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Comparative Analysis of Simulation Models of the Production of Ethylbenzene

by

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

Oxford

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DEDICATION

Foremost, I thank God, the author and finisher of my faith for the successful completion of this thesis. Through highs and lows, through times I was in doubt and times I stood strong, He is always my constant.

To the best family members I could ever dream of being blessed with, I dedicate this one, and many more to come, to you.

To the few special friends that have seen me through different times in life, I thank you. KGO, you have been amazing and the true definition of a friend. This one is specially dedicated to you as well.

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It is with utmost gratitude, I thank Dr. Alexander Lopez, my research professor, for always holding me accountable, demanding excellence from me, and supporting me all through my journey as a student in the honors college.

I extend my appreciation to Dr. Adam Smith and Dr. John O'Haver, who constantly believed in me; showing their utmost support academically and as friends. I would also like to thank Dr. Esteban Ureña-Benavides for his patience in the classroom and dedication to seeing me succeed; especially as a minority in the program.

Finally, I would like to thank my other distinguished teachers, friends, and coworkers for helping me succeed in school, work, and personal life.

ABSTRACT

Process Engineering is all about making sure a raw material can become the desired product with as little variation as possible, while achieving the customer's specifications. Many equipment used for chemical processes cannot be physically inspected during operation at steady state, hence, the need for simulation software. **The objective of this study was to compare the results of three different simulation** packages to evaluate their efficacy within process design.

This study focused on the economic analysis of the production of Ethylbenzene using various models. The base case variables were inputted into each model to simulate the calculations for a fully functioning operation. This model case was then optimized to yield a discrete optimum for conversion of benzene to ethylbenzene. Results and accuracy were determined based on the intricate assumptions made by the simulation software and the highest economic value.

It was found that the Excel result from using the ideal gas equations for the chemical reactions resulted in the least accurate results. This result was mainly attributed to the inaccurate assumption that the gases were monatomic and that they exhibit no attractive forces. The PRO/II simulation yielded more accurate results because mass and energy balance calculations accounted for non-ideal gas behavior. The SimCentral results could not be gotten due to the COVID-19 pandemic.

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Simulations

The chemical industry, especially upstream processes in the crude oil sector, rely heavily on simulations to make business, safety, and process design decisions. A simple tool often used in process simulation is spreadsheet software, such as Microsoft Excel, where calculations and assumptions are organized for users to modify process conditions and monitor economic models. More complex forms of simulations are done using additional software that incorporates rigorous mathematical models toward solving process mass and energy balances. These complex tools are programmed using semi-intuitive user interfaces to simulate chemical processes. While it is generally understood that complex process simulation software provides detailed chemical process estimations, an elective comparison among simulation packages and spreadsheet calculations are lacking from the literature. For this project, using a liquid phase reaction scheme to produce ethylbenzene was investigated. The goal was to develop a base case process for the liquid phase reaction scheme and perform discrete optimization on the process to convert 100 kmol/h each of ethylene and benzene into ethylbenzene.

Ideal Gas Assumption

The required process simulation was performed three different times using three different software packages: Microsoft Excel, Pro II and SimCentral. This was done to compare the results gotten from all three in terms of accuracy. The simulation performed by Excel was more simplistic than the rest because Excel calculations are done based on the ideal gas assumption. An ideal gas is a gas with molecules that have no intermolecular attractive forces and thus only undergo perfectly elastic collisions; they don't lose any energy from colliding. This assumption simplifies calculations significantly but is not entirely accurate except at high temperature and low pressure. Pro II and Sim Central on the other hand, use more complicated algorithms to mimic a real-world scenario. These optimizations were to be done on the given base case and as expected, each software yielded different results.

Process Diagram

Chemical plant design is a fundamental aspect of process engineering which is necessary for the sequence, production, and development of a chemical process. The design starts conceptually with a preliminary blueprint of what the entire process entails. These blueprints are in the form of process diagrams such as a process concept diagram and block flow diagram which are instrumental to chemical process design. These diagrams have various uses such as:

- Providing a starting point in building a process
- Presenting an overview and a comprehensive understanding of the process

- Identifying key unit operations involved in the process
- Giving a preliminary design to perform economic analysis before actual production

Considering some of the uses of process diagrams, it is important to note how useful these representations are. These diagrams are used as a basis for modeling realistic effects of variables on chemical process. The primary process diagram that is referenced for simulation is the Process Flow Diagram (PFD). This shows the flow of chemicals, unit operations, and equipment in the order in which they are intended to appear if the process is fully constructed. This diagram is drawn in a process simulation tool with base case scenarios or conditions that the plant is generally expected to operate. These tools will show or predict behavior of operating conditions that affect a process and can estimate whether the process specifications are feasible or not. Another benefit of being able to simulate a process is that optimization of process conditions can be performed on a computer to increase productivity, efficiency, and profitability. Being able to do this saves money in the earlier stages in the economic analysis and feasibility process. One can determine early on, what the estimated optimum operating condition is for plant design. To determine this optimum, whether globally or locally, an iterative process design procedure is often used. It is iterative because the manipulation of one decision variable in a process impacts all other variables and operating conditions in the whole process.

There are different models used to simulate a design. For these models to fully simulate a whole process, assumptions on the behavior of the chemical reactions, separations and recycle sections must be taken into consideration such that the simulation software can properly estimate what results to expect in a real case scenario. These assumptions are what are used to select the thermodynamic model to be used for the simulation. A thermodynamic package includes equation of states, activity models for solving non-idealities of phases and compositions of the chemical components. The selection of a thermodynamic package, however, does not provide a one for all answer regarding what the expected outcome of a fully operating plant will look like. There are different simulators for process design and operational analysis in chemical industries. The tools typically simulate steady-state processes, while some can simulate dynamic operations.

Optimization can be performed on these simulators as well. Although Excel can be used for calculations and local optimization, it is better to run multiple scenarios on different simulation tools to get more accurate estimates as excel results are based on more simplified equations of states and assumptions that may or may not be true in reality. It is still beneficial to have a base case scenario done in Excel to have a basis for comparing the simulated versions of the operation. **The purpose of this project is to compare the results obtained from ideal gas assumptions for the Excel calculations, and rigorous calculations done in two chemical process simulators, PRO/II and SimCentral.**

Optimization

Process optimization is done to make a certain process more efficient while satisfying certain constraints and is an important step in the design process. When optimizing a process, an engineer must vary certain characteristics of the process called design variables; these can be discrete or continuous variables. The goal of this is to find the optimal values that would make the process safer, more efficient and profitable. Ideally, the optimization would reach the global optimum; a point where the process is safest, most profitable and most efficient. However, decision variables tend to be dependent on each other making the global optimum almost unattainable. Therefore, engineers often aim for the discrete optimum which is found by varying the design variables to minimize or maximize a mathematical function called the objective function.

To ensure that the objective function is as close to the global optimum as possible while choosing design variables, a pattern should be followed. The base case should be tested first to minimize or maximize the objective function then a value close to the base case value. If the base case value gives the best results for the objective function then no other values need to be tested. Otherwise, a new value between the value close to the base case and the base case value should be tested. Curves that depict the effects of the decision variables could then be derived.

There are two types of optimization: parametric optimization and topological optimization. Parametric optimization involves changing parameters, such as temperature and pressure, to optimize the process. The decision variables chosen here are crucial to the efficiency of the optimization process. Topological optimizations deal with the arrangement of process equipment, such as the type of reactor, to optimize the process.

Afterward, a decision should be made of the scope of the process to consider first. A top-down approach would entail looking at the topological optimizations first. Alternatively, a bottom-up approach involves looking at the parametric optimizations first. Optimization should be completed in a certain order which is shown in a diagram often referred to as the process design onion model as seen in Figure 1. When optimizing, it is advisable to start at the center which is the reactor; where the formation of the product begins. Then move on to the separation section where the product and raw materials are recovered. After the recovery section, the heat exchanger networks should be optimized for areas in the plant where heat formed during operation is reused in other parts of the plant. Otherwise, it all amounts to wasted energy. At this point, most of the money and resources have been maximized and the plant operates at minimal cost, but minimizing cost of utilities is the final way to optimize a process. For example, if a process requires heat and utilizes high-pressure steam to gain the energy, it can be investigated, whether medium or low-pressure steam is sufficient to not generate more heat than needed.

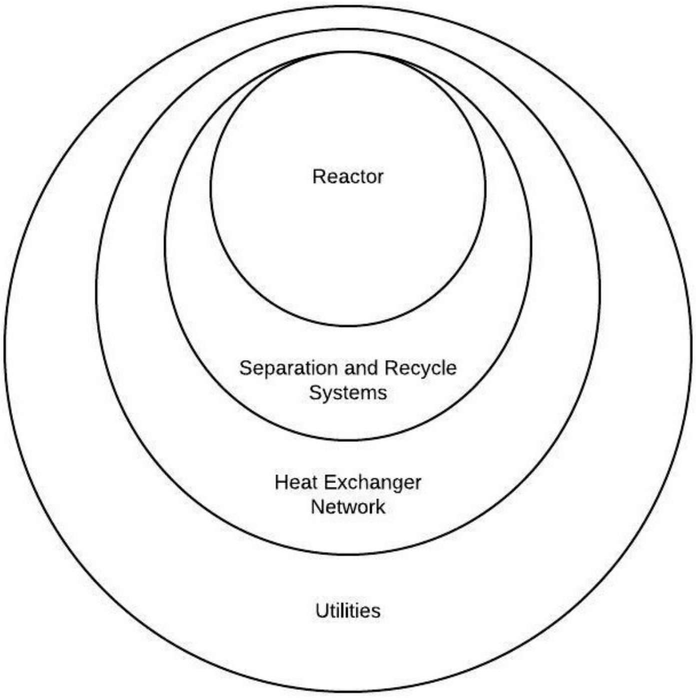


Figure 1: Process Design Onion

Chapter 1

Analysis

1.1 Ethylbenzene Manufacturing Process

Ethylbenzene was desired as a raw material for the downstream production of Styrene. The production of Ethylbenzene (EB) occurs in liquid phase in a Continous Stirred Tank Reactor (CSTR) with three reactions occuring.

The liquid phase production of EB takes place via the direct addition reaction between ethylene and benzene. Benzene and Ethylene both enter the process at fixed flow rates of 100kmol/hr, 1 atm and 25 ^oC. Both streams are combined and then cooled to meet the desired temperature for the reactor. The following equation describes the addition reaction:

$$\begin{array}{cccc} C_6H_6 & + & C_2H_4 \rightarrow & C_6H_5C_2H_5 \\ benzene & & ethylene & ethylbenzene \end{array}$$

A secondary reaction occurs between EB and ethylene to produce a by-product of diethylbenzene (DEB):

$$\begin{array}{llll} C_6H_5C_2H_5 & + & C_2H_4 \rightarrow & C_6H_4(C_2H_5)_2 \\ ethylbenzene & & ethylene & diethylbenzene \end{array}$$

A third reaction also occurs with formed diethylbenzene and benzene to yield ethylbenzene:

$$\begin{array}{llll} C_6H_4(C_2H_5)_2 & + & C_6H_6 \rightarrow & C_6H_5C_2H_5 \\ diethylbenzene & & benzene & ethylbenzene \end{array}$$

The reactor operates at 65^oC with pressure (in atm) described by the equation below:

$$P_{reactor} = -0.0005\frac{atm}{^oC^2}T^2{}_{reactor} + 0.4325\frac{atm}{^oC}T_{reactor} + 13.056atm \tag{1.1}$$

The first and third reactions both yield ethylbenzene so it is intuitive that we favor the reactions that give us our product. However, diethylbenzene is unfavorable to our process because it poses problems to Styrene production downstream. Hence, no more than 500ppm should be present in the final Ethylbenzene product. The reactor effluent is then sent to a heat exchanger to cool before the pressure is dropped to 2 atm. This drop in temperature and pressure is to achieve better separation of the lighter components, which is ethylene and benzene, from the heavier components, ethylbenzene and diethylbenzene. Utilizing the effects of operating conditions such as pressure and temperature greatly saves costs in utility and cost of raw materials if optimally recycled.

The separation section starts with a reflux drum which separates the gas from the components still in the liquid phase. Leaving the top of the flash drum is gaseous ethylene and benzene with the liquid leaving the bottom of the drum. The liquid stream goes into a distillation column that recovers the raw material, which is benzene. The recovered raw material is then sent to join the benzene feed thereby saving money by reducing the cost of raw materials. A second distillation column is what separates the desired product, ethylbenzene from the undesired product, diethylbenzene which is used for fuel gas on the plant.

A process flow diagram describing this operation is shown in Figure 1.1 below

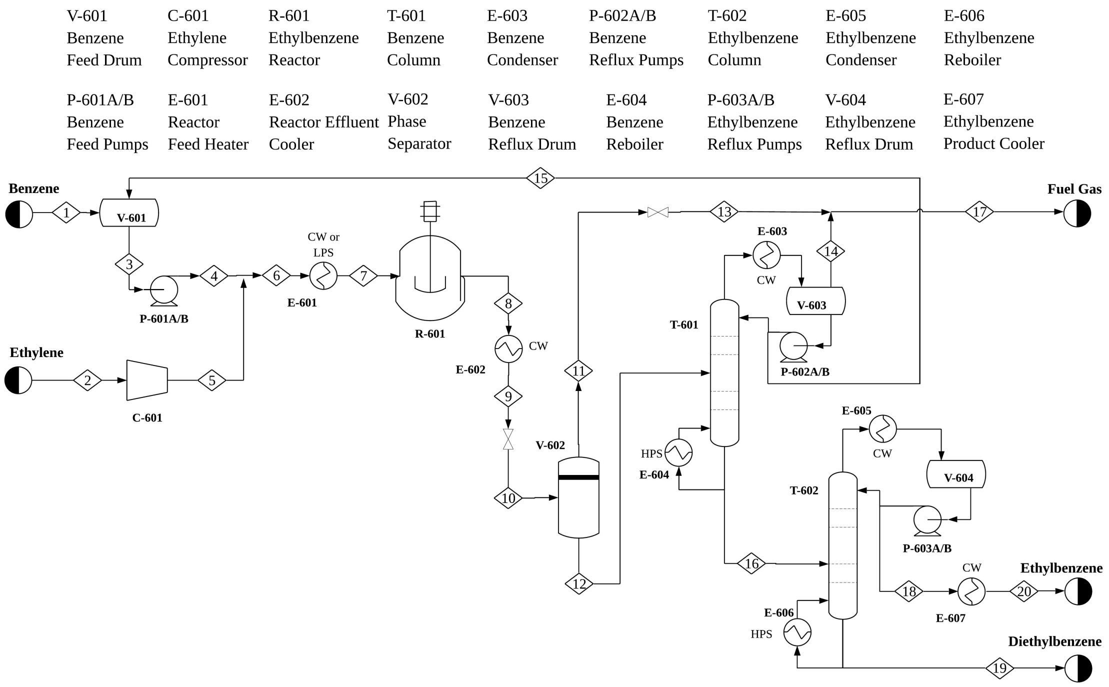


Figure 1.1: Preliminary Process Diagram for the Production of Ethylbenzene from Ethylene and Benzene

To investigate if this process is feasible or not, an economic analysis needs to be performed. To solve for the base case in excel, certain assumptions had to be made:

- assume ideal gases or solution of gases
- the Vapor-Liquid Equillibrium (VLE) calculations are performed based on Raoult's Law which is expressed as:

$$y_i P = x_i P_i^{sat} \tag{1.2}$$

- assume perfect separation in towers
- assume nothing lighter than the light key leaves the top of the and nothing heavier than the heavy key leaves the bottom of the distillation column
- assume the liquid volumes are additive
- assume that the liquid volume leaving the reactor is the same as the liquid volume entering the reactor

All these assumptions were made to simplify calculations and modeling of the base case. It is important to note that these assumptions might lead to incorrect mass balances and that is why simulations are very useful in process engineering. The modeling software helps to correct for errors in simplified assumptions made for calculations to be easier.

1.2 Equipment Sizing

In a chemical plant, the amount and size of equipment present, are based on the estimated amount of process fluid or gas that will be passed through it. The sizing of equipment is based on equations unique to the type of equipment being priced. There are specific parameters that are calculated to determine the cost of the equipment such as area, height, duty .etc. These were determined by following heuristics for designing a chemical facility (see Appendix A)[1].

For example, to size a distillation column, the number of trays, height and diameter were calculated based on certain rules and the flowrate of the process fluid in the vessel [1]. Once these values are determined, the Equivalent Annual Operating Costs (EAOC) is then calculated to determine the cost of each equipment; these equations can be found in Appendix A. These costs are then used to generate the Fixed Capital Cost (FCI) for the production process. Other costs generated are the Cost of Utilities (C_{UT}), Cost of Others (C_{OT}), Cost of Operating Labor (C_{OL}), Raw Materials Cost (C_{RM}), Revenue, all of which can be found in Chapter 7 and 8 of Analysis, Synthesis and Design of a Chemical Process text [1].

1.3 Economic Model

When the size of the equipment had been determined, series of equations were then used to estimate the cost of each equipment. These equations were gotten from the Analysis, Synthesis, and Design of Chemical Processes book[1].These prices were used in the economic analysis section to determine other costs associated with the start-up or continuation of running the plant.

For this case study, the parameter used to determine the feasibility of the project was the Net Present Value (NPV). If the NPV of producing ethylbenzene was higher than its alternative, then it was recommended that further investigation be done to improve the process. The goal was to improve the process to yield higher profit margin and NPV.

1.4 Optimization Process

The beginning of the optimization process started with picking out decision variables that would impact the objective function greatly. These variables are either expected to reduce the cost of raw materials by recovering almost all the benzene in the recycle stream to join the feed benzene or maximize the separation of the product, ethylbenzene from other components. The chosen decision variables were:

- Reactor volume - this variable was chosen because it has a direct impact on how much of the product can be obtained. Increasing the volume favors the conversion of reactant to product due to an increase in the residence time.

$$\tau = \frac{V}{\dot{v}} \tag{1.3}$$

- Reactor temperature - the rate of the reaction is highly dependent on temperature as can be seen in the Appendix A. The reaction kinetics is described by this equation:

$$-r_i = k_{o,i} e^{-\frac{E_i}{RT}} C_{ethylene}^a C_{EB}^b C_{benzene}^d C_{DEB}^e \tag{1.4}$$

- Temperature leaving E-602 - this temperature is critical in setting up the stage for the recovery of benzene. The higher the temperature, the more benzene is recovered to the overhead of T-601
- Pressure entering V-602 - this pressure provides the same set up as temperature exiting E-602

  - Temperature leaving T-601 Overhead - this temperature determined how much of the benzene can be condensed as opposed to burned with the ethylene leaving as fuel gas

These variables were varied to determine their optimum values and to derive a curve showing their effect on the NPV.

1.5 Simulation Process

For the simulation section, the first step in running any plant design on a software is determining what thermal package to use. The thermodynamics package chart in Figure 1.2 was followed to decide on a thermodynamics model.

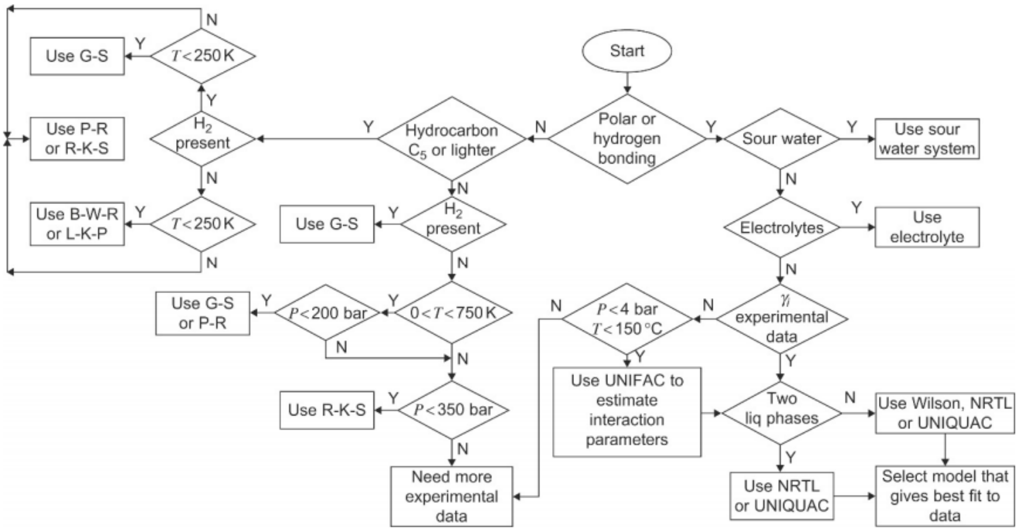


Figure 1.2: Selecting a Thermodynamic Package Chart

Once the thermo package was selected (SRK-SimSci in this case) , the components used were then added to the process in PRO/II. The next step was to reproduce the process flow diagram in the simulation workspace using the features in the software. For the variable conditions, the values calculated in the base case done in excel were entered as the initial estimates. After the PFD is completely drawn in PRO/II, the recovery section is linked to the feed and the process is recompiled to update the results of the simulation due to the more rigorous calculations the thermodynamic packet utilizes.

Chapter 2

Results

After the economic analysis of the plant was done, the base case NPV came out to be \$(75.3)M. The ethylbenzene yield and ethylene conversion were 87.5% and 67.9% at the end of the base case. The overall process was optimized discretely to obtain a local optimum. Excel was sufficient to determine the local optimum for the variables mentioned in the optimization section. The temperature values were varied during the optimization of the reactor from 65 ^oC to 84 ^oC. Table 2.1 below contains the results of the optimization iteration.

Table 2.1: Reactor Temperature Optimization Results (1st Run)

	Variable (^{o}C)	NPV (\$M)
Base Case	65	(103)
Optimized Case	84	(75.5)

Savings = \$ 27.5 M

Once the temperature was optimized, the new value was then used to continue optimization. The second variable optimized was the volume of the reactor. The base case had a liquid volume of 100 m^3 whereas the optimized case had a value of 125 m^3 as the amount of liquid that can be held for a given batch. The results are seen in Table 2.2 below.

Table 2.2: Reactor Volume Optimization Results (1st Run)

	Variable (m^3)	NPV ($M)
Base Case	100	(75.5)
Optimized Case	123	(75.3)

Savings = $ 0.2 M

This concludes the optimization of the reactor section. Next, the recovery of product and raw materials were optimized. The first variable in this was the temperature leading into the recovery section. The base case demands that the temperature into V-602 be 50 ^oC but the optimum temperature that yields the most recovery of raw materials and separation of product was found to be 95 ^oC. Table 2.3 below shows the relevant data collected from the optimization.

Table 2.3: Temperature leaving E-602 Optimization Results (1st Run)

	Variable (^{o}C)	NPV ($M)
Base Case	50	(75.3)
Optimized Case	95	(37.3)

Savings = $ 38 M

Next, the pressure into the flash drum was optimized. A valve regulates the pressure drop and the base case which was set at 2 atm was optimized as seen in Table 2.4 below.

Table 2.4: Pressure Entering V-602 Optimization Results (1st Run)

	Variable (atm)	NPV ($M)
Base Case	2	(37.3)
Optimized Case	1.85	(36.5)

Savings = $ 0.8 M

Finally, the temperature of the overhead condenser of the benzene column was optimized. This temperature is critical in recovering the majority of the unused liquid benzene instead of vaporizing it to be burned with the ethylene fuel gas. Although the gas is counted as a credit when calculating the cost of utilities, more money is saved when raw materials are utilized as this constitutes a major part of the costs associated with a plant. Table 2.5 below shows the base case and optimized case going from a temperature of 75^oC to 55^oC

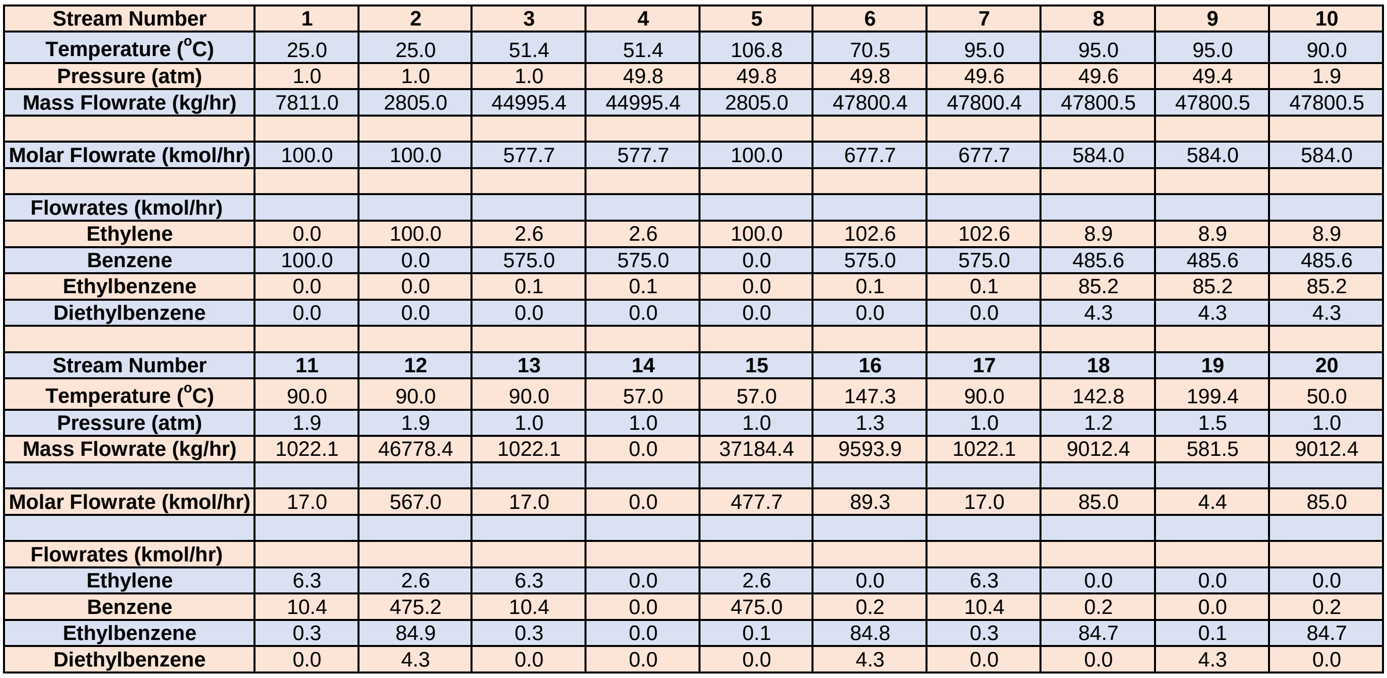
Table 2.5: Temperature leaving T-601 Optimization Results (1st Run)

	Variable (^{o}C)	NPV ($M)
Base Case	75	(36.5)
Optimized Case	55	(25.9)

Savings = $ 10.6 M

A second optimization set was done because it was discovered that changing each variable had an impact on the other variables, thereby affecting the overall outcome of the NPV. After a second run through of optimization, the final NPV determined from this simulation model came out to be \$1.4M. Although the NPV seems economically unattractive, it is still the better alternative compared to other options. If the company were to go the other economic route of buying ethylbenzene, instead of producing it, their NPV would be \$(700.2)M.

The figures below show the Stream tables derived from Excel and Pro II respectively. It is seen that there are disparities in the values from both simulation software. This can be attributed to the fundamental assumptions that they operate on.



Stream Number	1	2	3	4	5	6	7	8	9	10
Temperature (^oC)	25.0	25.0	51.4	51.4	106.8	70.5	95.0	95.0	95.0	90.0
Pressure (atm)	1.0	1.0	1.0	49.8	49.8	49.8	49.6	49.6	49.4	1.9
Mass Flowrate (kg/hr)	7811.0	2805.0	44995.4	44995.4	2805.0	47800.4	47800.4	47800.5	47800.5	47800.5
Molar Flowrate (kmol/hr)	100.0	100.0	577.7	577.7	100.0	677.7	677.7	584.0	584.0	584.0
Flowrates (kmol/hr)										
Ethylene	0.0	100.0	2.6	2.6	100.0	102.6	102.6	8.9	8.9	8.9
Benzene	100.0	0.0	575.0	575.0	0.0	575.0	575.0	485.6	485.6	485.6
Ethylbenzene	0.0	0.0	0.1	0.1	0.0	0.1	0.1	85.2	85.2	85.2
Diethylbenzene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.3	4.3	4.3
Stream Number	11	12	13	14	15	16	17	18	19	20
Temperature (^oC)	90.0	90.0	90.0	57.0	57.0	147.3	90.0	142.8	199.4	50.0
Pressure (atm)	1.9	1.9	1.0	1.0	1.0	1.3	1.0	1.2	1.5	1.0
Mass Flowrate (kg/hr)	1022.1	46778.4	1022.1	0.0	37184.4	9593.9	1022.1	9012.4	581.5	9012.4
Molar Flowrate (kmol/hr)	17.0	567.0	17.0	0.0	477.7	89.3	17.0	85.0	4.4	85.0
Flowrates (kmol/hr)										
Ethylene	6.3	2.6	6.3	0.0	2.6	0.0	6.3	0.0	0.0	0.0
Benzene	10.4	475.2	10.4	0.0	475.0	0.2	10.4	0.2	0.0	0.2
Ethylbenzene	0.3	84.9	0.3	0.0	0.1	84.8	0.3	84.7	0.1	84.7
Diethylbenzene	0.0	4.3	0.0	0.0	0.0	4.3	0.0	0.0	4.3	0.0

Figure 2.1: Excel Stream Table

Stream Number	1	2	3	4	5	6	7	8	9	10
Temperature (°C)	25.0	25.0	48.5	49.4	94.2	62.1	95.0	95.0	95.0	90.4
Pressure (atm)	1.0	1.0	1.0	49.8	49.8	49.8	49.6	49.6	49.4	1.9
Mass Flowrate (kg/hr)	7811.0	2805.0	35465.6	35465.6	2805.0	38270.6	38270.6	38270.6	38270.6	38270.6
Molar Flowrate (kmol/hr)	100.0	100.0	455.1	455.1	100.0	555.1	555.1	463.5	463.5	463.5
Flowrates (kmol/hr)										
Ethylene	0.0	100.0	1.7	1.7	100.0	101.7	101.7	10.1	10.1	10.1
Benzene	100.0	0.0	453.3	453.3	0.0	453.3	453.3	366.9	366.9	366.9
Ethylbenzene	0.0	0.0	0.1	0.1	0.0	0.1	0.1	81.2	81.2	81.2
Diethylbenzene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.3	5.3	5.3
Stream Number	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
Temperature (°C)	90.4	90.4	89.1	55.0	55.0	147.5	88.2	142.5	200.2	50.0
Pressure (atm)	1.9	1.9	1.0	1.0	1.0	1.3	1.0	1.2	1.5	1.0
Mass Flowrate (kg/hr)	1288.5	36982.1	1288.5	32.7	27654.7	9294.7	1321.2	8582.3	712.4	8582.3
Molar Flowrate (kmol/hr)	21.4	442.1	21.4	0.7	355.1	86.3	22.1	81.0	5.3	81.0
Flowrates (kmol/hr)										
Ethylene	8.0	2.1	8.0	0.4	1.7	0.0	8.4	0.0	0.0	0.0
Benzene	12.8	354.1	12.8	0.3	353.3	0.5	13.1	0.5	0.0	0.5
Ethylbenzene	0.6	80.6	0.6	0.0	0.1	80.5	0.6	80.4	0.1	80.4
Diethylbenzene	0.0	5.2	0.0	0.0	0.0	5.2	0.0	0.0	5.2	0.0

Figure 2.2: PRO/II Stream Table

As stated earlier; Excel uses a more simplistic approach by assuming an Ideal gas described by the ideal gas equation seen below.

$$pV_m = nRT \tag{2.1}$$

where p = Pressure

V$_m$ = molar Volume

n = number of moles of a substance

R = Ideal gas constant

T = Temperature

Pro II on the other hand uses more intricate algorithms to simulate a more realistic gas; specifically the Soave modification of Redlich-Kwong described by the equation below.

$$p = \frac{RT}{V_m - b} - \frac{a\alpha}{V_m(V_m + b)} \tag{2.2}$$

where $a = \frac{0.42747R^2T_c^2}{P_c}$

$b = \frac{0.08664RT_c}{P_c}$

$\alpha = (1 + (0.48508 + 1.55171\omega - 0.15613\omega^3)(1 - T_r^{0.5}))^2$

$T_r = \frac{T}{T_c}$

The ideal gas equation expresses an inverse relationship between the pressure and the molar volume whereas the Soave Redlich-Kwong equation expresses an inverse relationship between the pressure and the cube of the molar volume. This difference causes a variation in the results as the ideal gas operates linearly while the SRK equations operates exponentially. This variation is further compounded by the fact that the production process has so many interrelated variables affecting the resulting product. Of the two equations, the Soave Redlich-Kwong equation behaves more like a real gas and therefore yields more accurate results.

A case of the ideal gas assumption was run on PRO/II and resulted in slightly higher numbers in terms of the flowrate and conversion but lower values compared to when it was run on excel. The results of using PRO/II and Ideal Gas Law may differ in flowrates, the conversion and yield are relatively the same. This is because the process operates within the range were there is not much deviation from ideality, hence, delivering similar results. However, the SRK equation of state does not overestimate how much benzene is truly being recovered, nor the flowrate of ethylbenzene being sent to storage. Also, a liquid phase reaction should not be modeled using a law that describes ideal gases. This is where SRK is used and is the better fit of the data than Ideal Gas Law equation.

Chapter 3

Conclusion

The goal of this study was to evaluate the accuracy of three simulation models: Excel, PRO/II and SimCentral. Excel and Pro/II were used to perform an economic analysis of the production of Ethylbenzene however a SimCentral simulation could not be performed due to the COVID-19 pandemic. The base case variables were inputted into both models to simulate the calculations for a fully functioning operation. The reactor volume and temperature, temperature leaving E-602, pressure entering V-602 and the Temperature leaving the T-601 overhead condenser were used to optimize the base case to yield the discrete optimum for the process. The accuracy was determined based on the intricate assumptions made by the model and the highest economic value determined.

When optimizing,a higher temperature and volume than the base case is intuitively ideal for optimum conversion and residence time for more of the products to be formed. For the recovery section, there was first an increase in temperature into the flash drum and then a decrease in the temperature leaving the condenser of T-601. This does not initially make sense when looking at the process linearly as opposed to holistically. Since the process contains a recycle and goes through multiple iterations, new values are updated when there is a change upstream the production process. The increased temperature into the flashdrum drove more benzene to the overhead of the tower thereby resulting in more recovery of raw material. The increased benzene recycle changed the concentrations in the reactor, causing more ethylene to be reacted, therefore increasing the conversion rate of ethylene to ethylbenzene. Since less ethylene left the reactor, there was close to none leaving the flashdrum when the temperature was increased. So the high temperature aided the benzene to be driven overhead, as mentioned before and since there was a decrease in temperature of the overhead condenser, more liquid benzene was formed, recovering the raw material from the fuel gas stream out of the partial condenser. Since there was more unused benzene being recycled into the system, reaction 3 was favored, so the benzene reacted with the formed DEB to give more ethylbenzene, hence more products and higher revenue. This process shows why one cannot limit the analysis of an operating change to one piece of equipment and must look at the impact on the entire process.

The result of using the ideal gas equations for the chemical reactions resulted in the least accurate results. This is because of the simplified assumption that the gases are monatomic and that they exhibit no attractive forces. PRO/II simulation on the other hand, yielded more accurate results since they were calculated using exponential-based equations that take into consideration the non-ideality of the gases. The conversion and results from PRO/II show a slightly lower conversion and yield and this is expected because the calculations done on PRO/II are more strict in terms of the assumptions made, so there may not be as high a conversion as in Excel. The initial base case had a 87% conversion of the raw materials and a 69% yield of ethylbenzene. After optimization, Excel's values for conversion and yield were 91% and 92% respectively while that of PRO/II were 89% and 90%. It was expected that the conversion and yield in PRO/II results were lower because the calculations utilized the Soave-Redlich-Kwong cubic equation of state which is a more complex equation of state.

Bibliography

[1] R. Turton, R. C. Bailie, W. B. Whiting, and J. A. Shaeiwitz, *Analysis, synthesis and design of chemical processes*. Pearson Education, 2008.

Appendix A

Heuristics Tables

All the Heuristics tables in Appendix A were obtained from Analysis, Synthesis and Design of Chemical Processes Fifth Edition[1]

Table 3.1: Heuristics for Pumps

1. Power for pumping liquids: kW = (1.67)[Flow(m^3 /min)][ΔP(bar)]/ϵ, [hp = Flow(gpm) Δ(psi)/1714/ϵ], = Fractional Efficiency = ϵ (see Table 11.5).
2. Net positive suction head (NPSH) of a pump must be in excess of a certain number, depending upon the kind of pumps and the conditions, if damage is to be avoided. NPSH = (pressure at the eye of the impeller – vapor pressure)/(ρ g). Common range is 1.2–6.1 m of liquid (4–20 ft).
3. Specific speed N = (rpm)(gpm)^0.5 /(head in feet)^0.75 . Pump may be damaged if certain limits on N$_S$ are exceeded, and the efficiency is best in some ranges.
4. Centrifugal pumps: single stage for 0.057–18.9 m^3 /min (15–5000 gpm), 152 m (500 ft) maximum head; multistage for 0.076–41.6 m^3 /min (20–11,000 gpm), 1675 m (5500 ft) maximum head. Efficiency 45% at 0.378m^3 /min (100 gpm), 70% at 1.89 m^3/min (500 gpm), 80% at 37.8m^3 /min (10,000 gpm).
5. Axial pumps for 0.076–378 m /min (20–100,000 gpm), 12 m (40 ft) head, 65%–85% efficiency.
6. Rotary pumps for 0.00378–18.9 m /min (1–5000 gpm), 15,200 m (50,000 ft head), 50%–80% efficiency.
7. Reciprocating pumps for 0.0378–37.8 m /min (10–10,000 gpm), 300 km (1,000,000 ft) head max. Efficiency 70% at 7.46 kW (10 hp), 85% at 37.3 kW (50 hp), and 90% at 373 kW (500 hp).

Table 3.2: Heuristics for Heat Exchangers

1. For conservative estimate set F = 0.9 for shell-and-tube exchangers with no phase changes, q = UAF$\Delta T_i m$. When ΔT at exchanger ends differ greatly, then check F, and reconfigure if F is less than 0.85.
2. Standard tubes are 1.9 cm (3/4 in) OD, on a 2.54 cm (1 in) triangle spacing, 4.9 m (16 ft) long. A shell 30 cm (1 ft) dia. accommodates 9.3 m^2 (100 ft^2) 60 cm (2 ft) dia. accommodates 37.2 m^2 (400 ft^2) 90 cm (3 ft) dia. accommodates 102 m^2 (1100 ft^2)
3. Tube side is for corrosive, fouling, scaling, and high-pressure fluids.
4. Shell side is for viscous and condensing fluids.
5. Pressure drops are 0.1 bar (1.5 psi) for boiling and 0.2–0.62 bar (3–9 psi) for other services.
6. Minimum temperature approach is 10^{o}C (20^{o}F) for fluids and 5^{o}C(10^{o}F) for refrigerants.
7. Cooling water inlet is 30^{o}C (90^{o}F), maximum outlet 45^{o}C (115^{o}F).
8. Heat transfer coefficients for estimating purposes, W/m ^{o}C (Btu/hrft ^{o}F): water to liquid, 850 (150); condensers, 850 (150); liquid to liquid, 280 (50); liquid to gas, 60 (10); gas to gas 30 (5); reboiler 1140 (200). Maximum flux in reboiler 31.5 kW/m (10,000 Btu/hr ft). When phase changes occur, use a zoned analysis with appropriate coefficient for each zone.
9. Double pipe exchanger is competitive at duties requiring 9.3–18.6 m^2(100–200 ft^2).
10. Compact (plate and fin) exchangers have 1150 m^2 /m^3 (350 ft^2 /ft^3), and about 4 times the heat transfer per cut of shell-and-tube units.
11. Plate and frame exchangers are suited to high-sanitation services and are 25%–50% cheaper in stainless steel construction than shell-andtube units.
12. Air coolers: Tubes are 0.75–1.0 in. OD, total finned surface 15–20m^2 /m^2 (ft^2 /ft^2 bare surface), U = 450–570 W/m^2 ^{o}C (80–100 Btu/hr ft^2(bare surface) ^{o}F). Minimum approach temperature = 22^{o}C (40^{o}F). Fan input power = 1.4–3.6 kW/(MJ/h) [2–5 hp/(1000 Btu/hr)].
13. Fired heaters: Radiant rate, 37.6 kW/m^2 (12,000 Btu/hr ft^2); convection rate, 12.5 kW/m^2 (4000 Btu/hr ft^2); cold oil tube velocity = 1.8 m/s (6ft/sec); approximately equal transfer in the two sections; thermal efficiency 70%–90% based on lower heating value; flue gas temperature 140^{o}C–195^{o}C (250^{o}F–350^{o}F) above feed inlet; stack gas temperature 345^{o}C–510^{o}C (650^{o}F–950^{o}F).

Table 3.3: Heuristics for Compressor

1. Fans are used to raise the pressure about 3% 12 in (30 cm) water, blowers to raise less than 2.75 barg (40 psig), and compressors to higher pressures, although the blower range is commonly included in the compressor range.
2. Theoretical reversible adiabatic power = mz RT $[(P_2/P_1{}^3 - 1)]$/a where T is inlet temperature, R = gas constant, z = compressibility, m = molar flow rate, a = (k – 1)/k, and k = C_v/C_p . Values of R: = 8.314 J/mol K = 1.987 Btu/lbmol R = 0.7302 atm ft^3 /lbmol R
3. Outlet temperature for reversible adiabatic process T = T (P /P)^a .
4. Exit temperatures should not exceed 167^{o}C–204^{o}C (350^{o}F–400^{o}F); for diatomic gases C_p/C_v = 1.4. This corresponds to a compression ratio of about 4.
5. Compression ratio should be about the same in each stage of a multistage unit, ratio = $(P_n/P_1)^{1/n}$, with n stages.
6. Efficiencies of reciprocating compressors: 65% at compression ratios of 1.5, 75% at 2.0, and 80–85% at 3–6.
7. Efficiencies of large centrifugal compressors, 2.83–47.2 m /s (6000–100,000 acfm) at suction, are 76–78%.
8. For vacuum pumps use the following: Reciprocating piston type Down to 1 Torr, Rotary piston type Down to 0.001 Torr, Two-lobe rotary type Down to 0.0001 Torr, Steam jet ejectors 1-stage down to 100 Torr, 3-stage down to 1 Torr, 5-stage down to 0.05 Torr

6\. A three-stage ejector needs 100 kg steam/kg air to maintain a pressure of 1 Torr.

7\. In-leakage of air to evacuated equipment depends on the absolute pressure, Torr, and the volume of the equipment, V in m^3 (ft^3) according to W = kV$^{2/3}$ kg/h (lb/hr) with k = 0.98 (0.2) when P ¿ 90 Torr, k = 0.39 (0.08) between 3 and 20 Torr, and k = 0.12 (0.025) at less than 1 Torr. See Chapter 23 for more details.

Table 3.4: Heuristics for Process Vessels (Drums)

1. Drums are relatively small vessels that provide surge capacity or separation of entrained phases.
2. Liquid drums are usually horizontal.
3. Gas-liquid phase separators are usually vertical.
4. Optimum ratio of length to diameter = 3, but the range 2.5 to 5 is common.
5. Holdup time is 5 min for half-full reflux drums and gas/liquid separators, 5–10 min for a product feeding another tower.
6. In drums feeding a furnace, 30 min for half-full drum is allowed.
7. Knockout drums placed ahead of compressors should hold no less than times the liquid volume passing per minute.
8. Liquid-liquid separations are designed for settling velocity of 0.085–0.127 cm/s (2–3 in/min).
9. Gas velocity in gas/liquid separators, $u = k\sqrt{\rho_1/\rho_v - 1}$ m/s (ft sec)k = 0.11(0.35) for systems with mesh deentrainer, and k = 0.0305 (0.1) without mesh deentrainer.
10. Entrainment removal of 99% is attained with 10.2–30.5 cm (4–12 in) mesh pad thickness; 15.25 cm (6 in) thickness is popular.
11. For vertical pads, the value of the coefficient in Step 9 is reduced by a factor of 2/3.
12. Good performance can be expected at velocities of 30%–100% of those calculated with the given k; 75% is popular.
13. Disengaging spaces of 15.2–45.7 cm (6–18 in) ahead of the pad and 30.5cm (12 in) above the pad are suitable.
14. Cyclone separators can be designed for 95% collection at 5 μm particles,but usually only droplets greater than 50 μm need be removed.

Table 3.5: Heuristics for Distillation Towers (Gas Distillation and Absorption)

1. For reasons of accessibility, tray spacings are made 0.5–0.6 m (20–24in).
2. Peak efficiency of trays is at values of the vapor factor F = uρ in the range of 1.2–1.5 m/s kg/m^{30}.5 [1–1.2 ft/s lb/ft^{30}.5]. This range of F_s establishes the diameter of the tower. Roughly, linear velocities are 0.6 m/s (2 ft/sec) at moderate pressures, and 1.8 m/s (6 ft/sec) in vacuum.
3. Pressure drop per tray is on the order of 7.6 cm (3 in) of water or 0.007 bar (0.1 psi).
4. Tray efficiencies for distillation of light hydrocarbons and aqueous solutions are 60%–90%; for gas absorption and stripping, 10%–20%.
5. Sieve trays have holes 0.6–0.7 cm (0.25–0.5 in) dia., area being 10% of the active cross section.
6. Valve trays have holes 3.8 cm (1.5 in) dia. each provided with a liftable cap, 130–150 caps/m^2 (12–14 caps/ft^2) of active cross section. Valve trays are usually cheaper than sieve trays.
7. Bubblecap trays are used only when a liquid level must be maintained at low turndown ratio; they can be designed for lower pressure drop than either sieve or valve trays.
8. Weir heights are 5 cm (2 in), weir lengths are about 75% of tray diameter, liquid rate—a maximum of 1.2 m^3/min m of weir (8 gpm/in of weir); multipass arrangements are used at higher liquid rates.

Equipment Pricing

Installed Cost = Purchased Cost (4 + MF + PF)

where MF is the material factor and PF is the pressure factor.

Pressure Factors

Pressure (absolute)	Pressure Factor
P ≤ 10 atm	0
10 atm < P ≤ 20 atm	0.6
20 atm < P ≤ 40 atm	3.0
40 atm < P ≤ 60 atm	5.0
60 atm < P ≤ 100 atm	10

Compressors

$$PC_{compressor} = 500\dot{W}^{0.96} + 400\dot{W}^{0.6}$$

with the purchase cost ($PC_{compressor}$) in \$ and the power ($\dot{W}$) in kW.

Pumps

$$PC_{pump} = 5,000\dot{W}^{0.69}$$

with PC_{pump} in \$ and $\dot{W}$ in kW.

Vessels

$$PC_{vessel} = (1.67x10^{z})(0.959 + 0.041P_{vessel} - 8.3x10^{-6}P_{vessel}^{2})$$

$$z = 3.17 + 0.2D + 0.5\log_{10} L + 0.21\log_{10}(L^{2})$$

with PC_{vessel} in \$, the diameter (D) in m, the height or length (L) in m, and the absolute pressure (P_{vessel}) in bar.

Heat Exchangers

$$PC_{HX} = 1,030A^{0.6}$$

with PC_{HX} in \$ and A in m^2.

Reactors

$$PC_{reactor} = 5,000V_{reactor}^{0.85}$$

with $PC_{reactor}$ in \$ and $V_{reactor}$ in m^3.

Towers

$$PC_{tower} = 30,000V_{column}^{0.85}$$

with PC_{tower} in \$ and V_{tower} in m^3. PC_{tower} includes the cost of the reflux pumps.

Reboilers

$$PC_{reboiler} = 3PC_{condenser}$$

with the cost of steam 20 times the cost of cooling water in the condenser.

Appendix B

Optimization Results

Table 3.6: Reactor Temperature Optimization 1

Trial	Variable (^{o}C)	Revenue (\$M)	C$_{UT}$ (\$M)	C$_{OT}$ (\$M)	NPV (\$M)
1	50	400	(-12.3)	(-187)	(-246)
2	65	685	(-8.9)	(-184)	(-103)
3	75	737	(-8.01)	(-186)	(-78.5)
4	84	743	(-7.76)	(-186)	(-75.5)
5	90	742	(-7.69)	(-185)	(-76)

Table 3.7: Reactor Volume Optimization 1

Trial	Variable(m^3)	Revenue($M)	C_{UT} ($M)	C_{OT} ($M)	NPV ($M)
1	90	741	(-7.81)	(-185)	(-75.8)
2	100	743	(-7.76)	(-186)	(-75.5)
3	110	744	(-7.71)	(-186)	(-75.4)
4	123	746	(-7.66)	(-187)	(-75.3)
5	130	746	(-7.64)	(-187)	(-75.3)

Table 3.8: Temperature leaving E-602 Optimization 1

Trial	Variable (^{o}C)	Revenue($M)	C_{UT} ($M)	C_{OT} ($M)	NPV ($M)
1	50	746	(-7.66)	(-187)	(-75.3)
2	60	775	(-9.38)	(-188)	(-62.6)
3	75	812	(-9.58)	(-189)	(-45.8)
4	95	834	(-11.)	(-190)	(-37.3)
5	100	832	(-11.)	(-190)	(-38.3)

Table 3.9: Pressure Entering V-602 Optimization 1

Trial	Variable(atm)	Revenue($M)	C_{UT} ($M)	C_{OT} ($M)	NPV ($M)
1	1.5	833	(-11.2)	(-190)	(-37.9)
2	1.7	836	(-11.3)	(-190)	(-36.6)
3	1.85	836	(-11.3)	(-190)	(-36.5)
4	2	834	(-11.)	(-190)	(-37.3)
5	2.5	819	(-10.1)	(-189)	(-43.4)

Table 3.10: Temperature leaving T-601 Optimization 1

Trial	Variable (^{o}C)	Revenue($M)	C_{UT} ($M)	C_{OT} ($M)	NPV ($M)
1	50	876	(-17.6)	(-196)	(-26.)
2	55	876	(-17.7)	(-196)	(-25.9)
3	65	869	(-16.8)	(-195)	(-28.2)
4	70	864	(-14.9)	(-194)	(-28.3)
5	75	836	(-11.3)	(-190)	(-36.5)

Table 3.11: Reactor Temperature Optimization 2

Trial	Variable (^{o}C)	Revenue (\$M)	C$_{UT}$ (\$M)	C$_{OT}$ (\$M)	NPV (\$M)
1	80	841	(-18.3)	(-197)	(-43.6)
2	84	876	(-17.7)	(-196)	(-25.9)
3	90	911	(-17.7)	(-196)	(-9.5)
4	95	934	(-18.3)	(-197)	(1.16)

Table 3.12: Reactor Volume Optimization 2

Trial	Variable(m^3)	Revenue (\$M)	C$_{UT}$ (\$M)	C$_{OT}$ (\$M)	NPV (\$M)
1	120	932	(-18.3)	(-197)	(0.423)
2	123	934	(-18.3)	(-197)	(1.16)
3	124	935	(-18.4)	(-197)	(1.4)

Table 3.13: Temperature leaving E-602 Optimization 2

Trial	Variable (^{o}C)	Revenue (\$M)	C$_{UT}$ (\$M)	C$_{OT}$ (\$M)	NPV (\$M)
1	90	947	(-23.8)	(-202)	(0.0613)
2	95	935	(-18.4)	(-197)	(1.4)

Table 3.14: Pressure Entering V-602 Optimization 2

Trial	Variable (atm)	Revenue (\$M)	C$_{UT}$ (\$M)	C$_{OT}$ (\$M)	NPV (\$M)
1	1.85	935	(-18.4)	(-197)	(1.4)

Table 3.15: Temperature leaving T-601 Optimization 2

Trial	Variable (^{o}C)	Revenue ($M)	C$_{UT}$ ($M)	C$_{OT}$ ($M)	NPV ($M)
1	57	935	(-18.4)	(-197)	(1.4)
2	58	934	(-18.4)	(-197)	(0.979)
3	59	933	(-18.4)	(-197)	(0.559)
4	60	932	(-18.3)	(-197)	(0.136)