**Green Process Design Module - Case Study**

**Case Study Background**

Acrolein is an important specialty chemical intermediate. It is used as a feedstock in the production of the essential amino acid methionine or can be further oxidized to produce acrylic acid. Most acrolein is produced via the partial oxidation of crude oil derived propylene. However, acrolein can also be produced using a green chemistry based process via the catalytic dehydration of glycerol. Glycerol has been produced recently as a side product from the manufacture of biodiesel from vegetable oils or animal fats. In fact for every 9 kg of biodiesel produced, 1 kg of glycerol is produced as a side product. Finding additional markets for this glycerol is important to improving the economic viability of the biodiesel process.

This Inquiry Activity will focus on comparing and contrasting the chemical manufacture of acrolein from propylene with a green chemistry based process for manufacturing acrolein from glycerol from the perspective of a material and energy balance, potential environmental impacts and inherently safe process design. This Inquiry Activity will use process simulations created in an Aspen Plus environment. Students will be able to change feed stream input conditions as well as operating conditions in various unit operations and analyze the results in the spreadsheet environment. These activities assume the students are familiar with the fundamentals of Aspen Plus as well as material and energy balances.

There are five activities included in this package. The first examines the energy balance of the two processes and is geared to sophomore level students in a Material and Energy Balances course. Since the traditional process relies on an exothermic reaction and the green chemistry process relies on an endothermic process, the green chemistry process is at an energy disadvantage – a problem the students must reconcile. The second activity utilized the US EPA’s Waste Reduction (WAR) Algorithm to investigate the potential environmental impacts (PEI) of each process. This module is also geared towards students enrolled in the sophomore level Material and Energy Balances course. The third activity considers the inherently safer design aspects of the green chemistry based process. This activity is focused on students taking the Capstone Design course. The fourth activity focuses on life cycle assessment is could be implemented in either the Material and Energy Balances or Capstone Design Course. The fifth and final inquiry activity is based on the detailed design of the Product Column and is intended for students in the Capstone Design course.

Each activity has organized into three parts. Part 1 is intended to encourage the student group to think about what they expect from the activity. Part 2 will guide the student through the activity using the specified tools. Finally, Part 3 is intended as a graded exercise to be turned in. The purpose primary purpose of this graded component is to ensure that the student groups have completed the exercise prior to the lecture period. The entire exercise is intended to be performed by a group of 2 to 4 students.

There is additional functionality of these simulations not addressed in these activities which can be utilized at the discretion of the instructor or the initiative of the student. These parameters include detailed capital cost estimation, side product recovery and detailed design of individual unit operations.

Process Simulations included with this inquiry activity were created using Aspen Plus ver. 7.3.2.

**Pre- / Post-Test for Application of Green Chemistry to Manufacture Specialty Chemicals from Renewable Resources**

1. The three pillars of sustainability are:
   1. Health, Safety and the Environment
   2. People, Planet and Safety
   3. Economy, Environment and Society
   4. Health, Environment and Economy
2. Although there is no single universally accepted definition for sustainability, a widely adopted definition was proposed in 1987 by:
   1. The World Sustainability Forum
   2. The Bruntland Commission
   3. The United Nations Sustainability Initiative
   4. The Rio Commission
3. In general, the 12 Principles of Green Chemistry address:
   1. Alternative Feedstocks
   2. Green Solvents
   3. Synthesis Pathways
   4. Inherently Safer Chemistry
   5. All of the Above
4. The US EPA’s Waste Reduction Algorithm is a tool used to conduct what kind of assessment:
   1. Life Cycle Assessment
   2. Potential Environmental Impact Assessment
   3. Green Chemistry Impact Assessment
   4. Sustainability Assessment
5. TRUE/FALSE: The US EPA’s Waste Reduction Algorithm is NOT an effective tool for comparing processes based on renewable feedstocks to processes based on petroleum based feedstocks:
   1. True
   2. False
6. A Life Cycle Assessment considers the impacts of a product or process from:
   1. Cradle to Grave
   2. Gate to Gate
   3. Production to Landfill
   4. Raw Material to Product
7. Potential sources for uncertainty in a Life Cycle Assessment may include:
   1. Errors of omission
   2. Lack of sufficient data
   3. Reliance on aggregate data
   4. Supply chain variation
   5. All of the above
8. In general, increasing the number of stages in a distillation column:
   1. Increases the reflux ratio
   2. Decreases the energy needed to achieve a given separation
   3. Increases the energy needed to achieve a given separation
   4. Has no effect on the energy usage of the column
9. Inherently Safe Process Design:
   1. Decreases the Risk of a given chemical process
   2. Decreases the Hazard of a given chemical process
10. An example of Process Intensification as part of Inherently Safe Process Design would be:
    1. Continuous reactor vs. batch reactor
    2. Change of feedstock
    3. Gravity flow vs. pumping
    4. Minimization of storage volume

Answers: 1) c 2) b 3) e 4) b 5) a 6) a 7) e 8) b 9) b 10) a

**Guided Inquiry Activity 1: Material and Energy Balance Investigation**

Directions: Open the two Aspen Plus Simulation files “Glycerol Process Simulation for Inquiry.bkp” and “Propylene Process Simulation for Inquiry.bkp” provided by your instructor. This inquiry activity is intended to be completed in groups of 2 – 4 students, or as directed by your course instructor. Part I should be completed prior to beginning any work with the Aspen Plus files. Part II requires that you use the Aspen Plus files to investigate the differences in energy utilization between the propylene based process and the glycerol based process. Part III is intended for submission, but you should discuss your answers as a group.

**Part I: Predictions**

1. Based on your reading about the process chemistry, which process do you expect will use more energy? How do you think this will factor into the cost associated with operating the process? What factors other than energy usage do you think will factor into the operating cost of the process?
2. Which process which process do you believe will generate the least amount of waste? What do you base your decision on?
3. Without considering the overall product life cycle, which process do you believe will generate the least greenhouse gas emissions? What do you base your decision on?

**Part II: Exploring**

Start with the Propylene Process simulation.

1. Begin by exploring the results for the REACTOR block in the process simulation. Note the operating conditions, as well as the fractional conversions of each of the 4 reactions included in the model. Note the heats of these reactions – are they endothermic or exothermic?
2. Try changing the fractional conversions of one or more of the reactions by no more than +/- 10%. How do these changes affect the overall energy generated/consumed by the REACTOR? How do these changes affect the amount of wasted incinerated in the THERMAL OXIDIZER?
3. Now, take a look at the flow splitter block FS-2. This block controls the amount of gas being recycled to the REACTOR.
4. Try changing the recycle % by no more than +/- 10%. How do these changes affect the energy generated/consumed by the REACTOR?
5. Now open the UTILITIES folder in Aspen Plus and take a closer look at the available utilities: BRINE, COOLING TOWER WATER, ELECTRICITY, HIGH PRESSURE STEAM and MEDIUM PRESSURE STEAM. What do you notice about the relative costs of these utility sources?
6. Think about why we need so many choices. Would it be more efficient to just have one low temperature utility and one high temperature utility that could handle everything? Why or why not.
7. Go back and repeat items 2 and 4 above, but this time pay attention to the amounts of the individual utilities used. What trends do you notice?

Next, move on to the Glycerol Process simulation.

1. The Glycerol Process and the Propylene Process are very similar, with the exception of the feedstocks and the reactor itself. Take a moment to explore the Glycerol Process Aspen Plus simulation and not the differences between it and the Propylene Process simulation.
2. Repeat items 1 – 7 from the Propylene Process Simulation using the Glycerol Process simulation. What similarities/differences do you note between the two processes?

**Part III: Reflection:** To do outside of class and hand in. Your answers should be discussed with at least 2 other students and try to come to agreement on the answers and the reasons why.

1. How would you change your answers from Part 1 after exploring the two simulations?
2. What are the strengths and weaknesses of the two different approaches to producing Acrolein? What characteristics would you look for in an ideal process for producing Acrolein? What key indicators would you look for? What metrics would you use to evaluate your ideal process?
3. Based only of what you have learned from this activity, which process do you believe will have the lowest operating cost? Why?

Again, based only on what you have learned in this exercise, if you were in charge of choosing a process for producing Acrolein, which of these two process would you choose? Justify your answer.

**Guided Inquiry Activity 2: Potential Environmental Impacts**

Before beginning this module, it will be helpful to read the following journal article:

Young, Douglas, Richard Scharp and Heriberto Cabezas (2000): “The waste reduction (WAR) algorithm: environmental impacts, energy consumption, and engineering economics”, *Waste Management*, Vol. 20.

Directions: Launch the WAR Algorithm graphical user interface. This inquiry activity is intended to be completed in groups of 2 – 4 students, or as directed by your course instructor. Part I should be completed prior to beginning any work with the WAR Algorithm graphical user interface or Aspen Plus files. Part II requires that you use the WAR Algorithm to investigate the differences in potential environmental impacts between the propylene based process and the glycerol based process. Part III is intended for submission, but you should discuss your answers as a group.

In order to use the WAR Algorithm, you will need to download the free user interface from the EPA at the following URL, <http://www.epa.gov/nrmrl/std/war/sim_war.htm>.

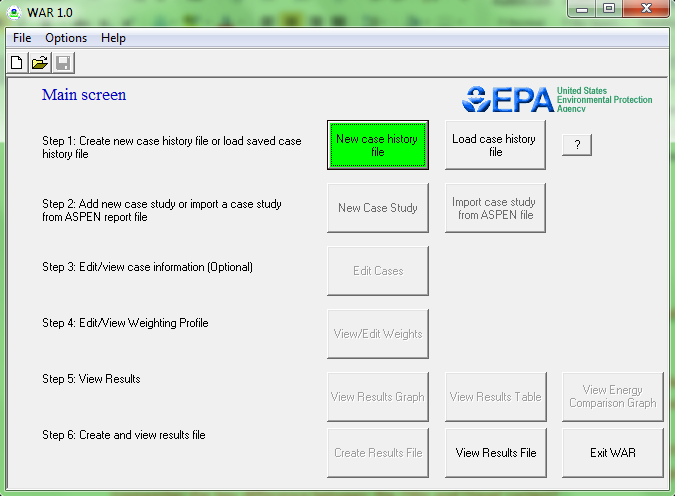
**Part I: Predictions**

1. How do you think the potential environmental impacts of the glycerol process will compare with the traditional, propylene based process? Do you think the impacts will be higher or lower?
2. Do you expect that the WAR algorithm will provide conclusive results on the environmental impacts of these two processes for producing Acrolein? Why or why not?

**Part II: Exploring**

Consider the traditional process for producing acrolein from propylene.

1. Begin by opening the two Aspen Plus .bkp files and creating a report file. The report file is created by selecting “Export” in the “File” dropdown tab and choosing “.rep” as the file type.
2. Launch the WAR Algorithm Graphical User Interface. Start a new Case History File, and begin the process of importing the process data from Aspen Plus. Alternatively, this data can be entered by hand.



1. Follow the on screen instructions to map the chemical species imported from Aspen to the correct chemical name in the WAR Algorithm database.
2. Next, view the streams that have been automatically imported. Change the Acrolein product stream from “Outlet Waste” to “Product”. This ensures that the product will not be included in the PEI calculations. NOTE: The WAR GUI sometimes fails to import all data properly from the Aspen Plus Report file. If this happens, simply type in the missing data by hand, being sure to note whether the stream is an input, output or product stream.
3. Finally, input the total energy requirement for the process. This data can be found by accessing the Utility Results in Aspen Plus.

Consider the green chemistry based process for producing acrolein from glycerol.

1. Create a new case in the WAR Algorithm GUI. Repeat the step above and use the WAR Algorithm to determine the Potential Environmental Impacts for the glycerol based process.
2. Look at the results for the two processes by selecting the “View Results Graph”. What do you notice? What conclusions can you draw? Are these results surprising?

**Part III: Reflection**: To do outside of class and hand in. Your answers should be discussed with at least 2 other students and try to come to agreement on the answers and the reasons why.

1. How would you change your answer from Part 1 after using the WAR Algorithm? If your guesses differed from the actual results, explain why that might be the case.
2. What are the strengths and weaknesses of the WAR Algorithm as a tool for assessing processes based on renewable feedstocks? How might you choose to modify the WAR Algorithm to improve upon its weaknesses? Can you explain the seemingly non-intuitive results?
3. How does the energy source affect the potential environmental impacts? What would happen if one of the processes were powered using renewable energy resources like wind power or solar? How could you investigate this using the WAR Algorithm?

**Guided Inquiry Activity 3: Process Safety and Inherently Safe Design**

Before beginning this module, it will be helpful to read the following journal article:

Seay, J. and M. Eden, “Incorporating Risk Assessment and Inherently Safer Design Practices into Chemical Engineering Education”, *Journal of Chemical Engineering Education*, 2008.

Directions: Open the 2 Aspen Plus Simulation files “Glycerol Process Simulation for Inquiry.bkp” and “Propylene Process Simulation for Inquiry.bkp” provided by your instructor. This inquiry activity is intended to be completed in groups of 2 – 4 students, or as directed by your course instructor. Part I should be completed prior to beginning any work with the Aspen Plus files. Part II requires that you use the process data found in the Aspen Plus files to investigate the differences in the potential process hazards between the propylene based process and the glycerol based process. Part III is intended for submission, but you should discuss your answers as a group.

**Part I: Predictions**

1. How do you think the inherent hazards of the traditional acrolein process compare with the green chemistry based process? Do you think the potential risk scenarios will be more or less severe?
2. What would you imagine to be the worst case upset scenario for these two processes? How do you come up with your scenarios?

**Part II: Exploring**

1. Make a list of the top 10 potential process upset scenarios you can think of for the traditional, propylene based acrolein production process as well as the green chemistry based process.
2. Create a spreadsheet and list the Initiating Cause and the Consequences for each of the 10 process upsets.
3. Considering the 5 categories of Inherently Safe Design Practice, suggest a process change for each of the 10 scenarios for each process to reduce the inherent risk of the process.
4. Based on your results, think about which process is inherently safer.

**Part III: Reflection**: To do outside of class and hand in. Your answers should be discussed with at least 2 other students and try to come to agreement on the answers and the reasons why.

1. How would you change your answer from Part 1 after going through the risk assessment exercise?
2. Although both acrolein production processes can be designed to achieve the same level of risk, why might an inherently safer process be preferred?
3. Are there any potential drawbacks to inherently safe design practice?

**Guided Inquiry Activity 4: Life Cycle Assessment**

Directions: Open the 2 Aspen Plus Simulation files “Glycerol Process Simulation for Inquiry.bkp” and “Propylene Process Simulation for Inquiry.bkp” provided by your instructor. This inquiry activity is intended to be completed in groups of 2 – 4 students, or as directed by your course instructor. Part I should be completed prior to beginning any work with the Aspen Plus files. Part II requires that you use the Aspen Plus files along with a spreadsheet to complete a very simple calculation to assess the differences in life cycle impacts between the propylene based process and the glycerol based process. Part III is intended for submission, but you should discuss your answers as a group.

**Part I: Predictions**

1. How do you think the life cycle inventory for the Glycerol based process differs from the propylene based process? In what ways will they be the same? What do you believe are the key fundamental differences between the two processes from a life cycle perspective?
2. Which process do you believe will have the lowest life cycle impacts?

**Part II: Exploring**

1. Considering the differences between the two manufacturing processes, come up with an appropriate functional unit for comparing the traditional process to the green chemistry based process.
2. Use a spreadsheet to make a list of all the chemical raw materials needed to manufacture acrolein from each process. Use the spreadsheet to calculate the feed rate for each raw material per functional unit.
3. Next, add a list of all the utilities used in the manufacture acrolein from each process to your spreadsheet. Use the spreadsheet to calculate the usage rate for each utility per functional unit.
4. Now, determine how each raw material will be delivered to the site – truck, rail or pipeline – and make an informed estimation of how far each raw material must be transported. Assume that your acrolein plant is located on the gulf coast of the United States.

**Part III: Reflection**: To do outside of class and hand in. Your answers should be discussed with at least 2 other students and try to come to agreement on the answers and the reasons why.

1. How are the life cycle impacts influenced by the reaction yield for the process?
2. What insights can you gain from this simple LCA that you could not get by just using the WAR Algorithm?
3. How does transportation affect the life cycle impacts of each process? What decisions can you then make regarding where to locate your production facility?
4. How, if at all, would you change your answer from Part 1 after completing Part II?

**Guided Inquiry Activity 5: Detailed Column Design**

Directions: Open the 2 Aspen Plus Simulation files “Glycerol Process Simulation for Inquiry.bkp” and “Propylene Process Simulation for Inquiry.bkp” provided by your instructor. This inquiry activity is intended to be completed in groups of 2 – 4 students, or as directed by your course instructor. Part I should be completed prior to beginning any work with the Aspen Plus files. Part II requires that you use the Aspen Plus files to prepare a detailed design for the Desorption Column used in both the propylene based process and the glycerol based processes. Both columns are similar, so either simulation can be used for this activity. Part III is intended for submission, but you should discuss your answers as a group.

**Part I: Predictions**

1. How do you think the geometry (number of stages and diameter) affect the total energy used by the column?
2. Do you believe that this separation will be easy (require relatively few stages) or difficult (require relatively many stages).

**Part II: Exploring**

1. Using the feed conditions from the Aspen Plus simulation, create a new unit operation using the DSTWU block.
2. Create a plot of reflux ratio vs. number of theoretical stages in the column (from total reflux to minimum reflux). Note the energy requirement in the reboiler and condenser over this range. List your conclusions about the potential environmental impacts, capital cost impacts and operating cost impacts for this design case.
3. Calculate the diameter of the column at total and minimum reflux.
4. Create a plot of column energy usage versus column diameter.

**Part III: Reflection**: To do outside of class and hand in. Your answers should be discussed with at least 2 other students and try to come to agreement on the answers and the reasons why.

1. How, if at all, would you change your answer from Part 1 after completing Part II?
2. How does the column geometry (number of stages and diameter) affect the energy usage for the column.
3. Considering what you know about Potential Environmental Impacts, how does the column geometry affect the PEI?
4. What are the potential drawbacks to a larger column?