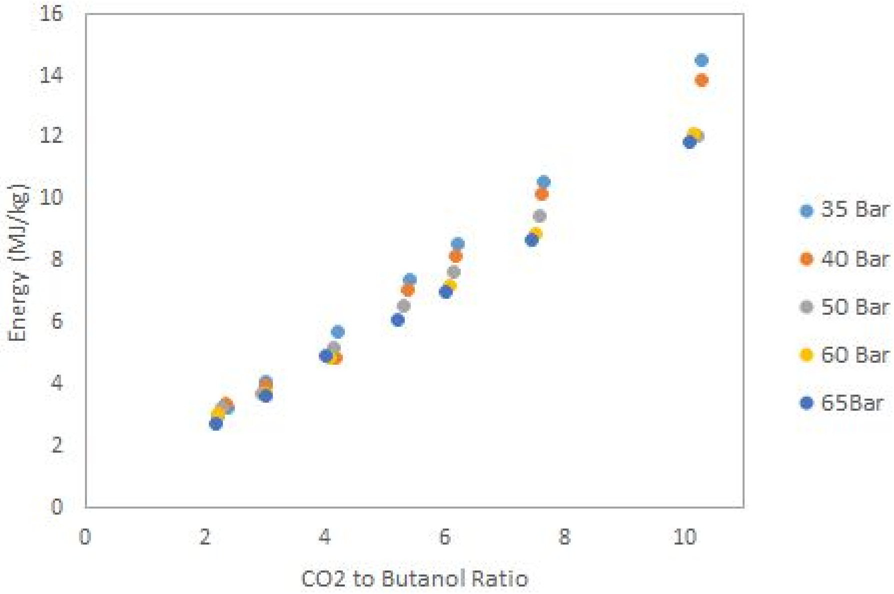

Figure 3: Graph of CO_2 to Butanol Ratio vs. Energy Requirement

The ratio of CO_2 to butanol is critical in the energy efficiency of the extraction process. Graph 2 shows that the lower the CO_2 to butanol ratio, the lower the energy requirement. This is because compressing carbon dioxide from 1 bar to 100 bar is a large portion of the energy, and a higher ratio means more carbon dioxide flowing into the system that needs to be compressed. In addition, Graph 2 shows that the higher the pressure, the less energy requirement. This is because the CO_2 in the recycle stream coming from the three phase separator started at a higher pressure and less energy was required to pressurize it.

After analyzing our data, the optimal parameters were determined to be a pressure of 65 bar in the three phase separator, and a CO_2:butanol mass ratio of 3:1 in the reactor. We chose a CO_2 to Butanol ratio of 3 because the energy requirement drops with lower ratio, and our literature data tells us that in order to achieve the 99% extraction we need a mass ratio of at least 3:1 (Laitinen, A., & Kaunisto, J. 1999).

4.3.2 Recovery Ratio and Product Purity

The recovery rate of butanol and the purity of the product were also tested and analyzed. Butanol recovery is the mass of butanol in the product stream divided by the mass of butanol produced in the reactor and tells us how well the butanol is recovered in the process.

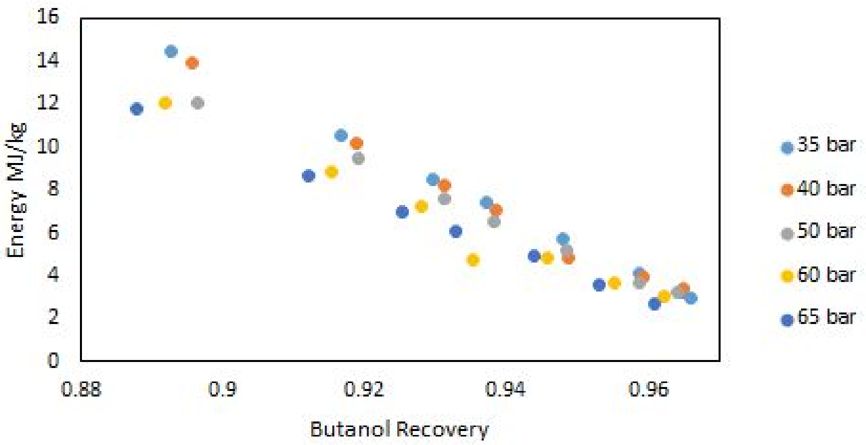

Figure 4: Butanol recovery mass ratio versus energy required per kilogram of product

Graph 3 shows that higher recovery rates are from runs that used less energy. This means that the runs with lower CO_2 to butanol ratios also had a higher rate of recovery. The graph also indicates that pressure impacts recovery rate, although not significantly. The lower the pressure, the better the recovery rate, by a very small fraction. In addition, recovery rate impacts the energy required per kilogram of product because it is calculated by dividing energy in megajoules per hour by the mass flow rate of the product, and less product means more energy per kilogram.

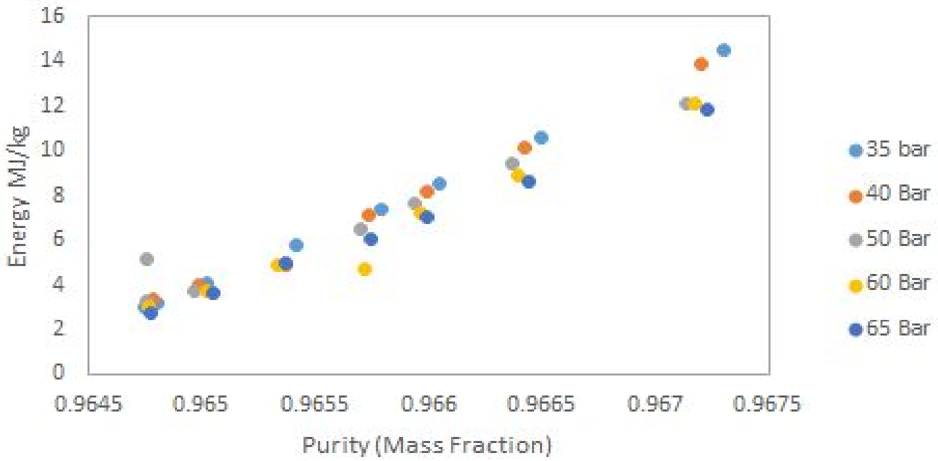

Figure 5: Mass fraction of butanol purity in the product stream versus energy required per kilogram of product for different pressures of the three-phase separator

The butanol purity of the product was examined using the mass fraction of butanol in the product stream. This is an important factor because the higher the butanol purity, the better the product. Graph 4 compares the purity of the product to the energy requirement per kilogram of the product stream. The trend in Graph 4 shows that there is marginally less purity when less energy is required. This difference is only by 0.001, so it is very marginal. If the purity is slightly less, it makes sense that the energy requirement is also less.

4.3.2 Recycle Ratio

The next parameter we explored was the recycle ratio of carbon dioxide. In the overall process, this is the CO_2 separated in the three-phase separator that is recycled back into the reactor. In these runs, the previously determined parameters of 65 bar in the three phase separator and a CO_2 to butanol mass ratio of 3:1 were used. Graph 5 shows the relationship between the recycle ratio and the energy required per kilogram of product. The trend shows that a higher recycle ratio reduces the energy requirement. However, the recycle ratio was only allowed to go to 0.7, where the energy requirement is 3.015 MJ/kg.

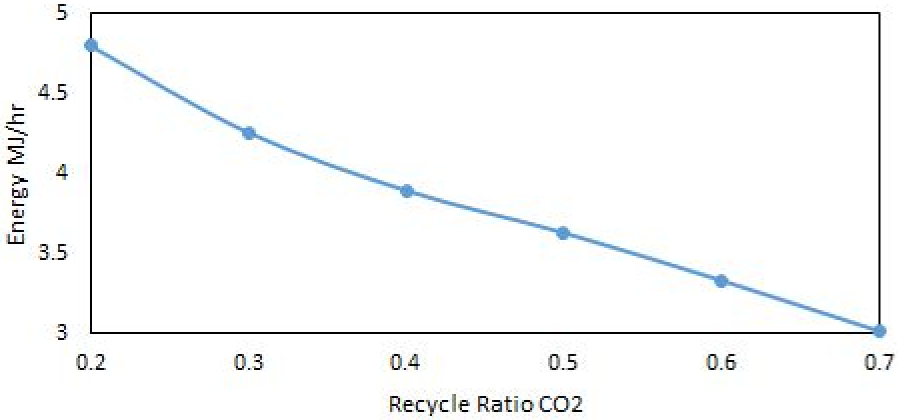

Figure 6: Recycle ratio of carbon dioxide compared to energy required per kilogram of product at 65 bar and a 3:1 mass ratio of carbon dioxide to butanol out of the reactor

The reason the recycle ratio only could go as high as 0.7 is shown in Graph 6. At a recycle ratio of 0.7, there is very little carbon dioxide entering the process, and in fact adding CO_2 to the process wouldn't be necessary.

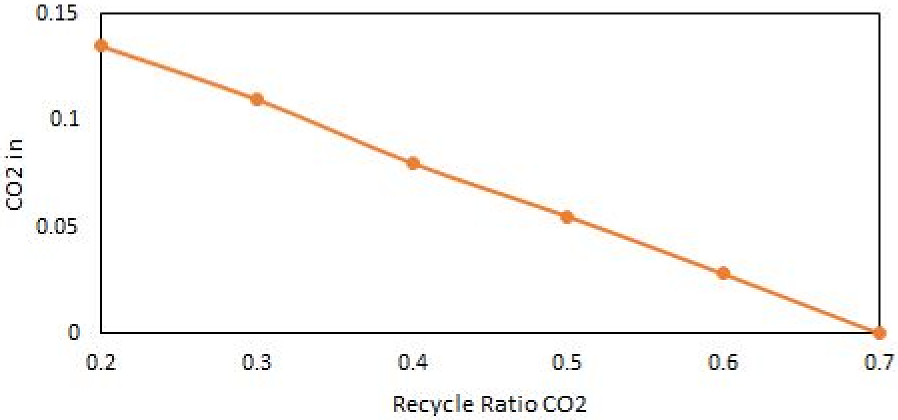

Figure 7: Recycle ratio of carbon dioxide versus carbon dioxide entering the process. 65 bar was used for the first flash and a CO_2 to butanol ratio out of the reactor was set to 3

This data introduced the idea that total recycle of carbon dioxide may be possible. That is, there is no need to feed a stream of carbon dioxide into the process because the reaction in the fermentation process creates enough carbon dioxide to run itself.

4.4 Final Process Designs

After doing the sensitivity analyses, we came up with four process design models we wanted to explore further. The first was similar to the basic model, run at optimal parameters and heat integrated. The next model was removing the three phase separator, and only having one separator that flashes the material from 100 to 1 bar. We then developed a total recycle process, based of the result from the recycle ratio analysis indicating that the process generates enough CO_2 to sustain itself. This means that we ran the process only using the CO_2 created by the fermentor. Finally, the fourth process model had a reactor at atmospheric conditions and pressurized the product from the reactor to be separated with supercritical carbon dioxide. This model was created in the event that the bacteria couldn't be engineered to grow and produce butanol as reliably as desired.

After choosing these four models, we heat integrated the processes in an effort to minimize the energy input. To incorporate the heat integration into the results we simply removed that heat duty or work requirement from the total energy requirement, as it was being done by a stream internal to the process. The effectiveness of the process models will be discussed in the following sections. The parameter details for each model are outlined in Table 4, as well as the energy requirements.

Model	**Regular**	**Total Depressurization**	**Total Recycle**	**Post Pressurization**
CO_2 Recycle Ratio	0.6	0.0	0.71	0.0
Pressure of First Separator (bar)	65	1	65	65
Inlet CO_2 (kg/hr)	0.028	0.185	0.000	0.300
CO_2 to Butanol Mass Ratio	3:1	3:1	3:1	3:1
Mass Fraction Butanol in Product	0.965	0.960	0.961	0.964
Product Energy Requirement (MJ/kg)	1.95	3.06	1.22	6.46
Butanol Energy Requirement (MJ/kg)	2.03	3.19	1.26	6.70

Table 4: Parameter specifications and results for the four analyzed process models

Table 4 shows that the process model with the best energy requirement is total recycle. These calculations were completed using numbers from Aspen plus, and do not contain the energy requirement of the reactor, because it is currently unknown and not estimable by Aspen. Further analysis if these results are in the following sections.

4.4.1 Regular Model

C-101	**C-102**	**E-101**	**C-103**	**V-101**	**E-102**	**C-104**
CO_2 Compressor	CO_2 Compressor	CO_2 Condensor	CO_2 Compressor	CO_2 Recycle Mixer	CO_2 Condenser	CO_2 Compressor
E-103	**R-101**	**V-102**	**V-103**	**V-104**	**V-105**	**P-101**
CO_2 Condensor	Butanol Reactor	Water Phase Separator	Three Phase Separator	CO_2 Recycle Splitter	Two Phase Separator	Liquid Pump

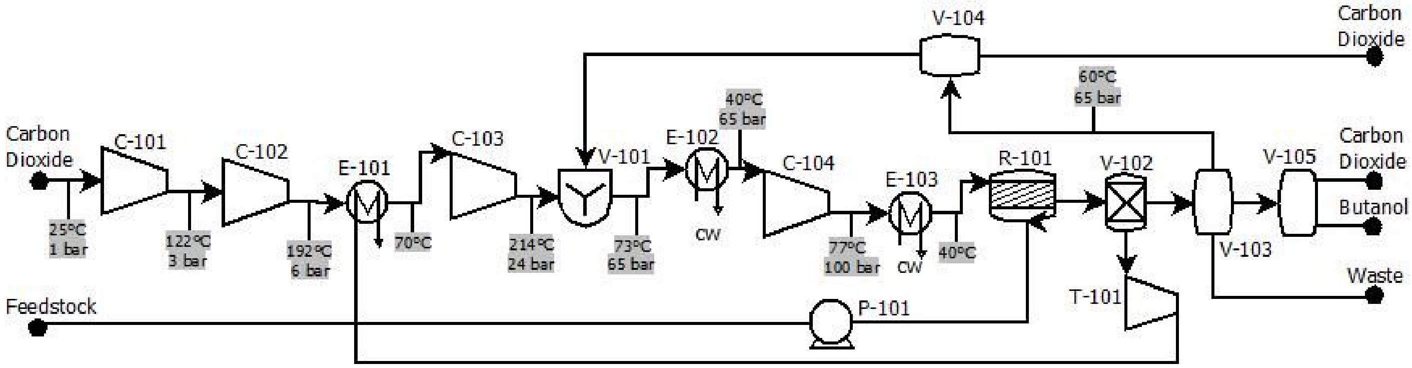

Figure 8: Regular Model

For this model, we ran the simulation using the optimal parameters we found doing our sensitivity analysis. The only part of the process that could be heat integrated was using the water we separated from the stream leaving the reactor to cool one of the heat exchangers. Most of the streams in this process need to be cooled and there aren't very many streams with a low enough temperature to do that. Of the four models this one had the second best energy requirement.

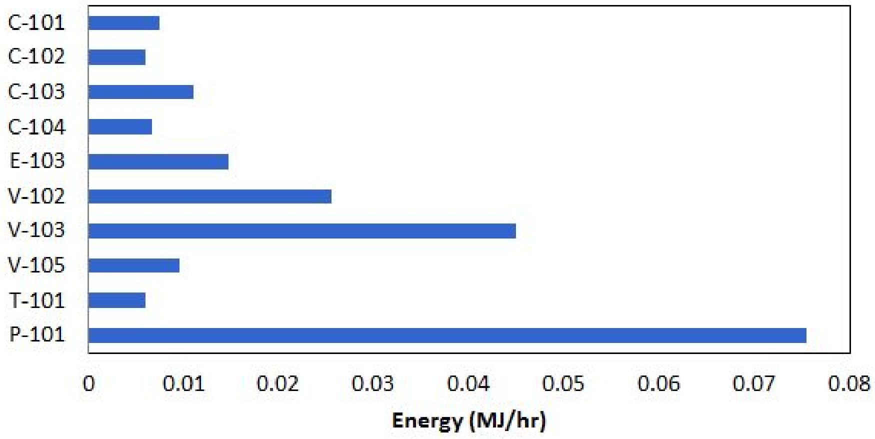

Figure 9: Tornado plot for base case process model showing energy use of various equipment

Graph 7 shows the different energy requirements of each piece of equipment that was not able to be heat integrated. From this graph, it is clear that the pump P-101 used to bring the feedstock pressure up to 100 bar requires the most energy. The second most energy requirement is V-103, which is the three phase separator that also recycles CO_2 back into the process.

4.4.2 Total Depressurization

C-301
CO_2
Compressor

C-302
CO_2
Compressor

E-301
CO_2
Condensor

C-303
CO_2
Compressor

E-302
CO2
Condenser

C-304
CO2
Compressor

E-303
CO_2 Condensor

R-301
Butanol
Reactor

V-301
Water Phase
Separator

V-302
Two Phase
Separator

T-301
CO2
Recycle
Splitter

P-301
Liquid Pump

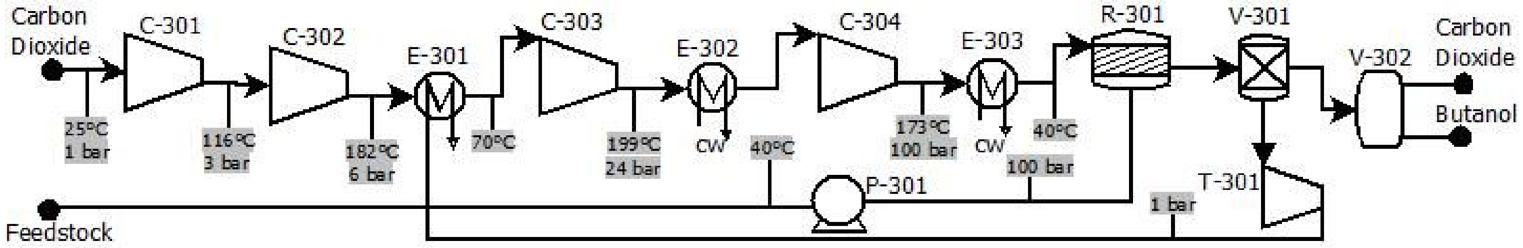

Figure 10: Total Depressurization Model

The next model we tested was the total depressurization model. In this model the three phase separator was removed. After the reactor, the first separator, or decanter, separates out the majority of the water and the butanol/CO_2 stream is depressurized to 1 bar. At 1 bar CO_2 is a gas and easily separates from the butanol product. In this model, the purity of the product remained high enough that we didn't need to add a distillation column or other kind of separator. We believe this is because the first separator attached to the reactor removes most of the water, and separating carbon dioxide and butanol is significantly easier than separating water and butanol. The necessity of the three phase separator is therefore minimal, and only necessary to recycle CO_2.

There was no recycle stream in this simulation. The purpose of the recycle stream for the other simulation was to provide a source of CO_2 that was at a higher pressure and didn't need to be compressed all the way from 1 to 100 bar. With total depressurization, a recycle stream wouldn't change the energy cost because there is no three phase separator and the recycle would have to be fully repressurized.

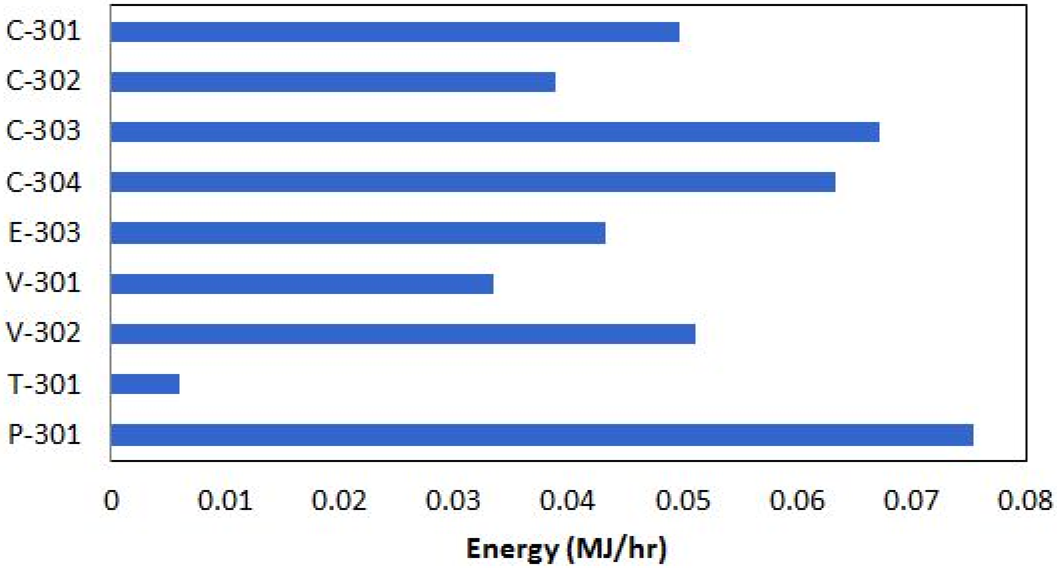

Figure 11: Tornado plot for total depressurization process model showing energy use for various equipment

In terms of heat integration, water from the first separator was used to cool one of the heat exchangers. We also let the temperature of the product drop all the way to 0º C in the flash (because temperature drops as it is depressurized), and used it to cool one of the heat exchangers, which brings it back to a reasonable temperature. This also saves energy in the separator because the stream doesn't need to be heated as much as the pressure is decreased. Overall, this process model was another practical simulation, although it had a higher energy requirement than the base case and total recycle model.

4.4.3 Total Recycle

E-201
CO_2 Condenser

C-201
CO_2 Compressor

E-202
CO_2 Condensor

R-201
Butanol Reactor

V-201
Water Phase Splitter

V-202
Three Phase Separator

V-203
CO_2 Recycle Splitter

V-204
CO_2 Recycle Splitter

T-201
Depressurizing Turbine

P-201
Liquid Pump

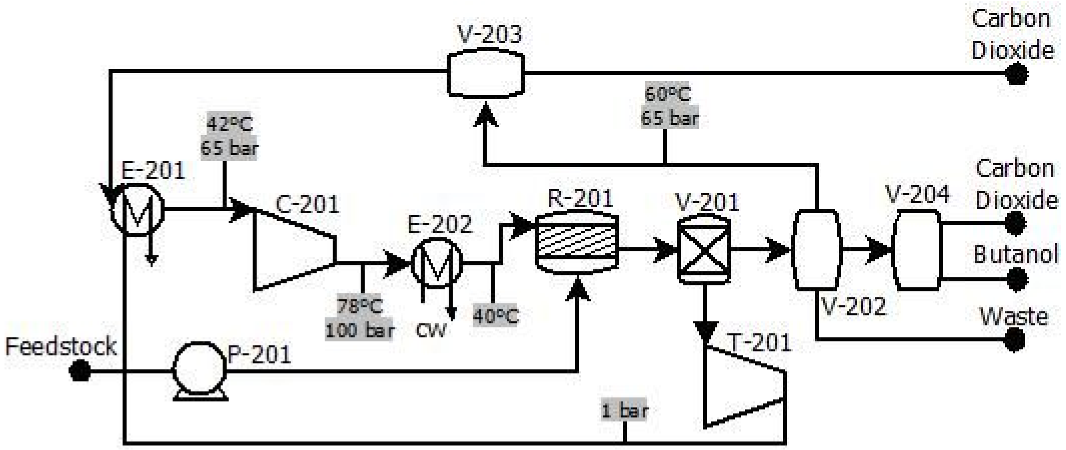

Figure 12: Total Recycle Model

The third model tested was total recycle. During the recycle ratio sensitivity analysis, it was found that the process could be run on the carbon dioxide that was produced by the fermentation alone, and that no carbon dioxide from outside the process was needed. This significantly dropped the energy requirement because aside from startup, the carbon dioxide in the process only had to be pressurized from 65 to 100 bar. This takes much less energy than pressurizing carbon dioxide from 1 to 100 bar.

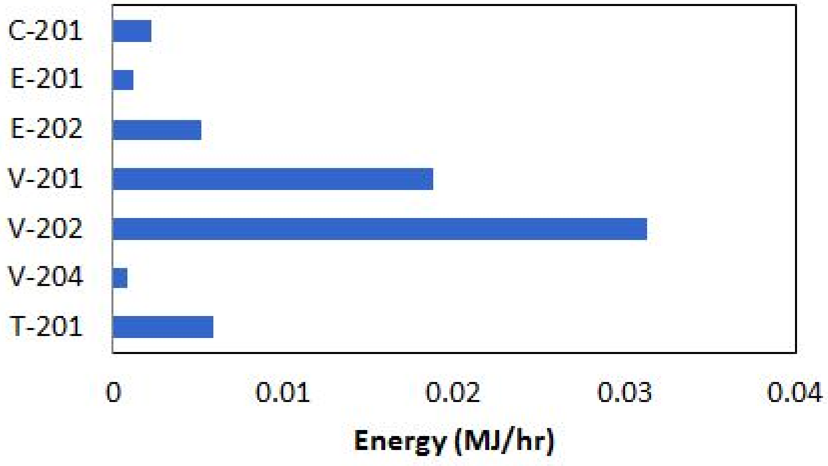

Figure 13: Tornado plot for total recycle process model showing energy use for various equipment

One concern with this model was the potential build up of butanol in the recycle stream. However, according to aspen, there is some butanol in the recycle stream but not enough to be concerned about. For this process the only heat integration that was possible was using the water from the first separator to cool the first heat exchanger. This process was the most promising of the models. Graph 8 shows that the most energy comes from the three phase separator, and also the liquid pump.

4.4.3 Post Reaction Pressurization

C-401 CO_2 Compressor	**C-402** CO_2 Compressor	**E-401** CO_2 Condensor	**C-403** CO_2 Compressor	**R-401** Butanol Reactor	**E-402** CO_2 Condenser	**C-404** CO_2 Compressor
E-403 CO_2 Condensor	**V-402** Mixer	**V-403** Water Phase Separator	**V-404** Three Phase Separator	**V-405** Two Phase Separator	**V-401** CO_2 Separator	**P-401** Liquid Pump

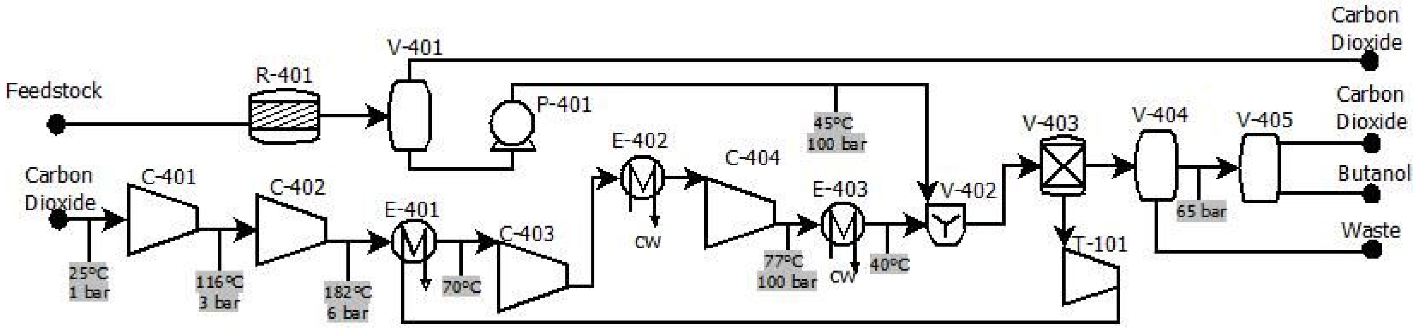

Figure 14: Post Pressurization Model

After running the previous simulations it came to our attention that it may be difficult for the bacteria to produce ethanol at 40ºC and 100 bar. To counter this, we tested a simulation in which the bacteria does the fermentation at atmospheric pressure and the product is then pressurized for separation. This may produce more reliable results in a lab or a plant. We found that this process required substantially more energy, however we did not recycle any of the CO_2. Still, the energy requirement is on par with the current industry standard of producing butanol.

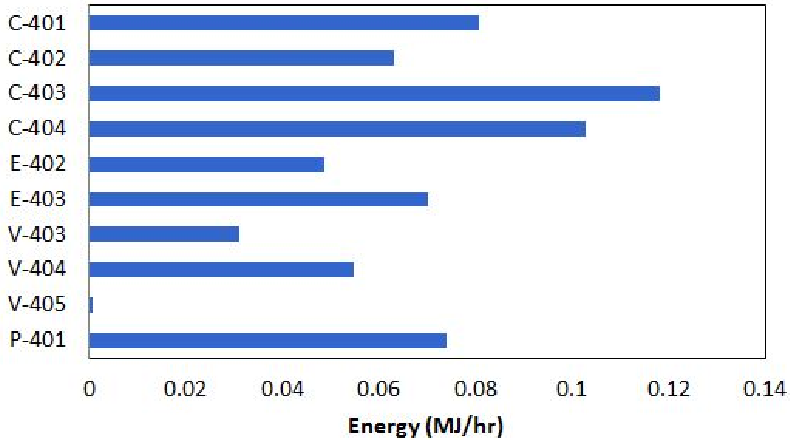

Figure 15: Tornado plot for post reaction pressurization model showing energy use for various equipment

Graph 9 shows the largest energy requirements come from the compressors that compress CO_2 for the extraction. This process should be altered so that there is a CO_2 recycle stream. Then, the energy requirement for the compressors would be much less and the overall energy requirement reduced. In addition, the effect of different parameters may be different on this model because it is altered more than the other models. Therefore, an investigation on optimal parameters should be conducted.

5.0 Conclusion

Our project was to determine the energy requirement of producing butanol by fermentation and purifying it using supercritical CO_2. We regressed data in Aspen Plus to adjust the parameters of an equation of state so it would accurately model the ternary behavior of our mixture, ran sensitivity analyses to determine what aspects of the process had the largest impact on energy input, and built and heat integrated several process models. We found that the best CO_2 to butanol mass ratio in the reactor was 3:1 (Laitinen, A., & Kaunisto, J.,1999). Having a middle flash is not necessary separation wise, but does allow for a high pressure recycle stream that will lower the energy cost. In addition, the process can be run at total recycle, just on the CO_2 it generates, which lowers the energy cost further.

In conclusion, our analysis finds the process for producing butanol using supercritical CO_2 to be energy efficient. However, equipment for high pressure operations is very expensive due to the need for safety features and high quality material that is strong enough to sustain high pressures. In addition, bacteria that can survive at supercritical conditions may not produce butanol at a reliable rate or as well as other bacteria that has previously been used. Further research must be done for bacteria butanol production at supercritical conditions and on costs for high pressure machinery. Because of these challenges, in industry the process may have to be run at the Post Pressurization model, in which the reaction to create butanol occurs at atmospheric conditions and the product from that reactor is pressurized and butanol extracted using supercritical carbon dioxide. In this case, we would recommend further exploration on the impact of different parameters for the post pressurization model, as well as looking into heat integration and finding a way to add a recycle stream.

If running the fermentor at 100 bar can be made cost effective and reliable, the total recycle model is the most energy efficient. We recommend further research be conducted on the startup procedures of a total recycle process and an in-depth analysis on whether total recycle is possible. If possible, a cost analysis should be completed and the cost of equipment that runs at high pressure plus the efficiency of the butanol producing bacteria should be explored. Also, research needs to be done into the kinetics of this reaction, our data did not include the energy for running the fermentor/water separator unit operation due to this lack of this information. According to our energy analysis, for the total recycle model it takes 1.22 MJ/kg of product with a 96.1 weight% butanol content, again without the reactor energy requirement taken into account.

With the energy density of butanol being 36 MJ/kg, this process should be energy efficient and comparable to the 20:1 energy return on investment (EROI) for gasoline. Energy required to obtain the feedstock and transport the butanol product to the user must be taken into account for the butanol EROI, but it is possible to have a 20:1 butanol EROI with our initial estimate of the extraction process at a 28:1. Further research must be completed to get a better estimate of the EROI with the reactor, feedstock, and transportation energy requirements taken into account. The feedstock especially may require a large amount of energy because it is sugar processed from energy crops or food crops such as corn and sugarcane.

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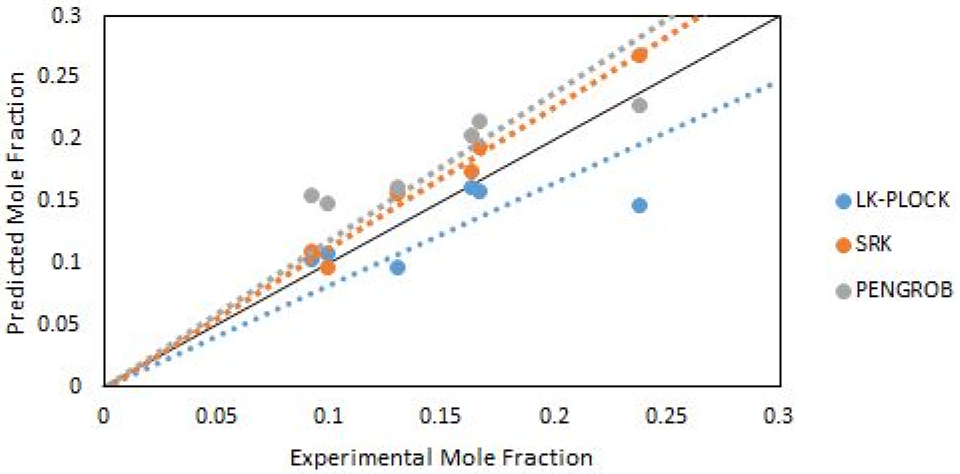
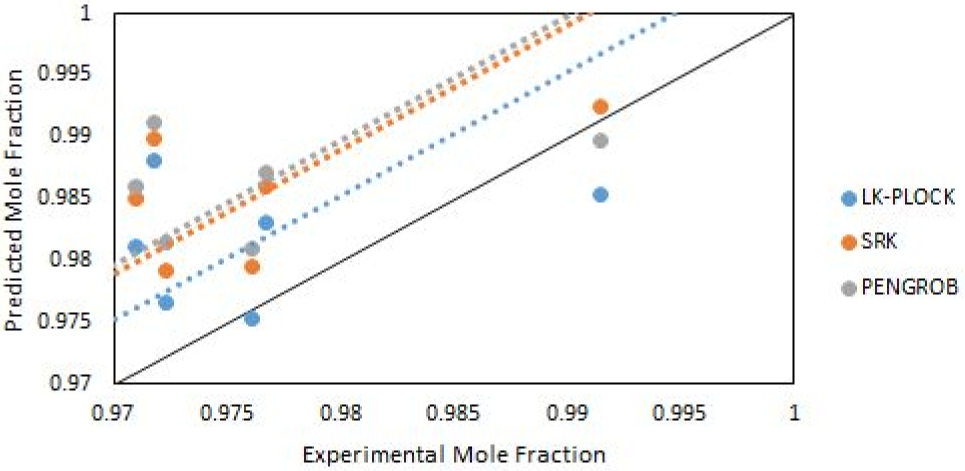
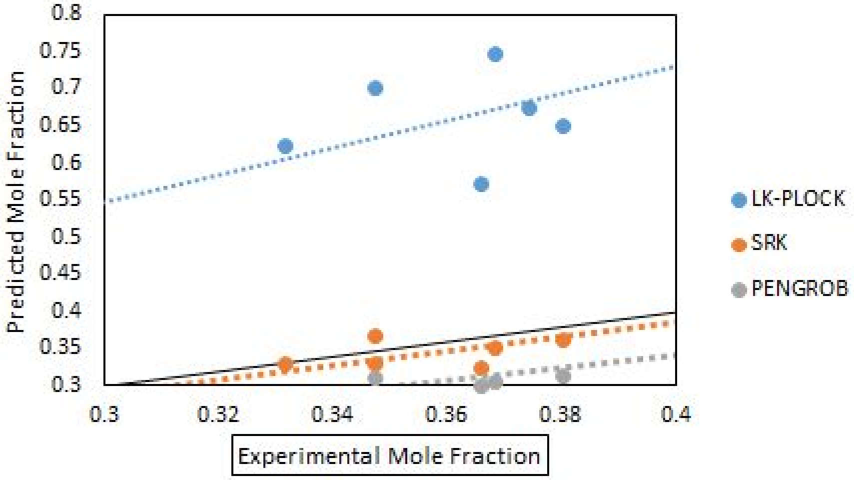
Appendix A: Equation of State Graphs



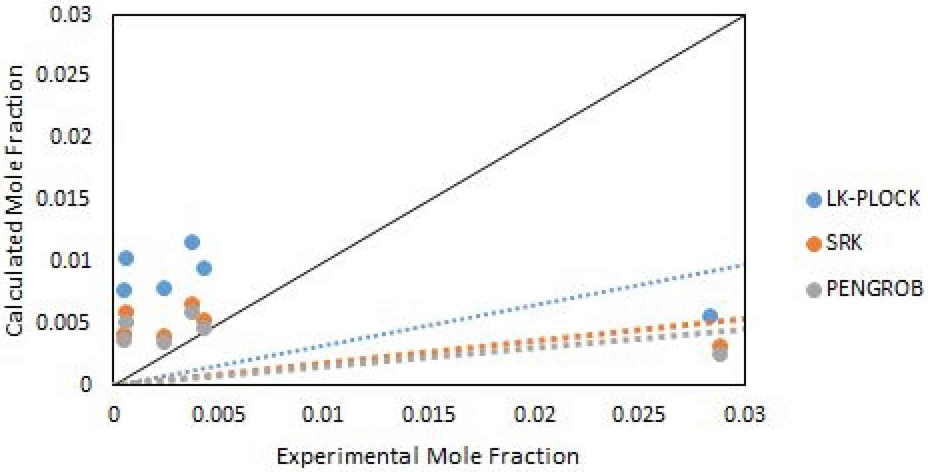
Graph 1: Comparison of experimentally found compositions versus calculated compositions for the Liquid 1 phase of CO_2 with a unity line



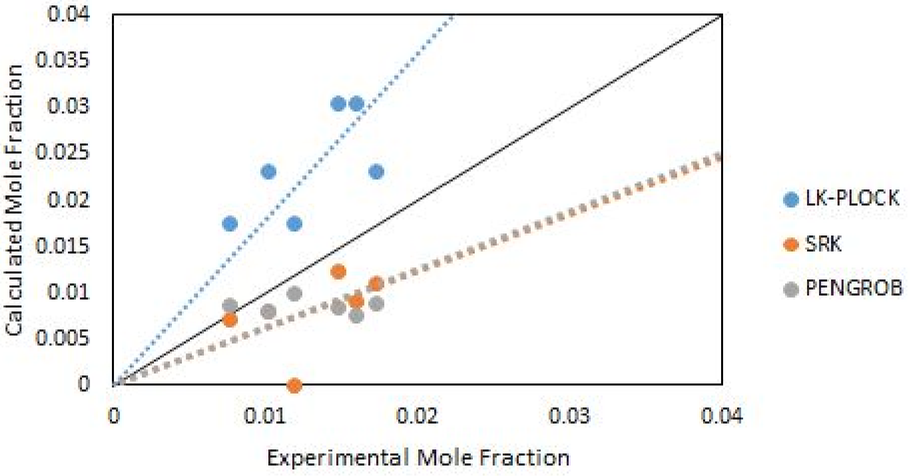
Graph 2: Comparison of experimentally found compositions versus calculated compositions for the Gas phase of CO_2 with a unity line



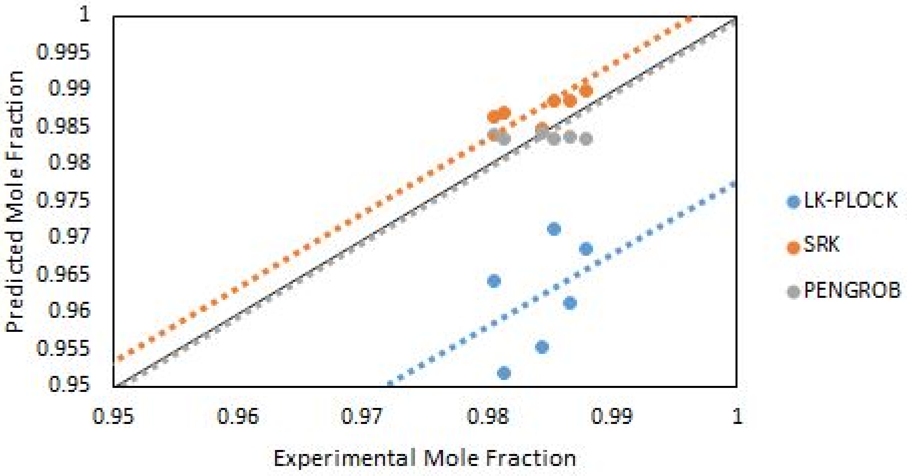
Graph 3: Comparison of experimentally found compositions versus calculated compositions for the Liquid 1 phase of Butanol with a unity line



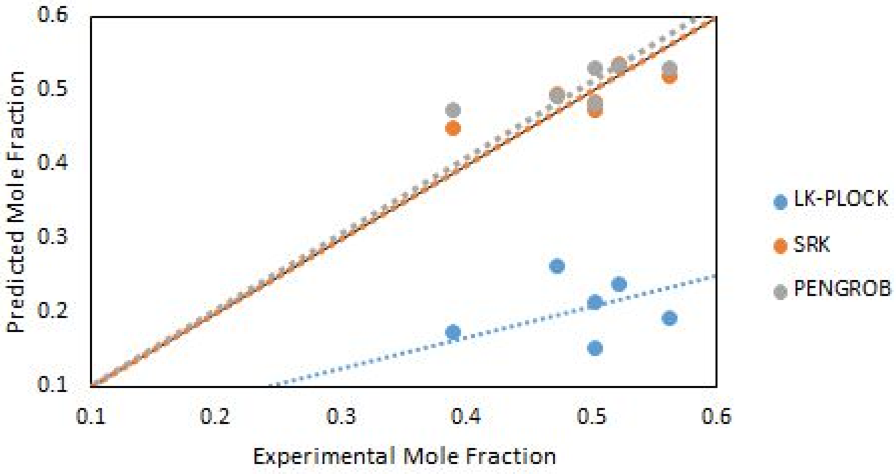
Graph 4: Comparison of experimentally found compositions versus calculated compositions for the gas phase of Butanol with a unity line



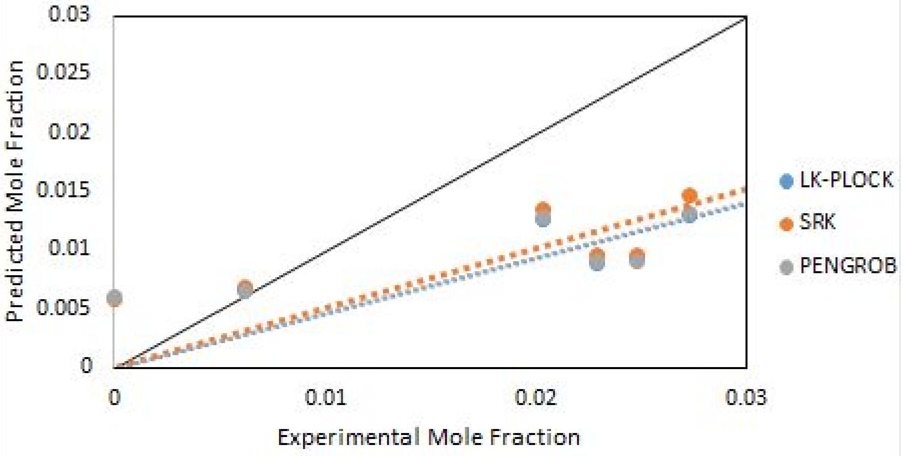
Graph 5: Comparison of experimentally found compositions versus calculated compositions for the Liquid 2 phase of Butanol with a unity line



Graph 6: Comparison of experimentally found compositions versus calculated compositions for the Liquid 2 phase of water with a unity line



Graph 7: Comparison of experimentally found compositions versus calculated compositions for the Liquid 1 phase of water with a unity line



Graph 8: Comparison of experimentally found compositions versus calculated compositions for the gas phase of water with a unity line

Appendix B: Aspen Input Files

Regular Model

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MODEL-OPTION
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COMPONENTS
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        WATER H2O /
        BUTANOL C4H10O-1 /
        GLUCOSE C6H12O6
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        BLOCK SEP IN=S2 OUT=LIQ1 LIQ2
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    OUTLETS-HOT TOREACT
    OUTLETS-COLD COLD3OUT
    HOT-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO
    COLD-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO
    TQ-PARAM CURVE=YES
BLOCK B3 RSTOIC
    PARAM TEMP=40. PRES=100.
    STOIC 1 MIXED GLUCOSE -1. / WATER 1. / BUTANOL 1. /  &
    CO2 2.
    CONV 1 MIXED GLUCOSE 1.
BLOCK COMP1 COMPR
    PARAM TYPE=ISENTROPIC PRES=3. SEFF=0.86 MEFF=0.3 NPHASE=2  &
    SB-MAXIT=30 SB-TOL=0.0001
    PROPERTIES LK-PLOCK FREE-WATER=STEAMNBS SOLU-WATER=3  &
    TRUE-COMPS=YES
    BLOCK-OPTION FREE-WATER=NO
BLOCK COMP2 COMPR
    PARAM TYPE=ISENTROPIC PRES=6. SEFF=0.86 MEFF=0.3 NPHASE=2  &
    SB-MAXIT=30 SB-TOL=0.0001
    PROPERTIES LK-PLOCK FREE-WATER=STEAMNBS SOLU-WATER=3  &
    TRUE-COMPS=YES
    BLOCK-OPTION FREE-WATER=NO
BLOCK COMP3 COMPR
    PARAM TYPE=ISENTROPIC PRES=24. SEFF=0.86 MEFF=0.3  &
    SB-MAXIT=30 SB-TOL=0.0001
```

```
    PROPERTIES LK-PLOCK FREE-WATER=STEAMNBS SOLU-WATER=3  &
    TRUE-COMPS=YES
BLOCK COMP4 COMPR
    PARAM TYPE=ISENTROPIC PRES=100. SEFF=0.86 MEFF=0.3  &
    SB-MAXIT=30 SB-TOL=0.0001
    PROPERTIES LK-PLOCK FREE-WATER=STEAMNBS SOLU-WATER=3  &
    TRUE-COMPS=YES
BLOCK TURB1 COMPR
    PARAM TYPE=ISENTROPIC PRES=1. SEFF=0.86 MEFF=0.3 NPHASE=2  &
    SB-MAXIT=30 SB-TOL=0.0001  MODEL-TYPE=TURBINE
    BLOCK-OPTION FREE-WATER=NO
EO-CONV-OPTI
STREAM-REPOR MOLEFLOW MASSFLOW MOLEFRAC MASSFRAC STDVOLFRAC
PROPERTY-REP PCES PROP-DATA DFMS
REACTIONS R-1 GENERAL
    REAC-DATA 1 NAME=FERMENT
    RATE-CON 1 PRE-EXP=1E-006 ACT-ENERGY=5. T-REF=40.
    STOIC 1 MIXED GLUCOSE -1. / BUTANOL 1. / CO2 2. /  &
    WATER 1.
```

Total Depressurization

```
;Input Summary created by Aspen Plus Rel. 34.0 at 21:49:41 Tue Apr 25, 2017
;Directory   Filename R:\total depressurization model.inp
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 OLD-DATABANK=YES
MODEL-OPTION
DATABANKS PURE32  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
    NOASPENPCD
PROP-SOURCES PURE32  / AQUEOUS  / SOLIDS  / INORGANIC
COMPONENTS
    CO2 CO2 /
    WATER H2O /
    BUTANOL C4H10O-1 /
    GLUCOSE C6H12O6
SOLVE
    RUN-MODE MODE=SIM
```

```
FLOWSHEET
        BLOCK COMP1 IN=CO2IN OUT=TOCOMP2
        BLOCK COMP2 IN=TOCOMP2 OUT=TOHEATX1
        BLOCK HEATEX1 IN=TOHEATX1 OULET OUT=TOCOMP3 COLD1OUT
        BLOCK COMP3 IN=TOCOMP3 OUT=TOHEATX2
        BLOCK HEATEX2 IN=TOHEATX2 COLD2IN OUT=TOCOMP4 COLD2OUT
        BLOCK COMP4 IN=TOCOMP4 OUT=TOHEATX3
        BLOCK HEATEX3 IN=TOHEATX3 COLD3IN OUT=TOREACT COLD3OUT
        BLOCK TURB1 IN=LIQ2 OUT=OULET
        BLOCK SEP2 IN=LIQ1 OUT=S1 S3
        BLOCK SEP IN=S2 OUT=LIQ1 LIQ2
        BLOCK B3 IN=TOREACT FEEDSTOC OUT=S2
PROPERTIES SRK FREE-WATER=STEAMNBS
        PROPERTIES LK-PLOCK
PROP-DATA LKPKIJ-1
        IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
        INVERSE-PRES='1/bar'
        PROP-LIST LKPKIJ
        BPVAL CO2 WATER -.0633000000
        BPVAL WATER CO2 -.0633000000
PROP-DATA ANDKIJ-1
        IN-UNITS ENG
        PROP-LIST ANDKIJ
        BPVAL CO2 WATER 0.0 0.0
        BPVAL WATER CO2 0.0 0.0
        BPVAL CO2 BUTANOL -5.2663133E-5 0.0
        BPVAL BUTANOL CO2 -5.2663133E-5 0.0
        BPVAL WATER BUTANOL -5.2663133E-5 0.0
        BPVAL BUTANOL WATER -5.2663133E-5 0.0
PROP-DATA SRKKIJ-1
        IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
        INVERSE-PRES='1/bar'
        PROP-LIST SRKKIJ
        BPVAL CO2 WATER -.0426522877 0.0 0.0 -273.1500000  &
        726.8500000
        BPVAL WATER CO2 -.0426522877 0.0 0.0 -273.1500000  &
        726.8500000
        BPVAL CO2 BUTANOL 0.0 2.45904104E-4 0.0 -273.1500000  &
        726.8500000
        BPVAL BUTANOL CO2 0.0 2.45904104E-4 0.0 -273.1500000  &
        726.8500000
        BPVAL WATER BUTANOL 0.0 0.0 -55.73644780 -273.1500000  &
        726.8500000
```

```
    BPVAL BUTANOL WATER 0.0 0.0 -55.73644780 -273.1500000  &
    726.8500000
PROP-DATA SRKLIJ-1
    IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
    INVERSE-PRES='1/bar'
    PROP-LIST SRKLIJ
    BPVAL CO2 WATER -.2016570920 0.0 0.0 -273.1500000  &
    726.8500000
    BPVAL WATER CO2 0.0 0.0 0.0 -273.1500000 726.8500000
    BPVAL WATER BUTANOL 0.0 6.18944746E-4 0.0 -273.1500000  &
    726.8500000
    BPVAL BUTANOL WATER 0.0 0.0 0.0 -273.1500000 726.8500000
    BPVAL CO2 BUTANOL 0.0 0.0 30.88241930 -273.1500000  &
    726.8500000
    BPVAL BUTANOL CO2 0.0 0.0 0.0 -273.1500000 726.8500000
STREAM CO2IN
    SUBSTREAM MIXED TEMP=25. PRES=1. MASS-FLOW=0.185
    MASS-FRAC CO2 1.
STREAM COLD2IN
    SUBSTREAM MIXED TEMP=0. PRES=10. MOLE-FLOW=100.
    MASS-FRAC WATER 1.
STREAM COLD3IN
    SUBSTREAM MIXED TEMP=0. PRES=10. MOLE-FLOW=100.
    MOLE-FLOW WATER 1.
STREAM FEEDSTOC
    SUBSTREAM MIXED TEMP=40. PRES=100. MASS-FLOW=2.21
    MASS-FRAC WATER 0.885 / GLUCOSE 0.115
BLOCK SEP SEP
    PARAM
    FRAC STREAM=LIQ1 SUBSTREAM=MIXED COMPS=CO2 WATER BUTANOL  &
    FRACS=0.995183 0.001658 0.99
BLOCK SEP2 FLASH2
    PARAM TEMP=0. PRES=1.
BLOCK HEATEX1 HEATX
    PARAM T-HOT=70. CALC-TYPE=DESIGN TYPE=COUNTERCURRE  &
    U-OPTION=PHASE F-OPTION=CONSTANT CALC-METHOD=SHORTCUT
    FEEDS HOT=TOHEATX1 COLD=OULET
    OUTLETS-HOT TOCOMP3
    OUTLETS-COLD COLD1OUT
    HOT-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO
    COLD-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO
    TQ-PARAM CURVE=YES
BLOCK HEATEX2 HEATX
```

```
        PARAM T-HOT=40. CALC-TYPE=DESIGN TYPE=COUNTERCURRE  &
        U-OPTION=PHASE F-OPTION=CONSTANT CALC-METHOD=SHORTCUT
        FEEDS HOT=TOHEATX2 COLD=COLD2IN
        OUTLETS-HOT TOCOMP4
        OUTLETS-COLD COLD2OUT
        HOT-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO
        COLD-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO
        TQ-PARAM CURVE=YES
BLOCK HEATEX3 HEATX
        PARAM T-HOT=40. CALC-TYPE=DESIGN U-OPTION=PHASE  &
        F-OPTION=CONSTANT CALC-METHOD=SHORTCUT
        FEEDS HOT=TOHEATX3 COLD=COLD3IN
        OUTLETS-HOT TOREACT
        OUTLETS-COLD COLD3OUT
        HOT-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO
        COLD-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO
        TQ-PARAM CURVE=YES
BLOCK B3 RSTOIC
        PARAM TEMP=40. PRES=100.
        STOIC 1 MIXED GLUCOSE -1. / WATER 1. / BUTANOL 1. /  &
        CO2 2.
        CONV 1 MIXED GLUCOSE 1.
BLOCK COMP1 COMPR
        PARAM TYPE=ISENTROPIC PRES=3. SEFF=0.86 MEFF=0.3 NPHASE=2  &
        SB-MAXIT=30 SB-TOL=0.0001
        PROPERTIES LK-PLOCK FREE-WATER=STEAMNBS SOLU-WATER=3  &
        TRUE-COMPS=YES
        BLOCK-OPTION FREE-WATER=NO
BLOCK COMP2 COMPR
        PARAM TYPE=ISENTROPIC PRES=6. SEFF=0.86 MEFF=0.3 NPHASE=2  &
        SB-MAXIT=30 SB-TOL=0.0001
        PROPERTIES LK-PLOCK FREE-WATER=STEAMNBS SOLU-WATER=3  &
        TRUE-COMPS=YES
        BLOCK-OPTION FREE-WATER=NO
BLOCK COMP3 COMPR
        PARAM TYPE=ISENTROPIC PRES=24. SEFF=0.86 MEFF=0.3  &
        SB-MAXIT=30 SB-TOL=0.0001
        PROPERTIES LK-PLOCK FREE-WATER=STEAMNBS SOLU-WATER=3  &
        TRUE-COMPS=YES
BLOCK COMP4 COMPR
        PARAM TYPE=ISENTROPIC PRES=100. SEFF=0.86 MEFF=0.3  &
        SB-MAXIT=30 SB-TOL=0.0001
        PROPERTIES LK-PLOCK FREE-WATER=STEAMNBS SOLU-WATER=3  &
```

```
        TRUE-COMPS=YES
BLOCK TURB1 COMPR
        PARAM TYPE=ISENTROPIC PRES=1. SEFF=0.86 MEFF=0.3 NPHASE=2  &
        SB-MAXIT=30 SB-TOL=0.0001  MODEL-TYPE=TURBINE
        BLOCK-OPTION FREE-WATER=NO
EO-CONV-OPTI
STREAM-REPOR MOLEFLOW MASSFLOW MOLEFRAC MASSFRAC STDVOLFRAC
PROPERTY-REP PCES PROP-DATA DFMS
REACTIONS R-1 GENERAL
        REAC-DATA 1 NAME=FERMENT
        RATE-CON 1 PRE-EXP=1E-006 ACT-ENERGY=5. T-REF=40.
        STOIC 1 MIXED GLUCOSE -1. / BUTANOL 1. / CO2 2. /  &
        WATER 1.
```

Total Recycle

```
;Input Summary created by Aspen Plus Rel. 34.0 at 21:52:06 Tue Apr 25, 2017
;Directory   Filename R:\total recycle model.inp
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 OLD-DATABANK=YES
MODEL-OPTION
DATABANKS PURE32  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
        NOASPENPCD
PROP-SOURCES PURE32  / AQUEOUS  / SOLIDS  / INORGANIC
COMPONENTS
        CO2 CO2 /
        WATER H2O /
        BUTANOL C4H10O-1 /
        GLUCOSE C6H12O6
SOLVE
        RUN-MODE MODE=SIM
FLOWSHEET
        BLOCK SEP1 IN=LIQ1 OUT=GAS LIQUID1 LIQUID2
        BLOCK HEATEX2 IN=4 OULET OUT=TOCOMP4 COLD2OUT
        BLOCK COMP4 IN=TOCOMP4 OUT=TOHEATX3
        BLOCK HEATEX3 IN=TOHEATX3 COLD3IN OUT=TOREACT COLD3OUT
        BLOCK TURB1 IN=LIQ2 OUT=OULET
        BLOCK SEP2 IN=LIQUID1 OUT=S1 S3
        BLOCK SEP IN=S2 OUT=LIQ1 LIQ2
```

```
    BLOCK B2 IN=GAS OUT=3 4
    BLOCK B3 IN=TOREACT 1 OUT=S2
    BLOCK B1 IN=FEEDSTOC OUT=1
PROPERTIES SRK FREE-WATER=STEAMNBS
    PROPERTIES LK-PLOCK
PROP-DATA LKPKIJ-1
    IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
    INVERSE-PRES='1/bar'
    PROP-LIST LKPKIJ
    BPVAL CO2 WATER -.0633000000
    BPVAL WATER CO2 -.0633000000
PROP-DATA ANDKIJ-1
    IN-UNITS ENG
    PROP-LIST ANDKIJ
    BPVAL CO2 WATER 0.0 0.0
    BPVAL WATER CO2 0.0 0.0
    BPVAL CO2 BUTANOL -5.2663133E-5 0.0
    BPVAL BUTANOL CO2 -5.2663133E-5 0.0
    BPVAL WATER BUTANOL -5.2663133E-5 0.0
    BPVAL BUTANOL WATER -5.2663133E-5 0.0
PROP-DATA SRKKIJ-1
    IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
    INVERSE-PRES='1/bar'
    PROP-LIST SRKKIJ
    BPVAL CO2 WATER -.0426522877 0.0 0.0 -273.1500000  &
    726.8500000
    BPVAL WATER CO2 -.0426522877 0.0 0.0 -273.1500000  &
    726.8500000
    BPVAL CO2 BUTANOL 0.0 2.45904104E-4 0.0 -273.1500000  &
    726.8500000
    BPVAL BUTANOL CO2 0.0 2.45904104E-4 0.0 -273.1500000  &
    726.8500000
    BPVAL WATER BUTANOL 0.0 0.0 -55.73644780 -273.1500000  &
    726.8500000
    BPVAL BUTANOL WATER 0.0 0.0 -55.73644780 -273.1500000  &
    726.8500000
PROP-DATA SRKLIJ-1
    IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
    INVERSE-PRES='1/bar'
    PROP-LIST SRKLIJ
    BPVAL CO2 WATER -.2016570920 0.0 0.0 -273.1500000  &
    726.8500000
    BPVAL WATER CO2 0.0 0.0 0.0 -273.1500000 726.8500000
```

```
          BPVAL WATER BUTANOL 0.0 6.18944746E-4 0.0 -273.1500000  &
          726.8500000
          BPVAL BUTANOL WATER 0.0 0.0 0.0 -273.1500000 726.8500000
          BPVAL CO2 BUTANOL 0.0 0.0 30.88241930 -273.1500000  &
          726.8500000
          BPVAL BUTANOL CO2 0.0 0.0 0.0 -273.1500000 726.8500000
STREAM COLD3IN
          SUBSTREAM MIXED TEMP=0. PRES=10. MOLE-FLOW=100.
          MOLE-FLOW WATER 1.
STREAM FEEDSTOC
          SUBSTREAM MIXED TEMP=40. PRES=1. MASS-FLOW=2.21
          MASS-FRAC WATER 0.885 / GLUCOSE 0.115
BLOCK B2 FSPLIT
          FRAC 3 0.71
BLOCK SEP SEP
          PARAM
          FRAC STREAM=LIQ1 SUBSTREAM=MIXED COMPS=CO2 WATER BUTANOL  &
          FRACS=0.995183 0.001658 0.99
BLOCK SEP2 FLASH2
          PARAM TEMP=30. PRES=1.
BLOCK SEP1 FLASH3
          PARAM TEMP=60. PRES=65. L2-COMP=WATER
BLOCK HEATEX2 HEATX
          PARAM T-HOT=42. CALC-TYPE=DESIGN TYPE=COUNTERCURRE  &
          U-OPTION=PHASE F-OPTION=CONSTANT CALC-METHOD=SHORTCUT
          FEEDS HOT=4 COLD=OULET
          OUTLETS-HOT TOCOMP4
          OUTLETS-COLD COLD2OUT
          HOT-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO
          COLD-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO
          TQ-PARAM CURVE=YES
BLOCK HEATEX3 HEATX
          PARAM T-HOT=40. CALC-TYPE=DESIGN U-OPTION=PHASE  &
          F-OPTION=CONSTANT CALC-METHOD=SHORTCUT
          FEEDS HOT=TOHEATX3 COLD=COLD3IN
          OUTLETS-HOT TOREACT
          OUTLETS-COLD COLD3OUT
          HOT-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO
          COLD-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO
          TQ-PARAM CURVE=YES
BLOCK B3 RSTOIC
          PARAM TEMP=40. PRES=100.
          STOIC 1 MIXED GLUCOSE -1. / WATER 1. / BUTANOL 1. /  &
```

```
        CO2 2.
        CONV 1 MIXED GLUCOSE 1.
BLOCK B1 PUMP
        PARAM PRES=100.
BLOCK COMP4 COMPR
        PARAM TYPE=ISENTROPIC PRES=100. SEFF=0.86 MEFF=0.3  &
        SB-MAXIT=30 SB-TOL=0.0001
        PROPERTIES LK-PLOCK FREE-WATER=STEAMNBS SOLU-WATER=3  &
        TRUE-COMPS=YES
BLOCK TURB1 COMPR
        PARAM TYPE=ISENTROPIC PRES=1. SEFF=0.86 MEFF=0.3 NPHASE=2  &
        SB-MAXIT=30 SB-TOL=0.0001  MODEL-TYPE=TURBINE
        BLOCK-OPTION FREE-WATER=NO
EO-CONV-OPTI
STREAM-REPOR MOLEFLOW MASSFLOW MOLEFRAC MASSFRAC STDVOLFRAC
PROPERTY-REP PCES PROP-DATA DFMS
REACTIONS R-1 GENERAL
        REAC-DATA 1 NAME=FERMENT
        RATE-CON 1 PRE-EXP=1E-006 ACT-ENERGY=5. T-REF=40.
        STOIC 1 MIXED GLUCOSE -1. / BUTANOL 1. / CO2 2. /  &
        WATER 1.
```

Post Pressurization

```
;
;Input Summary created by Aspen Plus Rel. 34.0 at 21:45:35 Tue Apr 25, 2017
;Directory   Filename R:\post pressurization model.inp
;

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 OLD-DATABANK=YES
MODEL-OPTION
DATABANKS PURE32  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
        NOASPENPCD
PROP-SOURCES PURE32  / AQUEOUS  / SOLIDS  / INORGANIC
COMPONENTS
        CO2 CO2 /
        WATER H2O /
        BUTANOL C4H10O-1 /
```

```
        GLUCOSE C6H12O6
SOLVE
        RUN-MODE MODE=SIM
FLOWSHEET
        BLOCK V-404 IN=1 OUT=GAS LIQUID1 LIQUID2
        BLOCK COMP1 IN=CO2IN OUT=TOCOMP2
        BLOCK COMP2 IN=TOCOMP2 OUT=TOHEATX1
        BLOCK HEATEX1 IN=TOHEATX1 COLDIN OUT=TOCOMP3 COLD1OUT
        BLOCK COMP3 IN=TOCOMP3 OUT=TOHEATX2
        BLOCK HEATEX2 IN=TOHEATX2 COLD2IN OUT=TOCOMP4 COLD2OUT
        BLOCK COMP4 IN=TOCOMP4 OUT=TOHEATX3
        BLOCK HEATEX3 IN=TOHEATX3 COLD3IN OUT=S9 COLD3OUT
        BLOCK V-405 IN=LIQUID1 OUT=S1 S3
        BLOCK B3 IN=FEEDSTOC OUT=S2
        BLOCK V-401 IN=S2 OUT=CO2OUT S8
        BLOCK B2 IN=S8 OUT=S6
        BLOCK V-402 IN=S9 S6 OUT=S10
        BLOCK V-403 IN=S10 OUT=1 2
PROPERTIES SRK FREE-WATER=STEAMNBS
        PROPERTIES LK-PLOCK
PROP-DATA LKPKIJ-1
        IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
        INVERSE-PRES='1/bar'
        PROP-LIST LKPKIJ
        BPVAL CO2 WATER -.0633000000
        BPVAL WATER CO2 -.0633000000
PROP-DATA ANDKIJ-1
        IN-UNITS ENG
        PROP-LIST ANDKIJ
        BPVAL CO2 WATER 0.0 0.0
        BPVAL WATER CO2 0.0 0.0
        BPVAL CO2 BUTANOL -5.2663133E-5 0.0
        BPVAL BUTANOL CO2 -5.2663133E-5 0.0
        BPVAL WATER BUTANOL -5.2663133E-5 0.0
        BPVAL BUTANOL WATER -5.2663133E-5 0.0
PROP-DATA SRKKIJ-1
        IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
        INVERSE-PRES='1/bar'
        PROP-LIST SRKKIJ
        BPVAL CO2 WATER -.0426522877 0.0 0.0 -273.1500000  &
        726.8500000
        BPVAL WATER CO2 -.0426522877 0.0 0.0 -273.1500000  &
        726.8500000
```

```
    BPVAL CO2 BUTANOL 0.0 2.45904104E-4 0.0 -273.1500000  &
    726.8500000
    BPVAL BUTANOL CO2 0.0 2.45904104E-4 0.0 -273.1500000  &
    726.8500000
    BPVAL WATER BUTANOL 0.0 0.0 -55.73644780 -273.1500000  &
    726.8500000
    BPVAL BUTANOL WATER 0.0 0.0 -55.73644780 -273.1500000  &
    726.8500000
PROP-DATA SRKLIJ-1
    IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
    INVERSE-PRES='1/bar'
    PROP-LIST SRKLIJ
    BPVAL CO2 WATER -.2016570920 0.0 0.0 -273.1500000  &
    726.8500000
    BPVAL WATER CO2 0.0 0.0 0.0 -273.1500000 726.8500000
    BPVAL WATER BUTANOL 0.0 6.18944746E-4 0.0 -273.1500000  &
    726.8500000
    BPVAL BUTANOL WATER 0.0 0.0 0.0 -273.1500000 726.8500000
    BPVAL CO2 BUTANOL 0.0 0.0 30.88241930 -273.1500000  &
    726.8500000
    BPVAL BUTANOL CO2 0.0 0.0 0.0 -273.1500000 726.8500000
STREAM CO2IN
    SUBSTREAM MIXED TEMP=25. PRES=1. MASS-FLOW=0.3
    MOLE-FLOW CO2 1. / WATER 0. / BUTANOL 0. / GLUCOSE 0.
STREAM CO2OUT
    SUBSTREAM MIXED TEMP=40. PRES=1.
STREAM COLD2IN
    SUBSTREAM MIXED TEMP=0. PRES=10. MOLE-FLOW=100.
    MASS-FRAC WATER 1.
STREAM COLD3IN
    SUBSTREAM MIXED TEMP=0. PRES=10. MOLE-FLOW=100.
    MOLE-FLOW WATER 1.
STREAM COLDIN
    SUBSTREAM MIXED TEMP=10. PRES=10. MOLE-FLOW=100.
    MOLE-FLOW WATER 1.
STREAM FEEDSTOC
    SUBSTREAM MIXED TEMP=40. PRES=1. MASS-FLOW=2.21
    MASS-FRAC WATER 0.885 / GLUCOSE 0.115
BLOCK V-402 MIXER
    PARAM
BLOCK V-403 SEP
    PARAM
    FRAC STREAM=1 SUBSTREAM=MIXED COMPS=CO2 WATER BUTANOL  &
```

```
        FRACS=0.995183 0.001658 0.99
BLOCK V-401 FLASH2
        PARAM TEMP=40. PRES=1.
BLOCK V-405 FLASH2
        PARAM TEMP=30. PRES=1.
BLOCK V-404 FLASH3
        PARAM TEMP=60. PRES=65. L2-COMP=WATER
BLOCK HEATEX1 HEATX
        PARAM T-HOT=70. CALC-TYPE=DESIGN TYPE=COUNTERCURRE  &
        U-OPTION=PHASE F-OPTION=CONSTANT CALC-METHOD=SHORTCUT
        FEEDS HOT=TOHEATX1 COLD=COLDIN
        OUTLETS-HOT TOCOMP3
        OUTLETS-COLD COLD1OUT
        HOT-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO
        COLD-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO
        TQ-PARAM CURVE=YES
BLOCK HEATEX2 HEATX
        PARAM T-HOT=40. CALC-TYPE=DESIGN TYPE=COUNTERCURRE  &
        U-OPTION=PHASE F-OPTION=CONSTANT CALC-METHOD=SHORTCUT
        FEEDS HOT=TOHEATX2 COLD=COLD2IN
        OUTLETS-HOT TOCOMP4
        OUTLETS-COLD COLD2OUT
        HOT-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO
        COLD-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO
        TQ-PARAM CURVE=YES
BLOCK HEATEX3 HEATX
        PARAM T-HOT=40. CALC-TYPE=DESIGN U-OPTION=PHASE  &
        F-OPTION=CONSTANT CALC-METHOD=SHORTCUT
        FEEDS HOT=TOHEATX3 COLD=COLD3IN
        OUTLETS-HOT S9
        OUTLETS-COLD COLD3OUT
        HOT-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO
        COLD-SIDE DP-OPTION=CONSTANT DPPARMOPT=NO
        TQ-PARAM CURVE=YES
BLOCK B3 RSTOIC
        PARAM TEMP=40. PRES=1.
        STOIC 1 MIXED GLUCOSE -1. / WATER 1. / BUTANOL 1. /  &
        CO2 2.
        CONV 1 MIXED GLUCOSE 1.
BLOCK B2 PUMP
        PARAM PRES=100.
BLOCK COMP1 COMPR
        PARAM TYPE=ISENTROPIC PRES=3. SEFF=0.86 MEFF=0.3 NPHASE=2  &
```

```
    SB-MAXIT=30 SB-TOL=0.0001
    PROPERTIES LK-PLOCK FREE-WATER=STEAMNBS SOLU-WATER=3  &
    TRUE-COMPS=YES
    BLOCK-OPTION FREE-WATER=NO
BLOCK COMP2 COMPR
    PARAM TYPE=ISENTROPIC PRES=6. SEFF=0.86 MEFF=0.3 NPHASE=2  &
    SB-MAXIT=30 SB-TOL=0.0001
    PROPERTIES LK-PLOCK FREE-WATER=STEAMNBS SOLU-WATER=3  &
    TRUE-COMPS=YES
    BLOCK-OPTION FREE-WATER=NO
BLOCK COMP3 COMPR
    PARAM TYPE=ISENTROPIC PRES=24. SEFF=0.86 MEFF=0.3  &
    SB-MAXIT=30 SB-TOL=0.0001
    PROPERTIES LK-PLOCK FREE-WATER=STEAMNBS SOLU-WATER=3  &
    TRUE-COMPS=YES
BLOCK COMP4 COMPR
    PARAM TYPE=ISENTROPIC PRES=100. SEFF=0.86 MEFF=0.3  &
    SB-MAXIT=30 SB-TOL=0.0001
    PROPERTIES LK-PLOCK FREE-WATER=STEAMNBS SOLU-WATER=3  &
    TRUE-COMPS=YES
EO-CONV-OPTI
STREAM-REPOR MOLEFLOW MASSFLOW MOLEFRAC MASSFRAC STDVOLFRAC
PROPERTY-REP PCES PROP-DATA DFMS
REACTIONS R-1 GENERAL
    REAC-DATA 1 NAME=FERMENT
    RATE-CON 1 PRE-EXP=1E-006 ACT-ENERGY=5. T-REF=40.
    STOIC 1 MIXED GLUCOSE -1. / BUTANOL 1. / CO2 2. /  &
    WATER 1.
```