AIChE®

2004
National Student Design Competition

If there are any questions about the design problem, student chapter advisors and design course instructors are asked to contact:

Professor Richard L. Long

New Mexico State University
Chemical Engineering Department
Las Cruces, NM 88003

Phone: (505) 646-2503
Fax: (505) 646-7706
Email: rilong@nmsu.edu

Please read the rules on the following pages carefully before submitting a solution to AIChE.

American Institute of Chemical Engineers
3 Park Avenue, New York, NY 10016-5991

AIChE National Student Design Competition
2004

Rules of the Contest

Solutions will be graded on (a) substantial correctness of results and soundness of conclusions, (b) ingenuity and logic employed, (c) accuracy of computations, and (d) form of presentation. Accuracy of computations is intended to mean primarily freedom from mistakes; extreme precision is not necessary.

It is to be assumed that the statement of the problem contains all the pertinent data except for those available in handbooks and literature references. The use of textbooks, handbooks, journal articles, and lecture notes is permitted.

Students may use any available commercial or library computer programs in preparing their solutions. Students are warned, however, that physical property data built into such programs may differ from data given in the problem statement. In such cases, as with data from literature sources, values given in the problem statement are most applicable. Students using commercial or library computer programs or other solution aids should so state in their reports and include proper references and documentation. Judging, however, will be based on the overall suitability of the solutions, not on skills in manipulating computer programs.

The 2004 National Student Design Competition is designed to be solved either by an individual chemical engineering student working entirely alone, or a group of no more than three students working together. Solutions will be judged in two categories: individual and team. There are, however, other academically sound approaches to using the problem, and it is expected that some Advisors will use the problem as classroom material. The following confidentiality rules therefore apply:

1. *For individual students or teams whose solutions may be considered for the contest:*
The problem may not be discussed with anyone (students, faculty, or others, in or out of class) before or during the period allowed for solutions. Discussion with faculty and students at that college or university is permitted only after complete final reports have been submitted to the Chapter Advisor.

2. *For students whose solutions are not intended for the contest:*
Discussion with faculty and with other students at that college or university who are not participating in the contest is permitted.

3. *For all students:*
The problem may not be discussed with students or faculty from other colleges and universities, or with individuals in the same institution who are still working on the problem for the contest, until after June 4, 2004. This is particularly important in cases where neighboring institutions may be using different schedules.

Submission of a solution for the competition implies strict adherence to the following conditions:

(Failure to comply will result in solutions being returned to the appropriate Faculty Advisor for revision. Revised submissions must meet the original deadline.)

ELIGIBILITY

- ONLY AIChE NATIONAL STUDENT MEMBERS MAY SUBMIT A SOLUTION. Non-member entries will not be considered. If you would like to become a National Student member, we must receive your membership application prior to submitting your solution. Application forms are found at **http://students.aiche.org/join/**.
- Entries must be submitted either by individuals or by teams of no more than three students. Each team member must meet all eligibility requirements.
- Each Faculty Advisor should select the best solution or solutions, not to exceed two from each category (individual and team), from his or her chapter and submit them per the instructions below.

TIMELINE FOR COMPLETING THE SOLUTION

- A period of no more than thirty (30) days is allowed for completion of the solution. This period may be selected at the discretion of the individual advisor, but in order to be eligible for an award, a solution must be emailed/postmarked no later than midnight June 4, 2004.
- The finished report should be submitted to the faculty advisor within the 30-day period.

REPORT FORMAT

- The body of the report must be suitable for reproduction, that is, typewritten or computer-generated. Tables, supporting calculations and other appendix material may be handwritten.
- The solution itself must bear no reference to the students' names and institution by which it might be identified. Please expunge all such references to the degree possible.
- *Entries as a PDF file are strongly encouraged.*

SENDING THE SOLUTION TO AIChE

- There should not be any variation in form or content between the solution submitted to the Faculty Advisor and that sent to AIChE National. The Student Chapter Advisor, or Faculty Advisor, sponsoring the student(s), is asked to maintain the original manuscript(s).
- Email a PDF file of the solution accompanied by its corresponding entry form to **awards@aiche.org**. **OR**
  Hard-copy entries should be sent in duplicate with their entry forms by registered mail to Awards Administrator, AIChE, 3 Park Avenue, New York, NY 10016-5991.
- **DEADLINE: Entries must be emailed/postmarked no later than midnight June 4, 2004.**

Disposal of Cavern-Stored Ethylchloroacetate by Reaction with Caustic (NaOH)
2004 AIChE Contest Problem

1.0 Introduction and Scope

Years ago a major producer (for anonymity purposes let's call the producer Chloroester Inc., CI for short) of ethylchloroacetate (ECA) pumped off-spec product into a salt-dome cavern located on the US Gulf Coast. Recently Federal and State authorities have informed CI that the ECA must be removed from the cavern and disposed of safely in an environmentally friendly manner.

You will define a project to dispose of the ECA by reacting it with caustic (NaOH) to produce a relatively non-volatile and olfactory benign organic salt – sodium chloroacetate (NaECA). This reaction also produces ethanol, which will be separated and sold into the power alcohol market.

The sodium chloroacetate organic salt is now being tested for disposal in CI's activated sludge waste treatment basins and in the neighboring city's waste treatment system. Based on preliminary testing, both biological disposal systems will degrade the NaECA to benign chemical species. A third disposal alternative, which is a bit more politically sensitive, is also being quietly investigated; that disposal method pumps the ethanol-free, pH neutral NaECA-containing waste stream out into the depths of the Gulf. With proper depth of disposal and dilution with seawater, it is expected that approval can be obtained to use this cost effective disposal alternative. The economic choice between these three disposal methods is the focus of a separate (to this study) project. The only link between the two projects is the premise that this project will provide (1) 8 hours of surge for the NaECA-containing waste stream and (2) a disposal pump will be provided, which provides 100 ft of dynamic head.

2.0 Cavern Storage

The ECA now resides in a 330 ft diameter, roughly spherical, cavern in a salt dome. The ECA phase, which occupies 55% of the cavern volume, is saturated with water. The remaining 45% of the cavern volume contains an aqueous saturated salt solution.

The top of the cavern is 3,300 ft below ground level.

There are three cemented, serviceable plastic-lined metal pipes (8", 10" and 12" inside diameter, respectively) extending from ground level into the top of the cavern.

The cavern is located in a remote area 3 miles from the CI plant site. Three serviceable plastic-lined metal pipelines (4", 6" and 8" inside diameter, respectively) exist between the plant site and the cavern site.

There are no pumps, tanks or any other process equipment located at ground-level at the cavern site or inside the cavern. All the old injection pumps, which were salvaged long ago, were located at the plant site.

3.0 Reaction Kinetics

Kinetics of the ECA + NaOH reaction in aqueous solutions are given in a thesis by S. Yu, "Micromixing and Parallel Reactions" at the Swiss Federal Institute of Technology, Zurich, Switzerland (1993).

This thesis can be a bit confusing because the reaction kinetics are buried in a discussion of micromixing and parallel reactions and different sets of units are used throughout the thesis. When the entire discussion is fully analyzed, it appear that the best (and conservative) kinetic model is the second order one given by equation 6.6 (page 120) with the second order reaction rate constant given by equation 6.7 (page 120) as

$$k_2 = 200{,}000\mathrm{Exp}(-38{,}910/RT) \tag{1}$$

where the units are SI and the units of k_2 are $m^3/[(kg\ mol)(s)]$, the units of T are K and the units of R are $(kPa)(m^3)/[(kg\ mol)(K)]$. The numerical value of R with these SI units is 8.314. Thus, the value of k_2 at T = 25 K is

$$k_2 = 200{,}000\mathrm{Exp}[-38{,}910/(8.314)(298)] = 0.03023\ m^3/[(kg\ mol)(s)],$$

4.0 Solubility of ECA in a Saturated Salt Solution

ECA is sparingly soluble in water. The solubility of ECA in water is given in Yu's thesis, page 124, as 2.25 Wt %. The solubility of ECA in a saturated salt solution can be determined from Appendix I, Experiment Number 2. (NOTE: Although the neck inside diameter of the 50 ml flask is not needed to calculate the solubility of ECA in the saturated salt solution, it was (for reference purposes) 9.45 mm). The experiments, which are documented in Appendix I, were performed in a University Chemical Engineering Laboratory.

5.0 Reaction Behavior and Phase Behavior

Experiments 3-6, Appendix I, document laboratory work which was done to determine reaction heat effects and solubility limits of reaction products. This information may not be available in the technical literature; therefore, these experiments were performed to provide sufficient technical information for reactor design.

6.0 Waste Treatment

The sodium chloroacetate and a modest amount of ethanol can be sent to waste treatment with the following provisos:

1. Any stream entering a waste treatment system or entering the Gulf must be a single liquid phase totally devoid of solids, and
2. The project must be charged with reasonable costs for treating the waste, both from a BOD and a hydraulic load standpoint. Disposal to the Gulf may prove to be the most economical

alternative; however, at present the project must be charged with the reasonable cost of disposal to either of the biological waste treatment systems.

3. ECA has very pungent odor and it is a lachrymatory chemical. There can be no detectable odor of ECA above the open-top, air-sparged waste treatment basins or at the water surface of any Gulf disposal site.

7.0 Ethanol Sales

Ethanol can be sold into the fuel market as "power alcohol" for blending with gasoline. The ethanol must either meet or be capable of being processed to meet fuel grade specifications. Fuel grade ethanol can be sold at market price, FOB Gulf Coast plant site. The Chemical Marketing Reporter is a good source of commodity chemical prices.

Power alcohol is 200 proof and is virtually free of water. It may not be economically attractive to break the azeotrope and remove virtually all the water from the ethanol with this project. It is likely that this project should produce 190 proof alcohol, which will be sold to a power alcohol producer. A reasonable price for 190 proof alcohol feed to a power alcohol plant is probably about 80% of the commodity price of power alcohol; because about 20% of the power alcohol market price will be required to remove the water from 190 proof ethanol.

The contaminants in the ECA and salt solution are not knows; thus, it is not realistic to expect that the ethanol could ever be sold as 190 proof USP fermentation grade ethanol, which can be used for food, personal care and medicinal purposes.

8.0 Cost Data

Peters, M. S., K. D. Timmerhaus and R. E. West, "Plant Design and Economics for Chemical Engineers", 5th Edition, McGraw-Hill (2003) is an excellent source of operating cost and capital cost data.

9.0 Fines for Late Disposal

The Federal and State Regulators are being pressured by lobbying groups to empty this cavern of ECA and place it in a proper, stable, environmentally sound, perpetuity condition. Consequently, the following schedule of fines will be levied.

DATE OF FINAL DISPOSAL	YEARLY FINE
1/1/07	$400,000 for 2006 or any portion thereof
1/1/08	$700,000 for 2007 or any portion thereof
1/1/09	$1,000,000 for 2008 or any portion thereof
1/1/10	$1,500,000 for 2009 or any portion thereof
After 1/1/10	Not Allowed

NOTE: The fines are cumulative; e.g., final disposal as of 1/1/10 will result in total fines of $400,000 + $700,000 + $1,000,000 + $1,500,000 = $3,600,000.

10.0 Design Keys

The following considerations must be handled extremely well for an acceptable optimum design.

1. The pumping equipment to remove the ECA and the saturated salt solution from the cavity must be well designed and properly documented. Any deviation from technical feasibility will invalidate the entire project design.
2. No solids whatever can enter waste treatment or the Gulf.
3. Any reactor system must be technically correct and economically optimum, with heat and phase equilibrium effects properly considered.
4. Any salable alcohol must be at least 190 proof.
5. Any distillation column must be technically correct and economically optimum.
6. Any economic optimization must maximize Net Present Worth using proper Discounted Cash Flow Economic Analysis.
7. The economically optimum time for final disposal must be properly determined.
8. The cavern must be placed in proper conditions for stable, environmentally sound, perpetuity existence.
9. A reasonable design and construction schedule must be developed. A reasonable premise for start of production is 1/1/05 with process definition starting 3rd Quarter 3003.
10. All process equipment necessary to implement the project must be included. Thus, all required storage and surge tanks must be included and each and every pump, including every pump required from the pump(s) required to remove the liquids from the cavern all the way to the alcohol loadout pump(s).

11.0 Reporting Requirements

The documentation you are preparing is properly called a "Preliminary Project Definition Report".

NOTE: FOR CONSISTENCY, CLARITY AND UNDERSTANDABILITY, ALL OF THE REPORT MUST BE DONE IN ENGLISH UNITS!!!!!!!!!

The report format must adhere to the following format.

1. Title Page.
2. Table of Contents.
3. Executive Summary - Two (2) page (maximum) condensation of the report.
4. Introduction - Orient the client to the assigned task.
5. Summary - Summarize the results of the study, emphasizing costs (operating, capital and NPW) and summarize the conclusions and recommendations. Briefly tell what was designed and when it will startup and shutdown.
6. Conclusions - Interpret your results. List your conclusions in decreasing order of significance.
7. Recommendations - Emphasize technical and operational feasibility and optimum economics.

8. Project Premises - Itemize all pertinent process and economic premises, including (1) the overall project schedule, battery limits etc., (2) feed and product specs, (3) costs of raw materials, utilities etc., (4) selling prices of all products (5) economics, including depreciation schedule, taxes, project life etc., (6) environmental requirements, (7) processing limitations, (9) extraordinary costs, (10) labor cost, (11) product quality considerations.
9. Process Flow Diagram (PFD) - Include all items of process equipment, include and number all process streams, indicate all utilities needed per individual process equipment item and include all process control loops required to fully automate the process (e.g., there is a minimum of 5 control loops needed for a distillation column).
10. Stream Attributes - For each and every stream on the PFD include on the PFD or on a separate page a Tabulation of Stream Attributes (SA's), including Stream Number, Mass Flow of Each Component, Total Mass Flow, Temperature, Pressure and Volumetric Flow Rate (GPM for liquids & CFM for gases). Proper SA's (lb/hr of each component, T, P etc) from a process simulator will suffice.
11. Process Description - Include process conditions, equipment type and size and how the process equipment is integrated to achieve process objectives. Explain the purpose of each process equipment item.
12. Safety and Environmental - Note and explain any special considerations. Explain and document how emission limits were achieved. Additionally:
    A. Include two or more safety review paragraphs to identify the major hazards and to highlight the technology that is added to improve the inherent and long term safety of the system.
    B. Include two or more environmental review paragraphs to identify the major environmental hazards and to highlight the technology that is added to improve the environmental impact of the project.

13. Utility Summary - Itemize each utility by user (i.e., by process equipment item). Include in the tabulation the unit cost of each utility and the yearly cost of each utility for each user.
14. Operating Cost Summary - Itemize using the categories given in Peters, Timmerhaus & West, 5th Edition, Tables 6-17 and 6-18, pages 273 and 274.
15. Equipment Information Summary - Itemize operating conditions, sizes, materials of construction for all processing equipment.
16. Capital Estimate - Itemize process equipment costs and itemize the overall estimate per Method C(or equivalent), page 250, Peters, Timmerhaus and West, 5th Edition.
17. Economic Analysis - Include a discussion of the economic methods and analysis. Include appropriate cash flow analysis tables. Include any graphical representations, such as NPW vs. Disposal Time
18. Innovation and Optimization - Explain and document what was done to economically optimize the project.
19. Engineering Calculations - Include all (not just samples and examples) pertinent hand calculations.
20. Computer Programs - Include input and output files, an explanation of the model(s) used and nomenclature.
21. Computer Process Simulation - Include input and output files and a simulator flow chart

for one set (the set for optimum conditions is preferred) of documented process conditions for any process simulation using standard process simulator programs.

NOTE: THERE MUST BE A ONE-TO-ONE CORRESPONDENCE BETWEEN STREAM NUMBERS IN THE PROCESS SIMULATION AND STREAM NUMBERS ON THE PROCESS FLOW DIAGRAM.

APPENDIX I

SOLUBILITY AND REACTION EXPERIMENTS

EXPERIMENT 1: Solubility of Ethylchloroacetate (ECA) in Water

Procedure:
1. Add 10 gm of De-ionized water to a 10 ml graduated cylinder.
2. Add 0.33 gm ECA.
3. Shake well for several minutes.
4. Allow to gravity separate.

Results:
1. As the graduated cylinder is inverted a small bead of ECA (about 2 mm diameter) falls through the water.

EXPERIMENT 2: Solubility of ECA in Saturated NaCl Solution

Procedure:
1. Add exactly 50 ml of saturated salt solution to a volumetric flask.
2. Add 1.016 gm ECA.
3. Shake well several times and allow ECA to settle upward.

Results:
1. The saltwater phase rose 3.5 mm above the 50 ml mark in the neck of the volumetric flask.
2. The ECA top phase was 9 mm deep; the top of the ECA phase was 12.5 mm above the 50 ml mark in the neck of the volumetric flask.

EXPERIMENT 3: Reaction of ECA with 50w% Caustic (NaOH)

Procedure:
1. Add 6 gm of ECA to a 10 ml graduated cylinder.
2. Immerse a sheathed thermocouple into the graduated cylinder.
3. On an analytical balance, incrementally add 4.3 gm of 50 w% caustic.
4. As the caustic is added, agitate by hand with the thermocouple wire.
5. Remove the thermocouple and cover the graduated cylinder top with parafilm.
6. Shake vigorously.

Results:
1. The thermocouple agitation was not sufficient to suspend the two liquid phases.
2. The temperature rose from 74 F to about 110 F as the caustic was incrementally added and as agitation was provided with the thermocouple.

3. As the caustic was added the bottom caustic phase became milky.
4. A couple of minutes after the vigorous shaking, the graduated cylinder became hot to the touch and continued to heat rapidly.
5. Vapor started to form in the batch and the batch contents erupted from the open top of the graduated cylinder. Intermittent puffs of white smoke erupted from the graduated cylinder, along with some solids.
6. After the "puffing" ceased, the graduated cylinder was filled with filled with bits of with un-consolidated, greasy-to-the-touch, white solids.

EXPERIMENT 4: Reaction of ECA with Caustic (NaOH) using a Reactor Charge of ½ 50w% Caustic and ½ Saturated Salt Solution

Procedure:
1. Add 12 gm ECA to a 125 ml flask.
2. Add 8.3 gm saturated salt solution.
3. Add incrementally 8.3 gm 50w% caustic solution.
4. Insert a thermocouple wire into the batch.
5. As the caustic is incrementally added, agitated by hand with a spatula.
6. After all the caustic is added place the flask on a magnetic stirring unit and agitate the batch for 10 hours with a Teflon stirring bar.
7. Stop the stirring and allow the batch to settle.

Results:
1. The batch became milky immediately upon caustic addition.
2. The temperature rose to about 115 F as the caustic was added.
3. The temperature remained about 115 F as the batch was agitated with the stirring bar.
4. After 10 hours of agitation, followed by an hour of settling, there was a clear liquid phase above and a settled solid phase below.

EXPERIMENT 5: Reaction of ECA with Caustic (NaOH) using a Reactor Charge of 50w% caustic, saturated salt solution & water

Procedure:
1. Add 124.1 gm ECA to a 125 ml flask.
2. Add 16.6 gm saturated salt solution.
3. Add 16.6 gm 50w% caustic.
4. Add 11 gm DI water.
5. Insert a magnetic stirring bar into the flask and sit the flask on a magnetic stirring unit.
6. Insert a thermocouple wire through a parafilm cover.
7. Start the stirrer, monitor batch temperature and batch appearance with time.

Results:
1. After the stirrer was started the batch temperature rose rather quickly from 74 F to about 105 F.
2. The temperature then rose to about 120 F over about 1 minute.
3. After the temperature rose to about 120 F, it started to rise very rapidly to 170 F in about 3 to 4 sec.

4. The batch temperature stayed constant at about 170 F for about 2 minutes and then started to cool slowly.
5. The batch was observed visually until the batch cooled to about 150 F at which point the batch was a clear single phase liquid.
6. The batch was again observed visually when the temperature was 85 F and the batch had become a milky white.
7. After 10 hours of agitation, followed by settling, the batch consisted of a clear upper layer and a lower layer which contained settled white solids.

EXPERIMENT 6: Solubility Limit of Solid Product from Experiment Number 3 Above.

Procedure:
1. Add 2.422 gm of solids from Experiment Number 3 in a 10 ml graduated cylinder.
2. Add 2.55 gm water, stir and observe the appearance.
3. Increase the added water to 3.507 gm and observe the appearance.
4. Add 0.258 gm of additional solid and observe the appearance.

Results:
1. Solids remained after stirring of the batch of 2.422 gm of solids and 2.55 gm of water.
2. All the solids dissolved after adding 3.507 gm of water total.
3. All the solids dissolved after adding an additional 0.258 gm of solids.

EXPERIMENT 7: Repeat of Experiment Number 3 in a 125 ml Agitated Flask

Procedure:
1. Add 60 gm of ECA to a 125 ml beaker agitated with a Teflon-covered stirring bar.
2. Immerse a thermocouple into the batch.
3. Add 43 gm of 50 w% caustic.

Results:
1. The temperature rose as follows:
   5 seconds----------100 F
   11 seconds---------110 F (probably the adiabatic rise for NaOH heat of solution)
   55 seconds---------120 F
   61 seconds---------130 F
   65 seconds---------186 F (the peak temperature)
   Thereafter----------The batch cooled slowly
2. Vapors were emitted as the reaction proceeded from 55 to 65 seconds.
3. The temperature peaked quickly and then started to cool slowly.
4. At room temperature the batch was completely solid.