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OPTIMIZATION AND ANALYSIS OF A STYRENE PRODUCTION PROCESS

By

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A thesis submitted to the faculty of The University of Mississippi in partial fulfillment of the requirement of the Sally McDonnell Barksdale Honors College.

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ABSTRACT

ALEXIS KATHLEEN KIMPEL: Optimization and Analysis of a Styrene Production Process
(Under the direction of Dr. Adam Smith)

The production of styrene from ethylbenzene in Unit 500 is designed to start up in 2024 and operate for 12 years after startup. The engineering team was tasked with designing the process, creating an economic model, and optimizing the net present value (NPV). The process was simulated in AVEVA PRO/II Simulation for the design process and to estimate the size of equipment. Parametric and topological optimization was performed subsequently on the unit operations in the process. The NPV was improved by $423M from a base case of -$919M to an optimized case of -$496M. The project is recommended to continue in terms of further optimization to make the project more financially attractive. However, a risk assessment and market analysis on the purchase of styrene is suggested before making a final decision. This optimization is detailed in part 1. A fluidized bed reactor was then simulated in PRO/II and optimized based on selectivity of the desired product, styrene. The fluidized bed optimization is discussed and compared to the adiabatic packed bed reactors that were originally designed to be used in the process. The fluidized bed reactor is detailed in part 2.

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PART 1: Styrene Production Optimization

Project Introduction

The objective of this project was to optimize a styrene production process by maximizing the net present value (NPV). NPV is a discounted cumulative cash flow that is used as the main measure of the economic feasibility of this project. The process was modeled and optimized using AVEVA's PRO/II process simulator. Stepwise optimization was performed to determine both parametric and topological variables that maximize the NPV while meeting all process constraints. Parametric optimization consists of manipulating operating conditions like temperature and pressure, whereas topological optimization deals with the arrangement and construction of equipment. Although both types are important, parametric optimization is more heavily focused on in the scope of this project.

The engineering team was able to improve the NPV of the process by $423 million (M) from a base case of -$919M to an optimized case of -$496M. The breakeven price of styrene improved from $2,650/tonne to $1,976/tonne. Although styrene can be purchased for $1,598/tonne, the minimized risk associated with producing styrene in terms of the accessibility, controllable production, and purity of styrene as well as the potential for profit in the downstream polymerization unit likely outweighs the lesser cost to purchase styrene.

Process Description

The styrene production process, Unit 500, is intended to start production in 2024 for a project life span of 12 years. It is designed to produce 100,000 tonnes per year of 99.8 wt%

styrene, which is then sent to a downstream polymerization unit. A block flow diagram of the major sections in the process is shown in Figure 1 below, and a full process flow diagram can be seen in Appendix A.

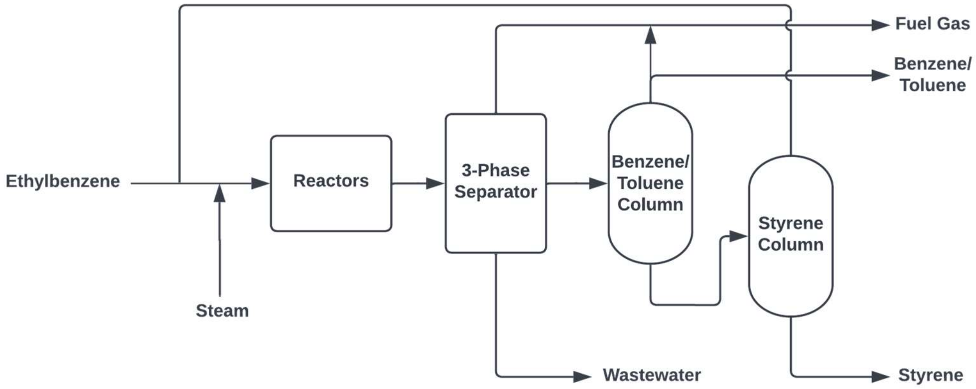


Figure 1: Unit 500 Block Flow Diagram

Styrene is produced from the dehydrogenation of ethylbenzene according to the following reaction.

$$C_6H_5C_2H_5 \leftrightarrow C_6H_5C_2H_3 + H_2$$

ethylbenzene styrene hydrogen

Side reactions producing both benzene and toluene also occur in the process as follows.

$$C_6H_5C_2H_5 \rightarrow C_6H_6 + C_2H_4$$

ethylbenzene benzene ethylene

$$C_6H_5C_2H_5 + H_2 \rightarrow C_6H_5CH_3 + CH_4$$

ethylbenzene hydrogen toluene methane

The unit utilizes 98% pure ethylbenzene as the fresh feed for the process, which is mixed with the ethylbenzene recycle stream. Superheated steam is injected into the reactor feed stream to heat the process stream to the required temperature for the reactors and to dilute the stream to increase the selectivity and yield of styrene. The superheated steam is generated in a fired heater from low pressure steam fed to the unit.

After the reactors section, the process is cooled and fed to a three-phase separator with three exit streams: a vapor stream, a liquid organic stream, and a wastewater stream that directly exits the unit. The liquid organic stream is sent to the separations section of the process where a benzene/toluene stream exits the top of the first distillation column as a byproduct. Fuel gas also exits the top of this column, which is combined with the vapor stream from the three-phase separator. The second distillation column separates the styrene product stream and the remaining ethylbenzene stream that is then recycled.

Process Safety and Environmental Considerations

Styrene has the potential to spontaneously polymerize above 125^{o}C at high concentrations. Polymerization can cause plugging in the process, which may require an unwanted shutdown and damage to equipment and piping. To prevent polymerization, a temperature control system should be placed throughout the system with alarms programmed to sound when streams with high concentrations of styrene approach 125^{o}C. The system should also have preventative measures in place when the temperature begins to increase. A product cooler on the styrene stream may be useful to minimize the risk of sending the styrene to the polymerization unit above 125^{o}C.

Another safety concern is the flammability of the components in the process, which influences the design of the pressure relief valves. Pressure relief valves in this process should be vented the vapor to safe locations like a flare system or to be recycled in the process. Proper grounding and bonding should also be maintained throughout the process to eliminate ignition sources.

There is also vacuum pressure in many pieces of equipment that should be designed for full vacuum pressure as a safeguard. Although this would increase the capital cost, it would prevent potential implosions and improve process safety and longevity of equipment.

Due to the toxicity of the components in the process, secondary containment systems need to be put in place to contain any spills to prevent contamination into the surrounding environment. Employees need to wear proper personal protective equipment (PPE) in the process areas to prevent irritation, burns, and other health concerns as well as be properly and routinely trained.

Base Case Assessment

The net present value for the base case process was -$919M and had a breakeven price of styrene of $2,650/tonne. Through the sensitivity analysis shown in Figure 2 below, the raw material cost has the largest impact on the NPV.

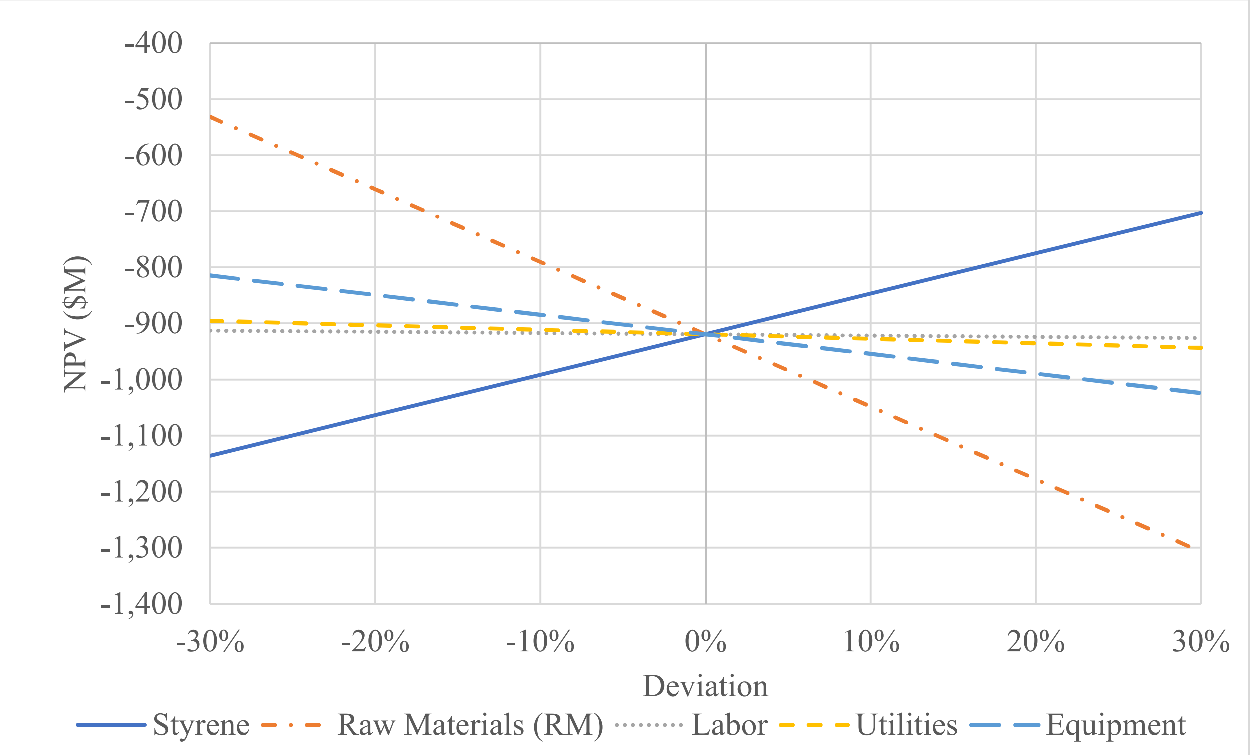


Figure 2: NPV Sensitivity Analysis

The raw material utilization proves to be of most importance in maximizing the NPV of this project, so the team focused on decreasing the fresh feed flowrate of ethylbenzene from the base case flowrate of 210 kmol/hr. This could be done by improving selectivity and yield in the reactors as well as minimizing the loss of ethylbenzene in the fuel gas stream. Reducing the equipment and utility costs was also investigated when optimizing the base case.

Other variables in the base case that need to be considered while optimizing are the constraints throughout the process. The main constraints include maintaining the styrene exit stream temperature below 125°C to avoid the risk of polymerization and producing the required production and purity of styrene. Other constraints included an L/D ratio of 2-10 in the reactors and temperature limitations on utilities used in the heat exchangers.

Optimization

The three main sections of the process include the reactors section, separation preparation section, and separation section. Each process condition that was an optimization variable was adjusted to maximize the NPV before moving on to the next variable. The stepwise optimization process began at the reactors and moved downstream through the subsequent unit operations. Two cycles of optimization were performed along with a heat integration analysis at the end. Additions of unit operations and adjustments to stream flows were also necessary to further optimize the process as well as to resolve safety concerns in the base case. Graphs for each variable are shown to visualize the optimization process with the tested values for each condition. On the graphs, the base case values are red and the chosen optimization values are green.

Before optimizing the reactors, the material of construction (MOC) of the distillation towers, T-501 and T-502, were investigated. In the base case, the MOC of the towers was titanium which was not necessary for the process conditions and compositions. When exploring various materials, carbon steel was an acceptable replacement and the most cost-effective. Replacing the MOC from titanium to carbon steel improved the NPV by $125M. However, consulting with a materials expert is advised to ensure that carbon steel is appropriate for the chemicals and conditions of the towers.

Following the MOC change for the towers, parametric optimization began in the reactors. Optimization in the reactors involved changes in temperature, pressure, and steam dilution to the process. An increase in raw material utilization while maintaining feasible downstream equipment costs was the primary goal in optimizing the reactors. Due to the reaction kinetics, a low temperature favors the production of styrene over benzene and toluene due to the lower activation energy of the styrene reaction. An increase in steam dilution and decrease in pressure also improves selectivity by decreasing the conversion of ethylbenzene and therefore the production of hydrogen in the styrene reaction which reduces the rate of the toluene reaction.

To find the optimum inlet temperature for the first styrene reactor, R-501, temperatures above and below the base case temperature were analyzed. The optimum condition was where the maximum NPV occurred, with 510°C improving the NPV the most. The temperature changes were achieved by varying the temperature of the steam injected into the process stream from the steam heater, H-501. The decrease in temperature improved the selectivity and yield which caused a decrease in the fresh feed requirement.

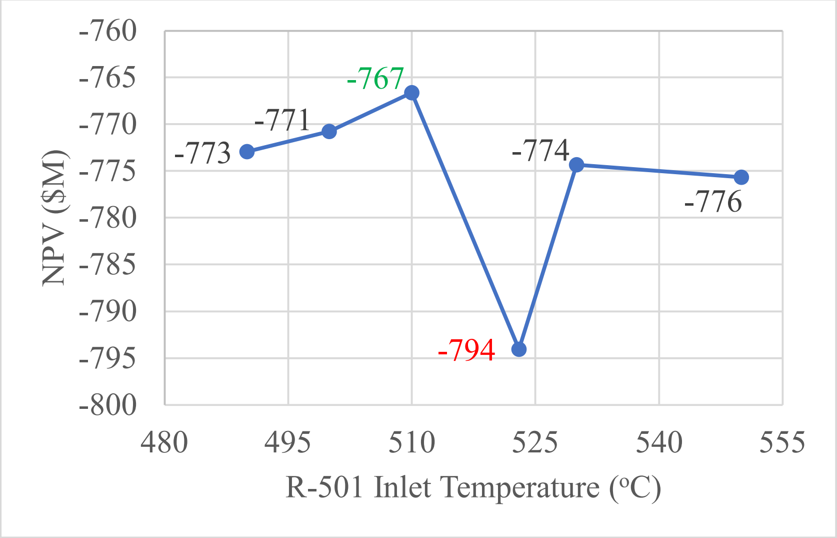


Figure 3: NPV vs. R-501 Temperature

Below 510°C, the NPV decreased due to a significant decrease in conversion causing downstream equipment to become too expensive. This was observed mainly in the separation section where the equipment became exceptionally large and outweighed the decrease in fresh feed required. The drastic spike in NPV as seen in Figure 3 was a concern to the engineering team. The fired heater duty was not properly updated in the economic model at the time this variable was considered but was resolved and did not have an impact on the optimized temperature for R-501.

The steam dilution rate to the process was then optimized. Although an increase in steam dilution improves the selectivity and yield, at this point in the process, it was optimal to increase the steam dilution rate, as seen in Figure 4, to increase the conversion of ethylbenzene to reduce the recycle flowrate, utility cost, and equipment costs.

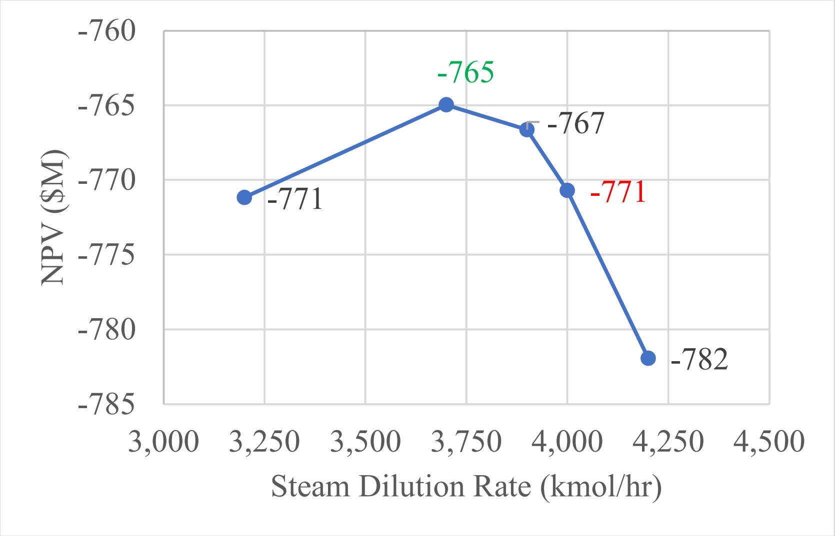


Figure 4: NPV vs. Steam Dilution Rate

Next, optimization of the inlet temperature of the second styrene reactor, R-502, was performed. Again, a decrease in temperature from 575°C to 550°C improved the NPV by reducing the fresh feed flowrate.

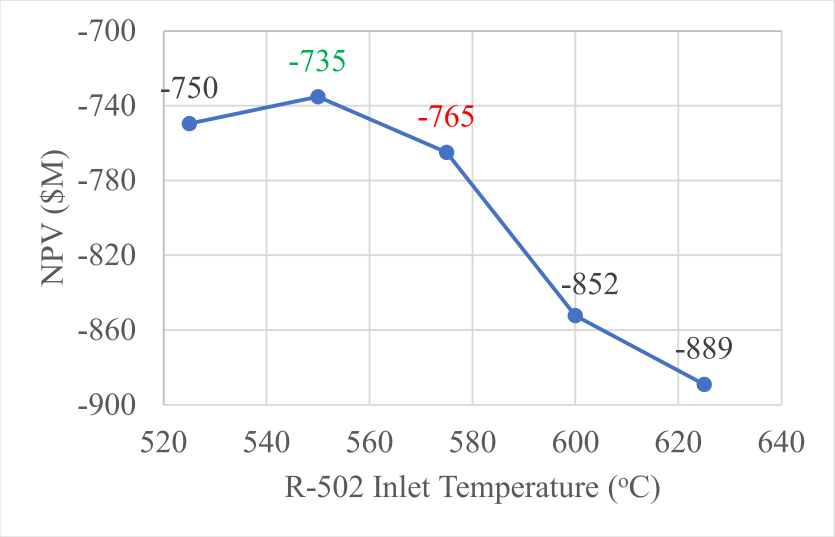


Figure 5: NPV vs R-501 Inlet Temperature

Like R-501, the yield and selectivity continue to increase at decreasing temperatures, but the conversion becomes too low which causes a drastic increase in the recycle flowrate and downstream equipment cost and is why a decrease in NPV at lower temperatures is seen in Figure 2. Reducing the inlet temperature in R-502 improved the NPV by $30M.

After optimizing the feed temperature to both reactors and the steam dilution flowrate to the process, further reactor optimization variables such as the inlet pressure to the first reactor, reactor volumes, and L/D ratio were investigated. However, when adjusting these variables, the engineering team noticed that these variables were having a larger downstream effect, mainly on the three-phase separator, rather than optimizing the reactors themselves. Because of these implications, the team moved forward with optimizing the separation preparation section before furthering reactor optimization.

The separation preparation section consists of the product coolers after the reactors section and the three-phase separator. The most important unit operation is the three-phase separator, V-501, as it separates the more volatile byproducts to the fuel gas stream, the wastewater, and the liquid organic stream that contains the desired product. However, at the base case inlet temperature of 65°C to V-501, 18 kmol/hr of ethylbenzene and 4 kmol/hr of the styrene product were lost to the fuel gas. This equated to a $20M loss per year of the fresh feed and desired product.

The inlet temperature to V-501 was adjusted by the product cooler E-505, which uses a utility of cooling water from 30°C to 40°C. With a decrease in temperature, there is a decrease in ethylbenzene and styrene in the vapor stream and therefore loss in the fuel gas stream. Because the minimum approach temperature for heat exchangers with cooling water is 10°C, the process stream temperature could be decreased to 40°C. However, the engineering team incorrectly analyzed the approach temperatures and only reduced the process temperature to 50°C. This issue was corrected later.

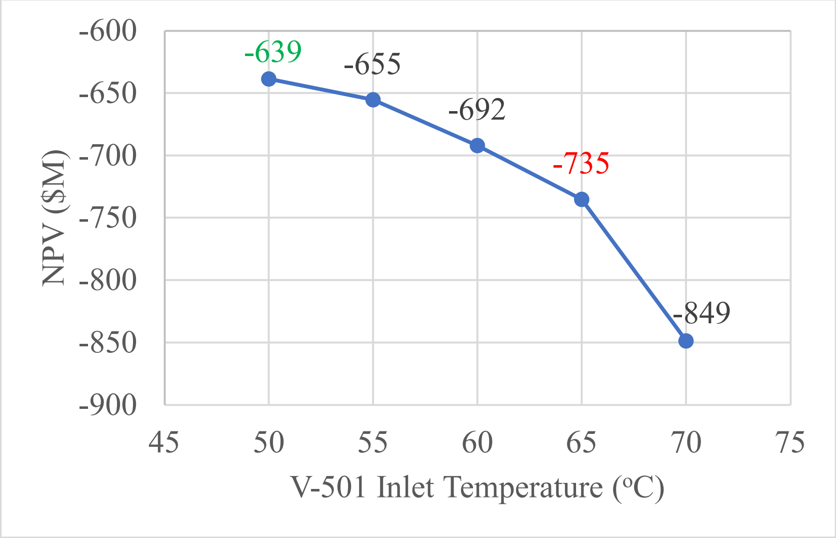


Figure 6: NPV vs. V-501 Temperature

The decrease in temperature in V-501 reduced the ethylbenzene loss to 6.7 kmol/hr and the styrene loss to 1.1 kmol/hr in the fuel gas stream and improved the NPV by $97M. Although a limitation on the cooling water temperature was thought to have been reached at this point in the process, there was still room for improvement as seen in Figure 6 and further optimization was reinvestigated in the second cycle.

After optimizing the three-phase separator, the reactor volumes and L/D ratios were observed. Reducing the volume of the reactors favored a higher selectivity of styrene but decreased the conversion of ethylbenzene. Again, this left the engineering team to find a balance between improving selectivity and equipment cost based on the largest NPV. Lowering the volume from 50 m^3 to 42 m^3 resulted in the largest improvement in NPV, shown in Figure 7. Additionally, a lower reactor volume results in less catalyst to be purchased each year. This optimization saved $13M.

Along with the volume, the team also explored the reactors' L/D ratio and found that the lower the ratio, the higher the NPV. This was because the pressure drop in the reactors decreased and caused the pressure in the three-phase separator downstream to increase. This led to an additional decrease in the loss of ethylbenzene and styrene in the fuel gas stream. With an L/D limitation of 2-10, the optimized ratio was 2 and improved the NPV by $5M.

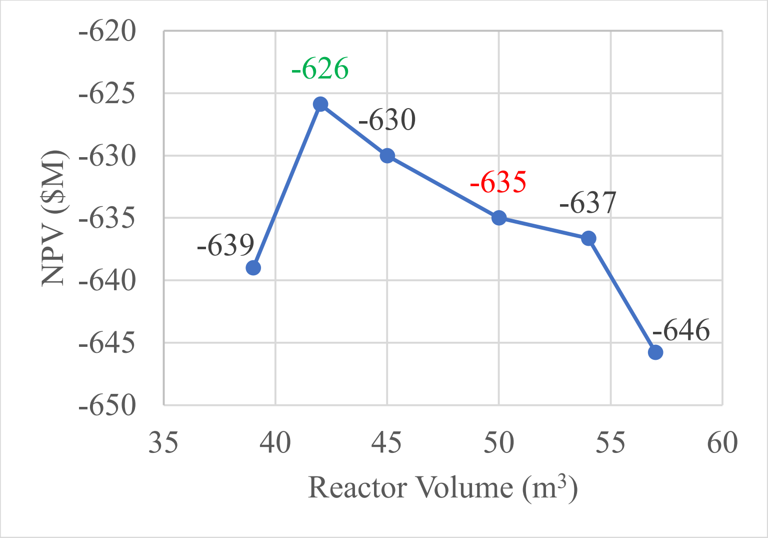


Figure 7: NPV vs. Reactor Volumes (R-501 & R-502)

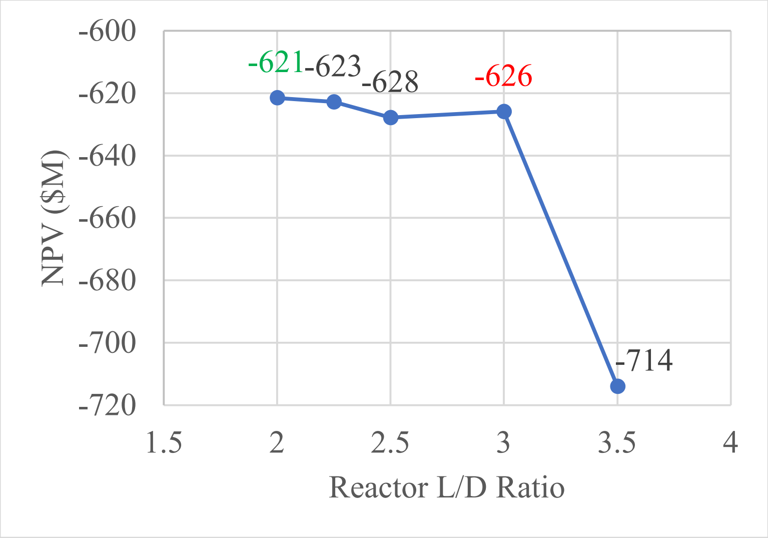


Figure 8: NPV vs. Reactor L/D Ratio (R-501 & R-502)

Lastly, for the reactors section, the team observed the inlet pressure to R-501. Although lower pressure improves the utilization of raw materials, there was an NPV improvement at higher pressure due to the increased conversion and decrease in utility and equipment cost. These improvements outweighed the increase in fresh feed cost. The results below in Figure 9 show that increasing the pressure from 190 kPa to 200 kPa was the most economical. However, the pressure had a minimal effect due to the reaction kinetics being based on partial pressure and only improved the NPV by $1M.

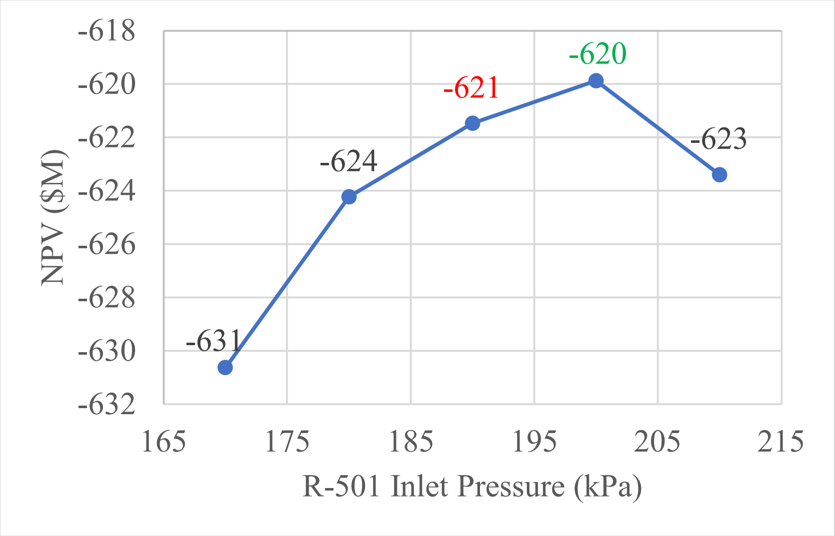


Figure 9: NPV vs. R-501 Inlet Pressure

Because the separation preparation section had already been optimized, the engineering team then moved to the separation section that includes the benzene/toluene column, T-501, and the styrene column, T-502.

In T-501, the optimization variables included the number of trays, the feed tray location, and the top tray pressure. Increasing the number of trays in T-501 decreased the vapor flowrate in the column, which reduces the diameter of the tower and therefore cost. The decrease in flowrate then decreases the duties of the reboiler and condenser, reducing utility costs. However, the increase in the number of trays increases the height of the column. The tower was marginally more expensive, but the decrease in utilities outweighed the increase in capital cost. The optimum number of trays was found to be 32, seen in Figure 10 below. Above 32 trays, the increase in capital cost outweighed the decrease in utility costs.

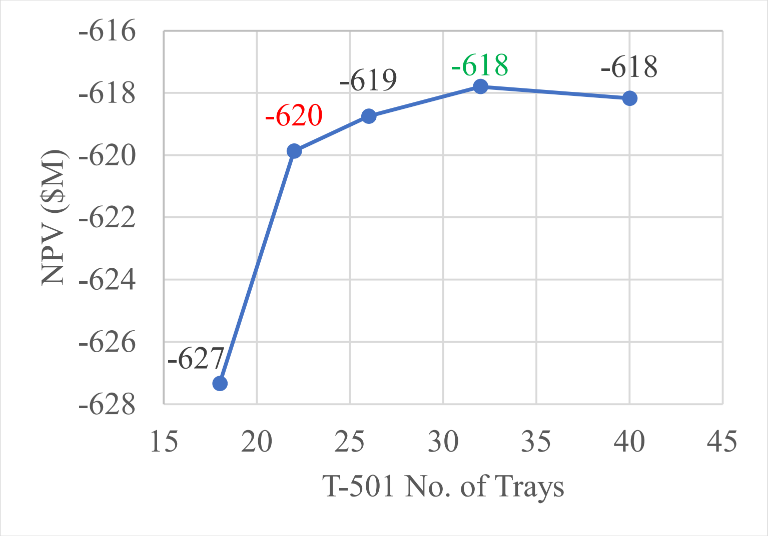


Figure 10: NPV vs. T-501 No. of Trays

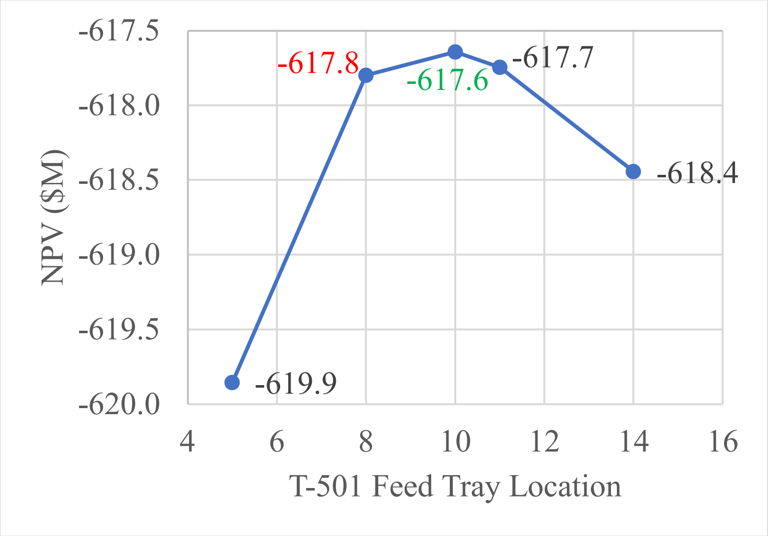


Figure 11: NPV vs. T-501 Feed Tray Location

Optimizing the feed tray location in a tower is effectively matching the feed composition and conditions to the tray composition and conditions. A feed tray that is too high causes excessive condenser duty to meet distillate specifications and a feed tray too low causes excessive reboiler duty to meet bottom specifications. At the optimized feed tray location of 10, there was a decrease in the vapor flowrate through the column as well as the reboiler and condenser duties. However, the NPV only improved by less than $1M.

The main impact of increasing the top tray pressure of T-501 was the effect it had on the fuel gas compressor, C-501. Increasing the top tray pressure in the column increases the pressure of the feed to C-501 so that the duty required to achieve the same desired pressure decreased. The top tray pressure was increased to 50 kPa.

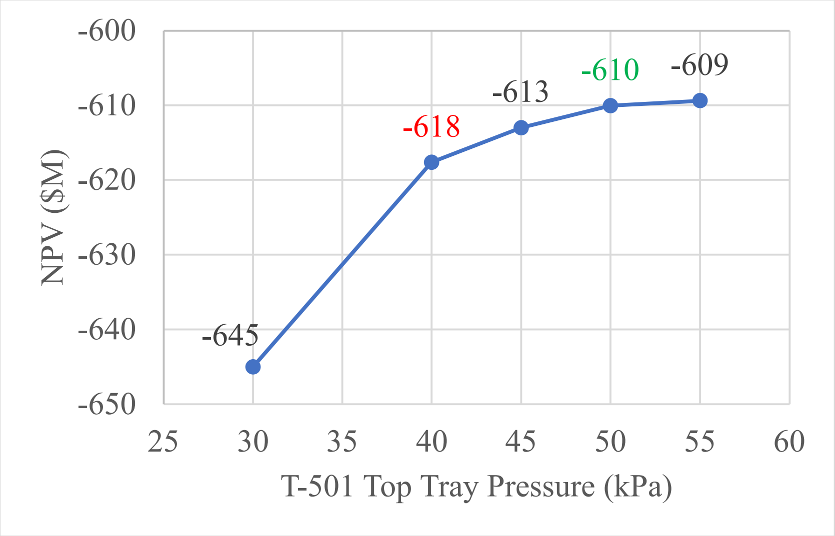


Figure 12: NPV vs. T-501 Top Tray Pressure

Although the NPV continued to increase with pressure as shown in Figure 12, above 50 kPa, the temperature at the bottom of the column exceeded 125°C, which is the temperature at which styrene can polymerize. The engineering team initially wanted to remain under this temperature as a preventative measure. However, styrene will spontaneously polymerize at high concentrations above this temperature and the bottom stream is about 15% styrene, so the only concern for auto-polymerization is in the styrene product stream. This information was taken into consideration in the second cycle of optimization. Increasing the top tray pressure improved the NPV by $8M.

The variables that were optimized in the styrene column were the number of trays and the feed tray location. The top tray pressure was not adjusted due to polymerization concerns at the bottom of the column. Increasing the pressure above the base case pressure of 55 kPa would increase the temperature and risk polymerization.

For the styrene column, T-502, it was more cost-effective to reduce the number of trays and therefore cost of the tower rather than to decrease the utility cost. The number of trays was reduced from 70 to 68.

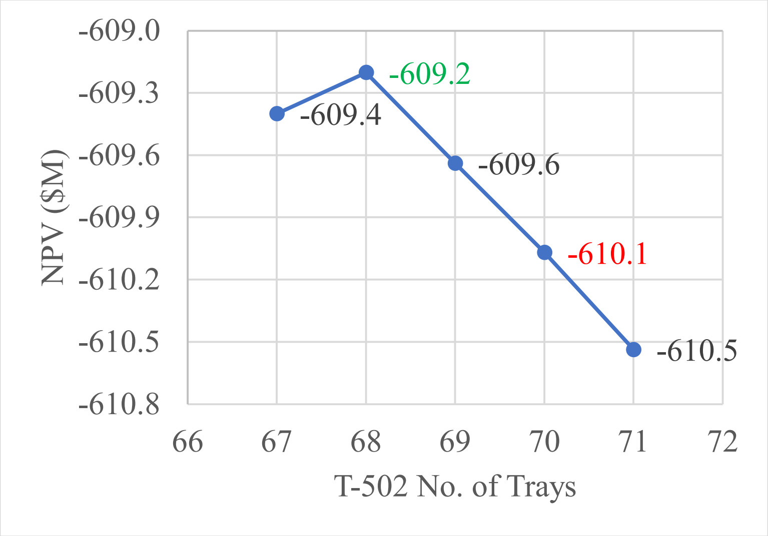


Figure 13: NPV vs. T-502 No. of Trays

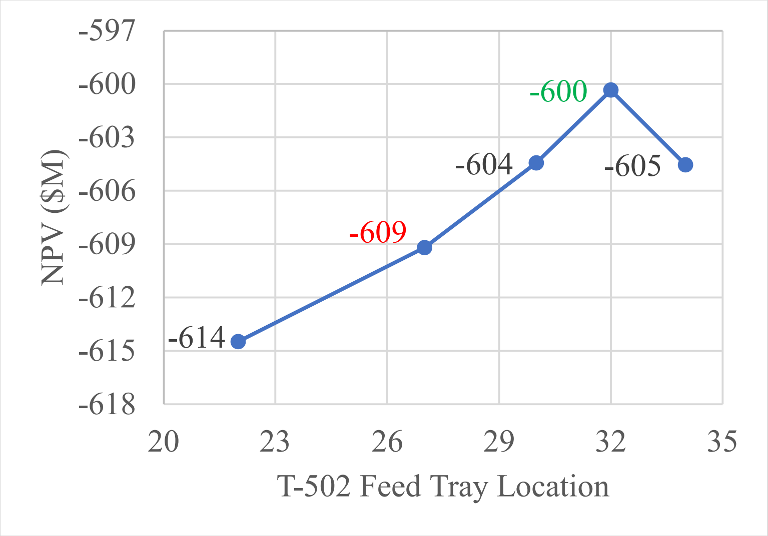


Figure 14: NPV vs. T-502 Feed Tray Location

Increasing the feed tray location from tray 27 to 32 in T-502 decreased the reboiler and condenser duties as well as the net liquid and vapor flowrates in the tower, resulting in a reduction in utility cost and capital cost.

The last optimization consideration for the first cycle was the addition of a second compressor, C-502, to the fuel gas compression section along with an intercooler, E-510. The base case compression ratio was 6 and is ideally 3 or less for safe operation.[i] With two compressors, the compression ratios in both C-501 and C-502 are under 3. Additionally, the temperature rise across a compressor with such a high compression ratio decreases the efficiency of the compressor. This brings the need for an intercooler into the process. The intercooler removes waste heat so that for the same compression ratio, less work is required. It also reduces the fuel gas to a safer exit temperature. Overall, this improves process safety in the plant as well as saved $11M for a first optimization cycle NPV of -$589M, a $330M improvement from the base case.

A second round of optimization was performed on the same variables as in the first cycle. Figure 15 below shows the improvement in NPV after optimization of each unit operation as well as the addition of heat integration in the process. Individual graphs for each variable are not shown, but the optimization process was performed like the first cycle.

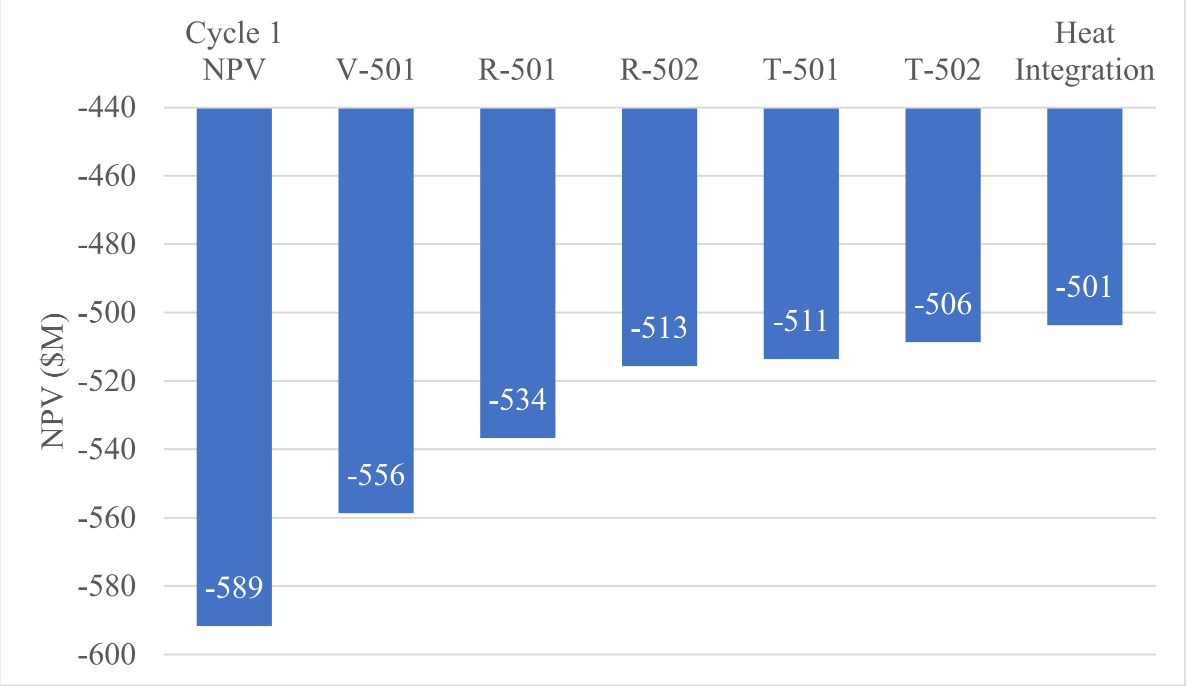


Figure 15: Optimization Cycle 2 Summary

This cycle began with optimization of V-501 due to the implications that were seen previously. Because a process limitation had been reached on the cooling water heat exchanger to feed V-501, an additional heat exchanger before the three-phase separator, E-511, that uses refrigerated water as a utility was added to the process. The minimum approach temperature for refrigerated water is 5ºC with a feed temperature of 5ºC and a return temperature of 15ºC. The temperature of the process stream was reduced to 20ºC. This further reduced the ethylbenzene and styrene loss in the fuel gas stream and therefore the fresh feed required for the process. This improved the NPV by $33M. However, again, the minimum approach temperature was incorrectly analyzed and could have been decreased to 10ºC. This issue was corrected and is discussed later. It is possible to replace the cooling water utility with refrigerated water in E-505, but the increase in utility cost for refrigerated water outweighs the increased capital cost of an additional heat exchanger.

In the first styrene reactor, it was now more cost-effective to increase the inlet temperature to 540°C and therefore increase conversion to reduce the recycle flowrate and downstream equipment size and cost rather than to improve selectivity and yield. The inlet pressure was also reduced to the inlet of the reactor to 180 kPa, reducing the required fresh ethylbenzene feed. The steam diluent to the process was also increased to 3,850 kmol/hr and improved the NPV due to the further increase in selectivity and yield of styrene in the reactors. The NPV was improved by $22M after R-501 optimization.

The temperature in the second reactor was decreased from the first cycle of optimization from 550°C to 520°C, which further decreased the fresh feed requirements and improved the NPV by $21M. Although the reactor volumes for R-501 and R-502 as well as the L/D ratios were analyzed separately rather than in conjunction as performed in cycle 1, there was no change in these variables from the previous cycle of a solid catalyst volume of 42 m^3 and an L/D ratio of 2.

In both distillation towers, it was more economical to reduce the utility costs by increasing the number of trays rather than decrease the capital cost by decreasing the number of trays. Optimal feed tray locations were again found by performing a tray-by-tray analysis. The optimal number of trays for T-501 was 40 with a feed tray location of 10. In T-502, the optimal number of trays was found to be 73 with a feed tray of 36. Additionally in T-501, the top tray pressure was further increased to 55 kPa to reduce the cost of the downstream compressors. Optimization of T-501 and T-502 improved the NPV by $2M and $5M respectively.

A comparison between the base case, cycle 1, and cycle 2 variables that were optimized and their values is in Appendix C.

The last step to finish optimizing the process was heat integration. The team used the R-502 effluent to preheat the reactor feed stream in E-501. This eliminated the steam utility in E-501 and reduced the utility requirements in the reactor effluent product cooler, E-503. However, heat integration can cause issues at startup. Solutions to reach the required temperature include increasing the steam injection temperature to the feed of the reactor or to valve in a high pressure steam utility that is only used at startup. This optimization improved the NPV by $5M.

As previously mentioned, the engineering team improperly analyzed approach temperatures in the product coolers before the three-phase separator. The process temperature could be reduced in the product cooler with cooling water, E-505, to 40^{o}C and in the product cooler using refrigerated water, E-511, to 10^{o}C. The decrease in temperature in E-505 reduces the more expensive utility required for E-511. The ethylbenzene and styrene loss further decreased in the fuel gas stream by reducing the process temperature in E-511 and therefore inlet temperature of V-501. This improved the NPV by reducing the fresh feed requirement. After these mistakes were corrected, the final optimized NPV of the process was increased to -$496M.

Optimized Design

	Base Case	Optimized	Improvement
NPV ($M)	-919	-496	423
Breakeven Cost ($/tonne)	2,650	1,976	-674
Fresh Feed Required (kmol/h)	209.6	171.7	-37.9
Overall Conversion	89%	96%	7%
Overall Yield	65%	74%	9%
Overall Selectivity	2.02	2.92	0.90

Table 1: Base Case vs. Optimized Case Metrics

Table 1 shows important metrics at the base and the optimized case of Unit 500. Overall, the NPV improved by $423M and the breakeven price to produce styrene decreased by

$674/tonne. The fresh feed required to the process, the factor that has the largest impact on the NPV, decreased by 37.9 kmol/hr. The overall conversion, yield, and selectivity all improved as well.

The major changes in the optimized design in comparison to the base case include the addition of the multistage compressor C-502 and intercooler E-510, the addition of product cooler E-511 that uses refrigerated water to cool the process stream to feed the three-phase separator, and the heat integration between the reactor effluent and the feed preheater, E-501. The reactor operating conditions mainly increased the selectivity and conversion of styrene in the process, the reduction of temperature in the three-phase separator significantly reduced the loss of ethylbenzene and styrene in the fuel gas stream, and optimization of the towers reduced utility and capital costs.

The optimized process flow diagram for Unit 500 and the stream table can be seen in Appendices D and E.

Further Considerations

Further optimization could be performed by completing more cycles on the process or by using an alternative software that can perform nonlinear optimization. However, topological changes to the process could yield a more optimized NPV such as exploring the option of a membrane reactor. Although a membrane reactor is more expensive than the adiabatic packed bed reactors currently designed in the process, it would offer improved raw material utilization, reduce side reactions, and remove and/or minimize downstream equipment. This could potentially make the cost of the reactor negligible in terms of the benefits it can provide.

Additionally, a suitable location for this plant would need to be selected. Although the plant would bring in additional jobs to the community, new development, especially a chemical plant, may be opposed by residents in many areas. A location with a low population that would provide communal and local governmental support for an industrial process would be ideal.

Recommendation

The breakeven price for the optimized case is $1,976/tonne, whereas it costs $1,598/tonne to purchase styrene. However, with Unit 500, there is a controllable styrene production and purity for the downstream units, whereas with purchasing styrene there is a supply chain risk associated with the accessibility of styrene. It also may not be possible to purchase styrene at the required purity for the polymerization unit. Additionally, any potential upstream units like the ethylbenzene production process where Unit 500 likely gets its feed from would need to be taken into consideration.

The potential for profit in downstream units and the minimized risk associated with producing styrene leads the engineering team to recommend moving forward with the project in terms of further optimization to make the production more attractive from an economic standpoint as well as determining additional specifications within the plant such as configuring a dynamic process and economic model, drawing P&IDs, and determining control systems. However, it is still in the company’s best interest to consult risk professionals to determine the risk premium on the purchase of styrene and conduct a market analysis before making a final decision.

PART 2: Fluidized Bed Reactor

Introduction

Using a single isothermal fluidized bed reactor was an additional consideration for the production process of styrene from ethylbenzene and was optimized apart from the previous case study, but it is important to note that reactions and reaction kinetics remain the same.

When a fluid flows upward with sufficient velocity to overcome the downward force of gravity, the particles become buoyant and is said to be fluidized. At high velocities, the particles become well mixed and approach isothermal behavior. This is the main advantage of fluidized bed reactors. However, fluidized bed reactors are "typically are more complex to design, build, and operate than other types of reactors, such as packed-bed reactors… [and] are prone to erosion and particle attrition caused by the moving particles"[ii]. These effects can increase the operating and maintenance costs, especially considering the use of expensive catalyst particles in the fluidized bed.

Specifications and Optimization

The fluidized bed was simulated in PRO/II as an isothermal plug flow reactor with an internal heat exchanger. A 10% bypass simulates part of the feed gas bypassing the catalyst due to the nature of the fluidized bed, meaning the reactor can never achieve above a 90% single-pass conversion.

The objective of this optimization was to maximize the selectivity of ethylbenzene to styrene by adjusting variables within the following limits: the inlet pressure between 0.75 bar and 5.0 bar, the inlet feed and reactor temperature between 300°C and 750°C, the reactor volume, and the reactor L/D ratio between 2 and 10. Additional constraints included that the superficial gas velocity at the conditions in the reactor must be between 3-10 times the minimum fluidization velocity, u_{mf}, using equation 1 where Ar is the Archimedes number described by equation 2, d_p is the particle diameter, ρ_g is the gas density, ρ_s is the catalyst density, μ_g is the gas viscosity, and g is the acceleration of gravity. Additionally, the minimum conversion of ethylbenzene is 5% and the pressure drop across the reactor is determined by equation 3 where ε is the void fraction of the particle in the fluidized bed. The catalyst diameter was 1 mm with a void fraction of 0.45 at minimum fluidizing conditions.

$$(1)\quad Re_{\rho,mf} = \frac{u_{mf} d_p \rho_g}{\mu_g} = [1135.69 + 0.0408Ar]^{0.5} - 33.7$$

$$(2)\quad Ar = \frac{d_p^3 (\rho_s - \rho_g) \rho_g g}{\mu_g^2}$$

$$(3)\quad \frac{\Delta P}{L} = g(1 - \varepsilon)(\rho_s - \rho_g)$$

An optimizer was used in PRO/II to maximize the selectivity by varying the above specifications within their limitations. An optimizer performs stepwise optimization where each variable is varied between the limits and the value that maximized the selectivity is then used to optimize the next variable. This is done in cycles until all the variables converge at the maximum selectivity between the limits and maintaining the required specifications.

Results

Because the reaction kinetics are unchanged, a low temperature and low pressure still favor the selectivity of styrene. However, to achieve the required conversion, the temperature and pressure are not at their lower limits. The optimized variables are shown below in Table 2.

Variable	Optimum Condition
Feed Temperature (^oC)	486
Feed Pressure (bar)	4.08
Reactor Volume (m^3)	196
L/D Ratio	2

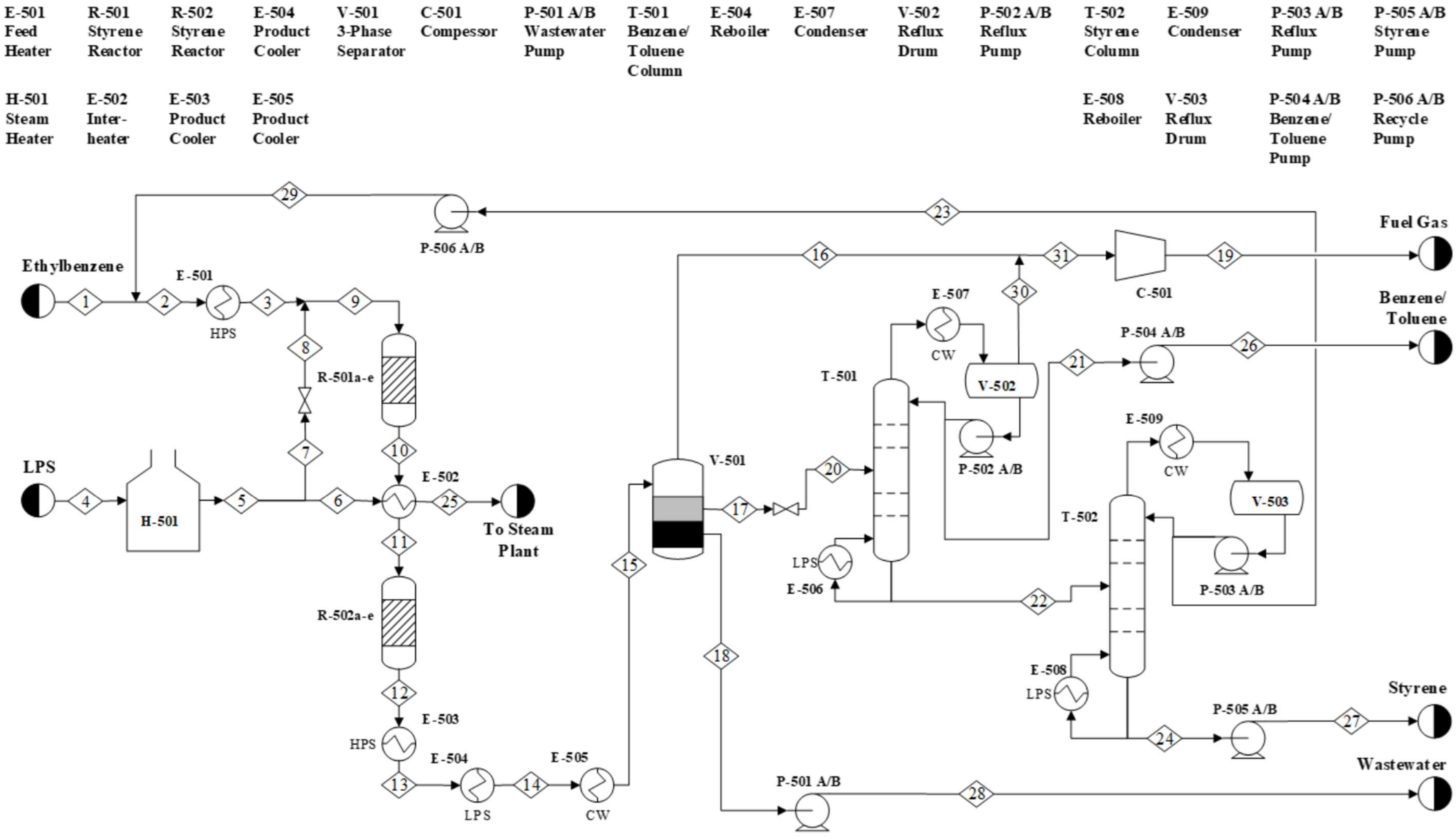
Table 2: Fluidized Bed Optimized Conditions

The selectivity of styrene is 12.14 and the conversion is at the minimum conversion of ethylbenzene at 5%. The minimum fluidization velocity of 0.4 m/s and the superficial gas velocity is 1.7 m/s into the reactor and 2.4 m/s out of the reactor which are 4.25x and 6x the u_{mf} respectively, meeting the requirements in the reactor.

Although the selectivity of 12.14 in the fluidized bed reactor is a significant improvement from the selectivity of 2.92 in the adiabatic packed bed reactors, there are some additional factors that need to be considered. The capital cost of the reactor, cost of the catalyst, frequency of catalyst replacement, the utility requirements for the internal heat exchanger, and the effect the reactor has on downstream equipment are major elements that will impact which type of reactor is the best for this process. Due to the significant negative impact that a low conversion had on the recycle flowrate and the distillation tower prices, the fluidized bed reactor may not be the most economical for the process. However, the high selectivity would reduce the fresh feed requirements greatly. An additional economic analysis needs to be completed before making a final decision on the feasibility of the fluidized bed reactor in the styrene production process.

APPENDICIES

Appendix A: Base Case Process Flow Diagram



Appendix B: Base Case Stream Table

Stream No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Temperature (°C)	136	108.7	225	159.0	800	800	800	799.0	523.7	499.2	575	549.7	270	180.0	65	65
Pressure (kPa)	210	210	190	600	565	565	565	190	190	172.6	157.6	133.8	118.8	103.8	88.8	88.8
Vapor Mole Fraction	0	0	1	1	1	1	1	1	1	1	1	1	1	1	0.1	1
Total Flow (kg/h)	22,164	62,338	62,338	174,587	174,587	104,327	70,260	70,260	132,597	132,597	132,597	132,597	132,597	132,597	132,597	5,942
Total Flow (kmol/h)	209.60	588.06	588.06	9691.04	9691.04	5791.04	3900.00	3900.00	4488.06	4555.74	4555.74	4638.50	4638.50	4638.50	4638.50	254.38
Component Flows																
Water	0.00	0.00	0.00	9691.04	9691.04	5791.04	3900.00	3900.00	3900.00	3900.00	3900.00	3900.00	3900.00	3900.00	3900.00	72.24
Ethylbenzene	205.41	582.34	582.34	0.00	0.00	0.00	0.00	0.00	582.34	506.71	506.71	399.17	399.17	399.17	399.17	18.13
Styrene	0.00	1.21	1.21	0.00	0.00	0.00	0.00	0.00	1.21	63.94	63.94	125.09	125.09	125.09	125.09	4.00
Hydrogen	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	54.78	54.78	91.14	91.14	91.14	91.14	91.07
Benzene	2.10	2.10	2.10	0.00	0.00	0.00	0.00	0.00	2.10	7.04	7.04	28.66	28.66	28.66	28.66	6.62
Toluene	2.10	2.41	2.41	0.00	0.00	0.00	0.00	0.00	2.41	10.36	10.36	35.14	35.14	35.14	35.14	3.75
Ethylene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4.95	4.95	26.56	26.56	26.56	26.56	26.07
Methane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	7.95	7.95	32.73	32.73	32.73	32.73	32.51

Stream No.	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
Temperature (°C)	65	65	241.1	64.9	50.8	119.7	90.8	123.6	700.0	50.8	120.9	65.0	93.0	50	62.9
Pressure (kPa)	88.8	88.8	240	60	40	60	25	55	550	200	200	200	210	40	40
Vapor Mole Fraction	0	0	1	0	0	0	0	0	1	0	0	0	0	1	1
Total Flow (kg/h)	57,892	68,763	7,046	57,892	4,111	52,672	40,173	12,499	104,327	4,111	12,499	68,768	40,173	1,104	7,046
Total Flow (kmol/h)	567.64	3816.48	276.48	567.64	46.80	498.46	378.46	120.00	5791.04	46.80	120.00	3816.76	378.46	22.09	276.48
Component Flows															
Water	11.40	3816.36	82.88	11.40	0.48	0.00	0.00	0.00	5791.04	0.48	0.00	3816.64	0.00	10.64	82.88
Ethylbenzene	380.98	0.06	18.34	380.98	3.60	377.17	376.94	0.24	0.00	3.60	0.24	0.06	376.94	0.21	18.34
Styrene	121.09	0.00	4.00	121.09	0.11	120.98	1.21	119.77	0.00	0.11	119.77	0.00	1.21	0.00	4.00
Hydrogen	0.08	0.00	91.14	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07	91.14
Benzene	22.03	0.01	13.15	22.03	15.49	0.00	0.00	0.00	0.00	15.49	0.00	0.01	0.00	6.54	13.15
Toluene	31.36	0.03	7.68	31.36	27.12	0.31	0.31	0.00	0.00	27.12	0.00	0.03	0.31	3.93	7.68
Ethylene	0.49	0.00	26.56	0.49	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.48	26.56
Methane	0.22	0.01	32.72	0.22	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.22	32.72

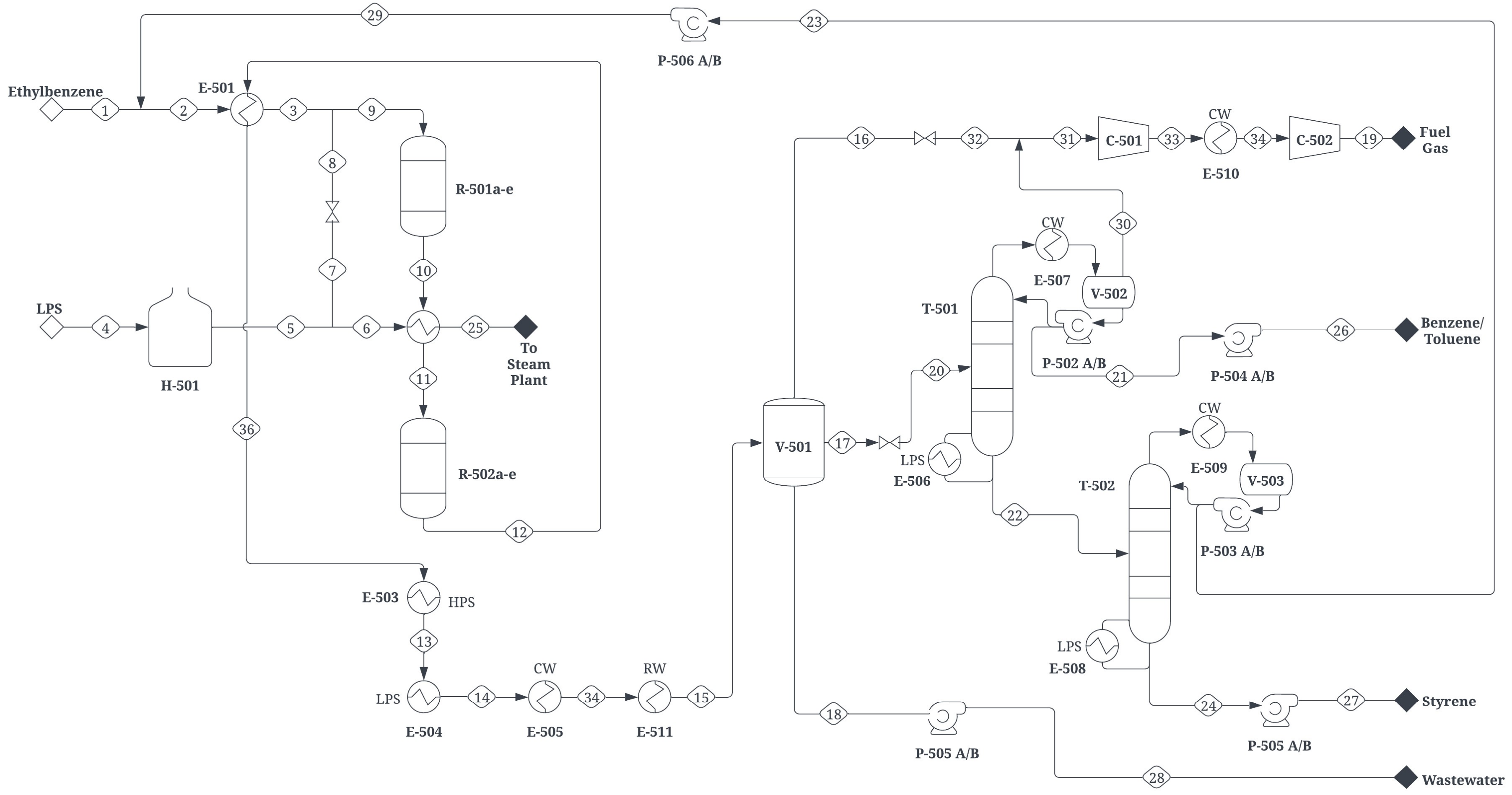
Appendix C: Optimization Variable Values

Variable	Tag	Variable	Base Case	Cycle 1 Optimization	Cycle 2 Optimization
3-Phase Separator	V-501	Temperature (°C)	65	50	20*
Styrene Reactor 1	R-501	Temperature (°C)	523	510	540
		Pressure (kPa)	190	200	180
		Solid Catalyst Volume (m^3)	50	42	42
		L/D Ratio	3	2	2
		Steam Diluent (kmol/h)	3,900	3,700	3,850
Styrene Reactor 2	R-502	Temperature (°C)	575	550	520
		Solid Catalyst Volume (m^3)	50	42	42
		L/D Ratio	3	2	2
Benzene/Toluene Column	T-501	No. of Trays	22	32	40
		Feed Tray	8	10	10
		Top Tray Pressure (kPa)	40	50	55
Styrene Column	T-502	No. of Trays	70	68	73
		Feed Tray	27	32	36

**Reduced to 10°C after further analysis*

Appendix D: Optimized Process Flow Diagram

E-501 Feed Heater
R-501 Styrene Reactor
R-502 Styrene Reactor
V-501 3-Phase Separator
E-511 Product Cooler
C-501 Compressor
E-510 Inter-cooler
C-502 Compressor
P-501 A/B Wastewater Pump
T-501 Benzene/ Toluene Column
E-506 Reboiler
E-507 Condenser
V-502 Reflux Drum
P-502 A/B Reflux Pump
T-502 Styrene Column
E-509 Condenser
P-503 A/B Reflux Pump
P-505 A/B Styrene Pump
H-501 Steam Heater
E-502 Inter-heater
E-503 Product Cooler
E-505 Product Cooler
E-504 Product Cooler
E-508 Reboiler
V-503 Reflux Drum
P-504 A/B Benzene/ Toluene Pump
P-506 A/B Recycle Pump



Appendix E: Optimized Stream Table

Stream No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Temperature (°C)	136	102.58	225	158.98	933.06	933.06	933.06	932.42	540.00	512.18	520	374.70	270	180	10	10	10	10
Pressure (kPa)	200	200	180	600	565	565	565	180	180	168.24	153.24	139.33	124.33	109.33	79.33	79.33	79.33	79.33
Vapor Mole Fraction	0	0	1	1	1	1	1	1	1	1	1	1	1	1	0.03	1	0	0
Total Flow (kg/h)	18,157	84,459	84,459	74,672	74,672	5,313	69,359	69,359	153,818	153,818	153,818	153,818	153,818	153,818	153,818	1,114	83,432	69,272
Total Flow (kmol/h)	171.70	796.27	796.27	4144.93	4144.93	294.93	3850.00	3850.00	4646.27	4739.44	4739.44	4779.91	4779.91	4779.91	4779.91	134.94	799.95	3845.02
Component Flows																		
Water	0.00	0.00	0.00	4144.93	4144.93	294.93	3850.00	3850.00	3850.00	3850.00	3850.00	3850.00	3850.00	3850.00	3850.00	2.10	2.95	3844.95
Ethylbenzene	168.27	791.33	791.33	0.00	0.00	0.00	0.00	0.00	791.33	685.02	685.02	630.32	630.32	630.32	630.32	0.70	629.60	0.02
Styrene	0.00	1.21	1.21	0.00	0.00	0.00	0.00	0.00	1.21	85.09	85.09	121.14	121.14	121.14	121.14	0.08	121.06	0.00
Hydrogen	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	70.75	70.75	92.56	92.56	92.56	92.56	92.44	0.12	0.00
Benzene	1.72	1.72	1.72	0.00	0.00	0.00	0.00	0.00	1.72	11.00	11.00	15.43	15.43	15.43	15.43	0.20	15.23	0.00
Toluene	1.72	2.01	2.01	0.00	0.00	0.00	0.00	0.00	2.01	15.15	15.15	29.38	29.38	29.38	29.38	0.11	29.25	0.02
Ethylene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	9.29	9.29	13.71	13.71	13.71	13.71	12.54	1.17	0.00
Methane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	13.14	13.14	27.37	27.37	27.37	27.37	26.78	0.56	0.03

Stream No.	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35
Temperature (°C)	177.35	10.00	50.85	126.72	90.81	123.60	699.94	50.88	120.95	10.01	93.05	50	12.72	9.97	112.20	60	40
Pressure (kPa)	240	75	55	75	25	55	550	200	200	200	200	55	55	55	120	105	94.33
Vapor Mole Fraction	1	0	0	0	0	0	1	0	0	0	0	1	1	1	1	1	0.03
Total Flow (kg/h)	1,353	83,432	4,386	78,801	66,302	12,498	5,313	4,386	12,498	69,278	66,302	239	1,353	1,114	1,353	1,353	153,818
Total Flow (kmol/h)	140.74	799.95	49.26	744.56	624.57	120.00	294.93	49.26	120.00	3845.35	624.57	5.80	140.74	134.94	140.74	140.74	4779.91
Component Flows																	
Water	4.20	2.95	0.51	0.00	0.00	0.00	294.93	0.51	0.00	3845.29	0.00	2.10	4.20	2.10	4.20	4.20	3850.00
Ethylbenzene	0.77	629.60	6.23	623.30	623.07	0.24	0.00	6.23	0.24	0.02	623.07	0.07	0.77	0.70	0.77	0.77	630.32
Styrene	0.08	121.06	0.09	120.97	1.21	119.76	0.00	0.09	119.76	0.00	1.21	0.00	0.08	0.08	0.08	0.08	121.14
Hydrogen	92.56	0.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.12	92.56	92.44	92.56	92.56	92.56
Benzene	1.29	15.23	14.14	0.00	0.00	0.00	0.00	14.14	0.00	0.00	0.00	1.09	1.29	0.20	1.29	1.29	15.43
Toluene	0.85	29.25	28.22	0.29	0.29	0.00	0.00	28.22	0.00	0.02	0.29	0.74	0.85	0.11	0.85	0.85	29.38
Ethylene	13.65	1.17	0.06	0.00	0.00	0.00	0.00	0.06	0.00	0.00	0.00	1.11	13.65	12.54	13.65	13.65	13.71
Methane	27.34	0.56	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.03	0.00	0.56	27.34	26.78	27.34	27.34	27.37

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[ii] Cocco, Ray & Karri, Sb & Knowlton, Ted. (2014). Introduction to Fluidization. Chemical Engineering Progress. 110. 21-29.