**Carbon Dioxide Mitigation- Case Study**

**Case Study Background**

The largest Ammonia plant in the U.S, owned by CF industries and located in Donaldsonville, LA, is estimated to have total CO2 emissions of around 2.1 Million tones per year. There is rising pressing needs for the plant to reduce its carbon emissions according to new environmental laws in an attempt to reduce global warming effects. The plant managers investigate the possibility of sequestering the emitted carbon dioxide into value-added chemicals by scaling up few of the novel processing routes reported in research literature. Alternatively, the plant is required to pay expensive carbon social cost for each tonne of CO2 emitted. In order to maximize the profit, the plant chemical engineers thoroughly studied the process chemistry literature of the four most in demand value-added chemicals: Propylene Carbonate (PC), Phenol (Ph), Benzoic Acid(BA) and Ethylene Glycol(EG).

This series of activities focus on using process integration and optimization tools to select the most profitable process or processes that would fix as much of the available CO2 as possible. The activity starts by formulating empirical profit maximization function, and then stepwise guided activities would allow the students to gradually build on the profit function to integrate important process economics factors. Basic knowledge of material and energy balance is expected to take on this activity. Although prior knowledge of process design and economics could be helpful, the concepts could be learned by the students as they go through the activity as well. The activity would also use process simulation and optimization software including ASPEN PLUS and LINGO respectively. The LINGO optimization software would allow students to create different scenarios for price sensitivity, capacity constraints, utility prices, carbon credit, and carbon social cost to take the decision that would result in the maximum profit possible.

The first activity starts with benchmarking the potential profitability of the four processes by calculating the MISR ratios. Afterwards, the students are prompted to calculate the Modified-MISR to take into account the possible effect of the utility cost of the reactor. The results from these two calculations would serve as an important reference for the results of the subsequent activities. Material balance calculations for each process is then performed to serve as optimization constraints. An empirical profit equation is formulated, and the subsequent activities would allow the students to add total plant utility cost, fixed capital investment, carbon credit and carbon social cost to mimic the real industrial profit case study. Assigning dollar value to carbon credit for fixing CO2 and carbon social cost to CO2 from utility production depicts the bigger picture of product lifecycle assessment. In a sense, the case study embeds the actual CO2 fixed in terms of profit value which is the significant metric for company stakeholders. The are guided seven activities in this educational module. Each activity includes three parts. Part I is aimed to be an introduction to the main goal of the activity. Part II guides the students to carry out the activity through detailed instructions. Part III provides students with additional insights and allows them to explore and evaluate their results. In addition, part III is a graded activity to be turned in for credit.

**Activity 1: Benchmarking profitability of the processes**

It is advisable to go through the following source before proceeding with this activity. Read chapter 2 about process economics and profitability.

“Halwagi M. M. 2012, Sustainable Design Through Process Integration: Fundamentals and Applications to Industrial Pollution Prevention, Resource Conservation, and Profitability Enhancement”. ISBN 978-1-85617-744-3”.

**Part I: Purpose**

Before trying to optimize profit for chemical processes, we need first to have some reference or “initial guess” about the profitability of the four possible chemical processes. Calculating the MISR ratio would give us an initial idea about how profitable one process is, and we can rank the processes according to their profitability. However, you need to be careful that the actual results of the profit maximization function may not match the MISR predictions, and that is fine. A process might seem very profitable according to MISR, but when accounting for other process economic factors like plant utilities, fixed capital investment, or even carbon tax, it may not stand profitable at all. Nonetheless, it is always useful in the engineering and science fields to base your decisions on a reference.

**Part II: Exploring**

Directions:

1-After reading about the four possible processing routes, find out the selling prices of the raw materials and main products of each process. For now, assume that the carbon dioxide is obtained free of charge. A good place to start searching for selling prices of chemicals is <http://www.icis.com/chemicals/channel-info-chemicals-a-z/>. If you cannot find the price of your chemical in this list, try to look for chemical vendors in Google or otherwise.

2-Now that you have determined the selling prices of your chemicals, open your spreadsheet program. Populate your selling price values, and calculate the MISR ratios as outlined in the overview document or the resource above.

**Part III: Reflection**

Now that you have determined your MISR, try to reflect and find answers to the following questions. Try to base your argument on facts not opinions, and state why or why not the results the way they are

1. According to the MISR ratio results, which process is the most profitable? Which is the least profitable? Is it always that the most profitable process is the one that is most in demand in the chemicals market? Why or why not?
2. You may have found prices that are not up-to-date and that is because chemical vendors try to keep such sensitive information or the price reports are usually overpriced. Nonetheless, do you think that prices of the chemicals in these processes change drastically over time? If yes, what factors led to such changes? If not, what are plausible reasons do you think that might explain the stability of chemical prices? Does it depend on the individual chemical?

**Activity 2: Effect of utilities on benchmarking results**

This activity requires the use of ASPEN PLUS. Your instructor should give you initial tutorial about how to access and use the software. Try to save all your files for future reference.

**Part I: Purpose**

You might notice that the MISR ratios is dependent only on the selling prices of chemicals, and there are a lot of other factors that affect the profitability of the process. Some claims state that the utility cost of the reactor might be one of the determining factors in the profitability since there is usually considerable heating or cooling requirement for any endothermic or exothermic respectively in a chemical plant. In this activity, you will use ASPEN PLUS software to calculate the actual heat of reaction to determine the heating or cooling duty on a process. Afterwards, you would recalculate the MISR ratios while taking into account this utility cost. For simplification purposes, you would assume that all the available CO2 from the ammonia plant goes into each of the four processes, and you would base all your calculations on that assumption.

**Part II: Exploring**

1. From the supplied process chemistry readings, determine the operating conditions like temperature and pressure of the reaction. (Ignore all kinetics data because it is out of the scope of this module).
2. As prompted by your instructor, open the *Rstoic* model in ASPEN PLUS, enter all your reactants and products component. Mark all your chemical species to be in stoichiometric ratios in molar amount. Designate one stream for each chemical species. The reactants should be at room temperature, and the product stream conditions should be as that of the reactor.
3. Run the model, and go to “Results” tab. You will find the molar enthalpy of each stream. Take the difference between the summation of the molar enthalpies of the products and that of the reactants. This should be your actual heat of raction.
4. Calculate your utility cost of each reaction assuming 100% conversion of CO2 (Take the utility price of HP steam to be $4/MM Btu and that of cooling water to be $1/MMBtu)
5. Multiply your yearly capacity of the product and reactants by their respective selling prices. Add your utility cost per year to the yearly cost of the raw material. Now, recalculate the MISR ratios.

**Part III: Reflection**

Now that you have taken into account the potential utility cost of the reactor, try to re-evaluate your decisions from the previous activity, and answer the following questions. Give reasons.

1-How does the utility cost affect the MISR ratio? Did the process profitability rank change after accounting for the utility costs? Explain your answer.

2-Which process is the most utility consuming? Why? Why do you think the cost of HP steam is higher than that of cooling water? Do you think that utility cost of the reactor accurately represents the actual plant utility cost? Explain your reasoning.

**Activity 3: Material balance for the processes**

**Part I: Reflection**

This activity is aimed to write the material balance equations that govern the conversion of raw materials into products. These equations are important as we start to develop the profit optimization problem. The equations would serve as constraints to the profit maximization function. This activity is simple, but yet crucial for successful implementation of the model. It is advisable to go through your old notes of your mass balance class and brush on your skills to carry out this activity.

**Part II: Exploring**

1. Draw a Process box for all your inputs and outputs for each process. It is advisable to designate one stream for each chemical species for simplification purposes. Try to choose your variables carefully, and make sure to distinguish between raw material variables that might go into more than one process.
2. Write down your overall mass balance for each process; in such a way that the summation of all the species to be zero (This step will make it easier to write up the optimization problem in the next activity in LINGO software). Make sure your all your variables are in tones/year. (Also notice the difference between Metric tone and U.S ton).
3. Write down the component mass balance for N-1 components for each process. Where N is the number of components in a given process. Make sure again that your equations have all the variables add up to zero.

**Part III: Reflection**

1. Looking at your mass balance equations, which process gives the most amount of product for every tone of CO2 fixed? Which process do you think has the maximum CO2 fixture? Which process do you think has the maximum carbon element fixture into main product?
2. In part II, you were instructed to write only N-1 component balance equations. Explain why doing so is crucial for an optimization problem?

**Activity 4: Formulating basic profit maximization function**

**Part I: Reflection**

This main purpose of this activity is to learn and get used to using LINGO optimization software via formulating an empirical profit function. By empirical, we mean that no complex process economics factors are taken into consideration. Empirical profit is the gross profit collected by selling the chemical commodity less than the price of raw materials and reactor utilities. As you will see in upcoming activities, the empirical profit maximization function can be modified to incorporate more complex factors like fixed capital investment and other significant profit factors. However, for now this activity focuses on building the backbone of profit optimization. You will compare the results obtained from this empirical function to the benchmark results for reference and analysis.

**Part II: Exploring**

1-Open LINGO software as directed by your instructor. Save a new file with your initials. You can have a look at this example problem video that introduces LINGO language. It is a short video that teaches you the syntax quickly and clearly: https://www.youtube.com/watch?v=8K5lwGfXVF8

2-Write down all the selling prices of all the raw materials and products of all processes.

3-Write down the optimization function in linear format. You should think on how to convert the flow rate of product into dollar value via the selling price. Take care of unit analysis and make sure you are consistent throughout.

4-Write your mass balance equation constraints you developed in activity 3.

5-Write down all non-zero inequality constraints where applicable.

6-Run the code, and copy/paste the results into the interactive Excel spreadsheet named “CaseStudy-Results” in the “LINGORawResults” tab at your designated case study column.

**Part III: Reflection**

1. According to your results, which process so far is the most profitable? Can you rank them in order of decreasing profitability? Does this result match that predicted by MISR?
2. Explain possible reasons that made that particular process the most profitable?
3. Try to take out the reactor utility cost by commenting your code, and run the code again. How does your profit change? Provide your insights.
4. If you were prompted to write this code without the mass balance equations, how the results would look like? Explain your answer.

**Activity 5: Integrating plant utilities**

**Part I: Reflection**

In the previous activities 2 and 4, you took into account the reactor utility cost. However, the actual utility costs for a plant extends beyond that of the reactor. A typical plant would usually encompass dryers, compressors, heaters, and mixers where each of them require some form of heating or cooling. Typically, you would be prompted to design a generic process in ASPEN and calculate the heat duties according to the capacities set by this problem. However, due to the timeframe of this module, we would search literature for typical equipment, heat duties, and utility costs for each chemical process under investigation. A good place to start with are the chemical industry reports provided by SRI consulting (<https://chemical.ihs.com/IHS/Public/Aboutus.html)> . The reports for a wide variety of chemicals are available free of charge at the Process Safety Library.

The reports found may not be recent. However, the typical equipment of a process remains barely unchanged. Therefore, you can always get updated heat duty values for each of the process equipment of the typical process. Again, you will compare your results with those provided by the benchmark and those from activity 4.

**Part II: Exploring**

1. Find a typical process flow diagram for each of the four chemical products. Depending on the literature source, you might also find the heat duty and the utility cost of each unit. If you cannot find the required values, ask your instructor for assistance. Remember literature sources can be of great variety including senior design reports, industry reports, and technical journals. Alternatively, you can use ASPEN to generate generic process design (This step can be carried later for your learning experience, and results to be compared with your literature values)
2. Integrate the total utility cost of all the units for each process into the profit maximization function. Take care not to account for the reactor cost twice.
3. Integrate all capacity constraints as set by your literature search for demand of each chemical commodity. Remember the capacity you have to integrate is not the one you found to calculate the plant utility cost.

**Part III: Reflection**

1. According to your results, what is the most profitable chemical process? Did the profitability rank change from activity 4?
2. Do you think that the plant utility cost significantly accounted for the profit? Explain your answer.
3. Do processes with the high capacities necessarily end up with the highest utility costs? Do you think doubling capacity, doubles utility cost? Explain your answer.

**Activity 6: Integrating fixed capital investment cost**

**Part I: Reflection**

One significant profit factor that should be taken into consideration is the fixed capital investment cost (FCI). This cost refers to that of the land, machinery, pipelines, equipment, and other fixed assets for the chemical plant to be set up before production. In this exercise, we will calculate the fixed capital investment based off the sample process design you found in activity 5. The fixed capital investment is related to the capacity via a mathematical relationship indicated in the book reference in activity 1 (Refer to chapter 3). The mathematical relationship correlated FCI to the capacity via the a-factor which is product specific value. You will be prompted to find the fixed capital investment cost per year using this mathematical relationship.

**Part II: Exploring**

1. From the literature source you found in activity 5, find the product capacity and the estimated fixed capital investment cost for the plant.
2. Use the appropriate mathematical relationship to calculate the a-factor for the five processes. (Use x-exponent to be 0.6)
3. Use the a-factor value you calculated to calculate the FCI installement. (Assume 10- year installment plan)
4. Integrate the FCI into your profit maximization function for all of the four processes.

**Part III: Reflection**

1. After integrating the fixed capital cost, which process is the most profitable? Did the profitability rank change? Why/Why not?
2. Using your model, does doubling the capacity automatically doubles the fixed capital investment cost? Explain your answer.
3. For simplification purposes, you used x-exponent of 0.6. Find reasons on why the x-component may not be necessarily 0.6 for all the process equipment. What factors might influence the x-component value?

**Activity 7: Carbon credit and Carbon social cost**

**Part I: Reflection**

In this activity, you will examine the effect of possible environmental regulations and how these could possibly impact the profit of the chemical manufacturer. Suppose that the U.S government proposes to apply carbon social cost (CSC) to all chemical manufacturers (which is an anticipated to be a realistic one!) to reduce the government’s greenhouse gases emission global share. This cost is defined as the total cost paid by society from public health to other environmental impacts as a result of one tonne CO2 emitted. On the other hand, the government could give financial incentives called “carbon credit” for every tonne of CO2 utilized. This scenario could put firms to ask whether it is profitable to convert CO2 at all. In this activity, you will further extend your profit maximization function for different governmental scenarios to make decisions on whether it is profitable to convert CO2 or just pay the CSC.

**Part II: Exploring**

1. Save a copy of your code in different name to be used for this activity.
2. Search journals, news, or environmental agencies on possible values for carbon credit and carbon social cost. You certainly would find different values for each, and write down all these values along with the references.
3. For each value of carbon credit and CSC, create a copy of the code and integrate the two variables accordingly. Remember that carbon credit is dollar positive and CSC is dollar negative. Remember to use the same flow rate variables you used for the rest of your code.

**Part III: Reflection**

1. List some factors that affect the carbon social cost.
2. Which scenario yields the most profit? Which one has the least profit? Describe your answer
3. How much CO2 is being fixed into each process in the most profitable scenario? Answer the same question for the least profitable scenario.
4. According to your analysis, is it overall more profitable for CF industries to build new chemical plant(s) to utilize CO2? Explain your answer.