# Energy Analysis of Butanol Extraction Using Supercritical Carbon Dioxide


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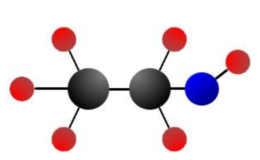
## Abstract


The goal of this project was to model a butanol extraction process using supercritical carbon dioxide ($CO_2$) in Aspen Plus and then complete an energy analysis for various probable process models. A large part of modeling the process was determining an Equation of State (EOS) that accurately modeled the $CO_2$/Water/Butanol ternary system at critical conditions. Following the design of a process model and the completion of the energy analysis, recommendations were proposed on the best method of butanol production from an energy standpoint.

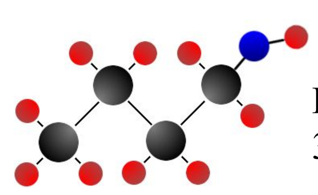

## Background

Butanol has the potential to be a better renewable liquid fuel option than ethanol because of its superior energy density.



**Ethanol** 20 MJ/L


**Gasoline** 33 MJ/L



**Butanol** 30 MJ/L

Supercritical extraction of higher alcohols implements supercritical fluids as solvents, most commonly $CO_2$, to extract an alcohol product. This method of extraction has been found to be a simpler and a more economic process than other extraction methods, and is recently receiving more attention because of this potential.

The Massachusetts Institute of Technology (MIT) recently discovered that a butanol producing bacteria (*B. megaterium*) can survive at $CO_2$ supercritical conditions. With butanol extraction using supercritical $CO_2$ now a possibility, butanol production has the potential to be energy efficient.

## Objectives

1. Determine an EOS that accurately models the ternary system $CO_2$/Water/Butanol at supercritical conditions
2. Perform a sensitivity analysis on the basic process model to determine optimal parameters
3. Design different models for the butanol extraction process in Aspen Plus
4. Determine the most energy efficient and viable process design with heat integration and energy analysis
5. Provide recommendations for further research and development

## References


Bioalcohols. (2010). Retrieved April 19, 2017, from http://biofuel.org.uk/bioalcohols.html

Cody, R., Sabo, V., & Vandenberg, H. (2016, April 28). *Energy Analysis of Butanol Extraction* [Scholarly project]. In *WPI MQP report*. Retrieved March 2, 2017.

Gasoline. (2017, April 18). Retrieved April 19, 2017, from https://en.wikipedia.org/wiki/Gasoline#/media/File:HAZMAT_Class_3_Gasoline.png Picture

Laitinen, A., & Kaunisto, J. (1999). Supercritical fluid extraction of 1-butanol from aqueous solutions. *The Journal of supercritical fluids*, *15*(3), 245-252.

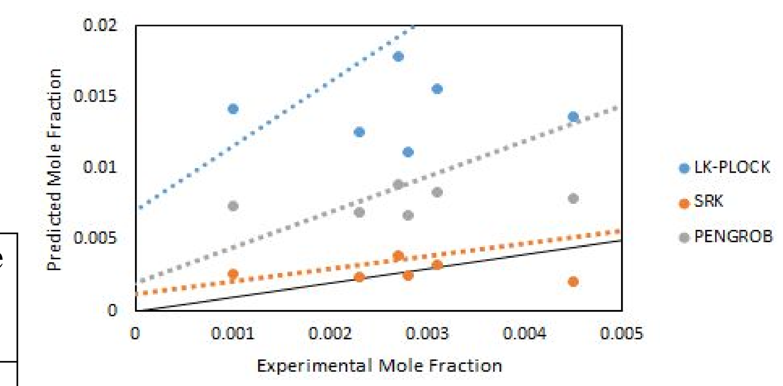

## Equation of State Results

We explored three equations of state (EOS) that we predicted would best model the ternary system $CO_2$/water/butanol at our desired temperature and pressure: SRK, LK-PLOCK, and PENGROB.

| 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 1:** Altered EOS analyzed for accuracy of representing $CO_2$/water/butanol system at critical conditions

**Graph 1**: Comparison of experimentally found compositions versus calculated compositions for the Liquid 2 phase of $CO_2$ with a unity line (example graph)




SRK equation of state accurately predicts the phase composition of the $CO_2$/water/butanol at our desired temperature and pressure

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

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

## Sensitivity Analysis Results

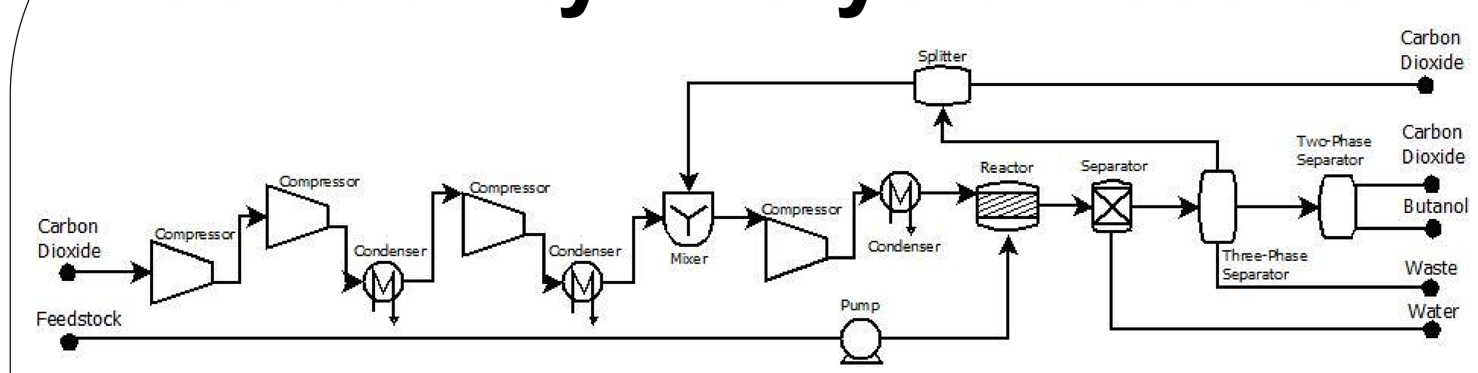
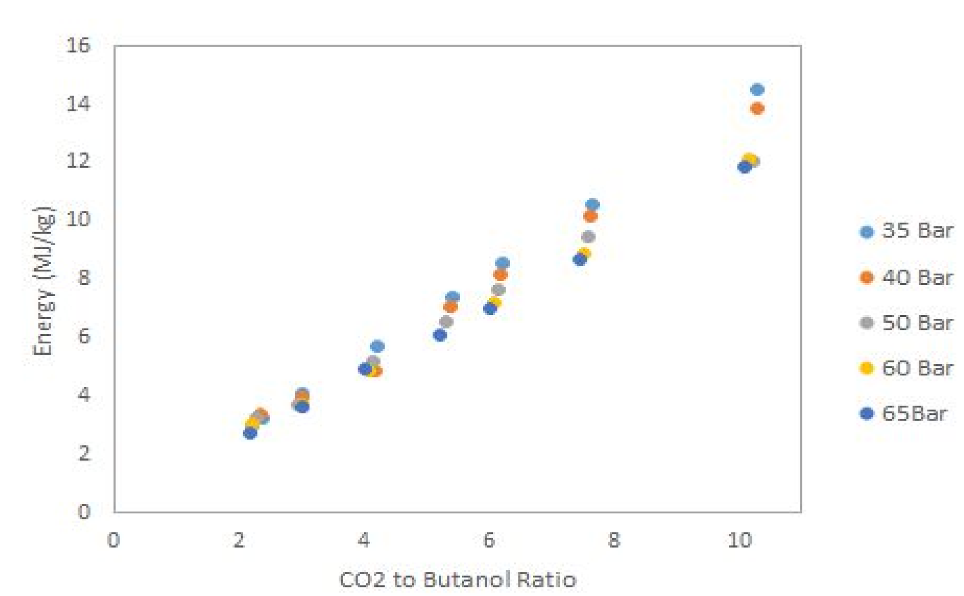


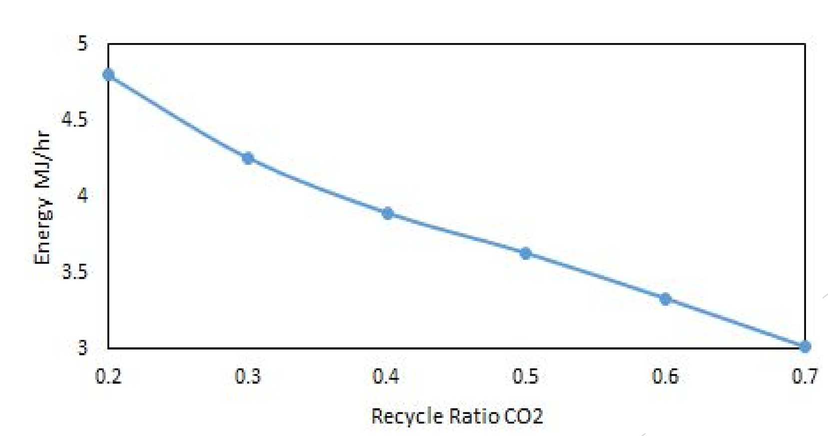

**Figure 1**: Basic Process Model Design

**Graph 2**: Energy requirement per kilogram product for varying: pressure of the first flash, and $CO_2$ to butanol mass ratio in the reactor




The optimal pressure of the first separator is 65 bar and the lower the ratio of $CO_2$ to butanol in the reactor, the better the energy requirement. We chose an optimal ratio to be 3:1 based on butanol purity results in the product stream and the energy requirement.

The higher the recycle ratio, the lower the energy requirement per kilogram product. At a rate around 0.71 the system is at total recycle.




**Graph 3**:Impact of $CO_2$ recycle ratio on energy requirement

## Final Models and Results

Unless specified: 3:1 $CO_2$ to butanol mass ratio and 100 bar pressure was used in the reactor. Pressure of the first separator set to 65 bar.

- **Regular model**: $CO_2$ recycle ratio of 0.6
- **Total depressurization**: pressure of the first separator is 1 bar. Therefore no $CO_2$ recycle stream or third separator.
- **Total recycle**: no inlet $CO_2$ and a $CO_2$ recycle ratio of 0.71.
- **Post pressurization**: the reactor is at atmospheric conditions and pressurization and extraction post reaction.

| | Regular | Total Depressurization | Total Recycle | Post Pressurization |
|---|---|---|---|---|
| **Mass % Butanol in Product** | 96.5% | 96.0% | 96.1% | 96.4% |
| **Product Energy Requirement (MJ/kg)** | 2.0 | 3.1 | 1.2 | 8.0 |
| **Butanol Energy Requirement (MJ/kg)** | 2.0 | 3.2 | 1.3 | 8.3 |

**Table 2:** Results for the four analyzed process models

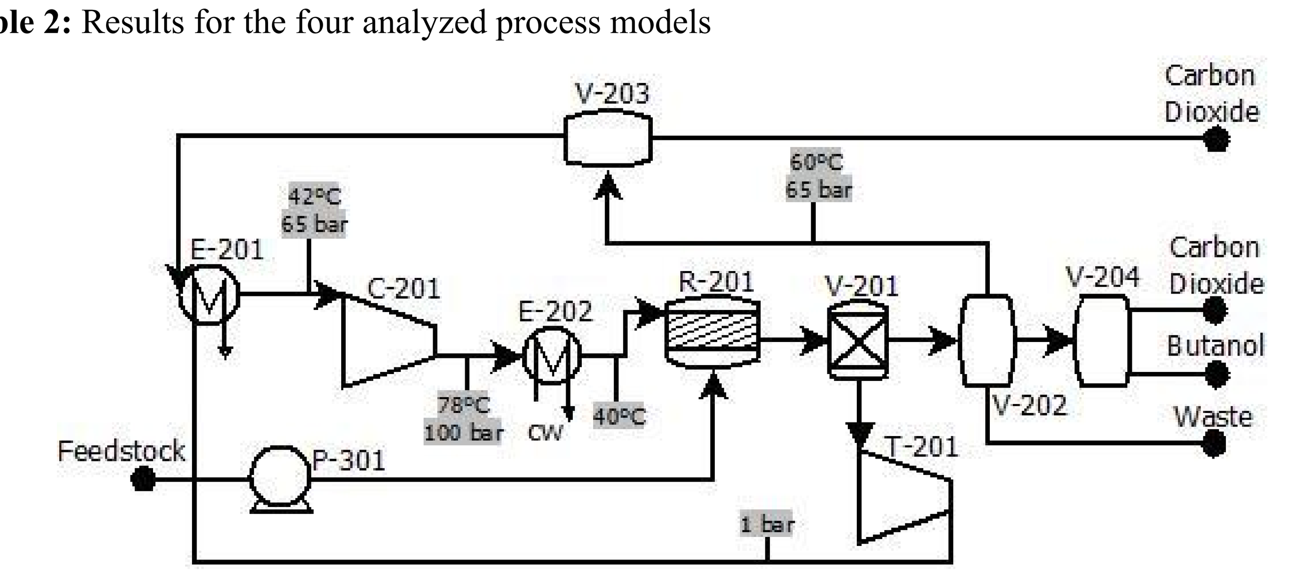
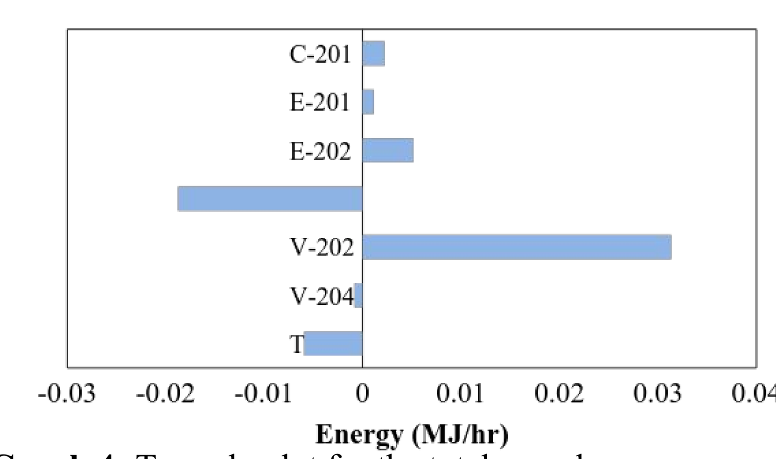



**Figure 2**: Total Recycle Model Design




**Graph 4:** Tornado plot for the total recycle process model that shows energy requirement for each piece of equipment.

Total Recycle has the best calculated energy requirement.

## Recommendations

1. Use SRK as an altered EOS to model the ternary system $CO_2$/Water/Butanol
2. The most energy efficient model variation is Total Recycle, with a $CO_2$ recycle ratio of 7.1, a pressure of 65 bar for the first separation, and a $CO_2$ to butanol mass ratio of 3:1 in the reactor.
3. We recommend further research be done on the following:
   - Start-up procedure and feasibility of the Total Recycle process
   - The necessity of the three phase separator
   - Energy requirement of the reactor
   - Cost analysis of different process models

## Acknowledgments


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 DOE for funding the project and MIT for collaborating with us.