AMERICAN INSTITUTE OF
CHEMICAL ENGINEERS

1999 National Student Design Competition

American Institute of Chemical Engineers
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If there are any questions about the design problem, Student Chapter Advisors and design course instructors are asked to contact:

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

1999 AIChE NATIONAL STUDENT DESIGN COMPETITION

Dicyclopentadiene Recovery from By-Product of Naphtha Steam-Cracking

DEADLINE FOR MAILING:

Solutions must be postmarked no later than midnight, June 4, 1999.

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 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 other 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 1999 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. Solution 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 or universities, or with individuals in the same institution who are still working on the problem for the contest, until after June 4, 1999. 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.
- ✓ Entries may 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 send these by registered mail, as per the below instructions, to the Institute.

TIMELINE FOR COMPLETING THE SOLUTION

- A period of no more than thirty 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 postmarked no later than midnight, June 4, 1999.
- **The finished report must 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 may be written in ink. Supporting calculations and other appendix material may be in pencil.
- The solution itself must bear no reference to the students' names or institution by which it might be identified. In this connection, graph paper bearing the name of the institution should not be used.

SENDING THE SOLUTION TO AIChE

- Two copies of each of the solution(s) must be sent to the address below; original manuscript(s) must remain in the possession of the Student Chapter Advisor, or Faculty Advisor, sponsoring the student(s)
- There should not be any variation in form of content between the solution submitted to the Faculty Advisor and that sent to the AIChE office.
- Each copy must be accompanied by the enclosed ENTRY FORM giving each contestant's name, AIChE membership number, college or university, Faculty Advisor name, address, home address, home telephone number, and student chapter, lightly attached to the report. This form will be retained for identification by the executive director of the Institute.
- DEADLINE: Entries must be postmarked no later than midnight, June 4, 1999. As soon as the winners have been notified, original manuscripts must be forwarded to the office of the executive director as soon as possible.

SEND TO:

Administrator, AIChE Awards
American Institute of Chemical Engineers
3 Park Avenue
New York, New York 10016-5901

DEADLINE: JUNE 4, 1999

1999 AIChE National Student Design Competition

Dicyclopentadiene Recovery from By-Product of Naphtha Steam-Cracking

I. OBJECTIVE AND SCOPE

Steam cracking of naphtha to produce ethylene and propylene is one of the largest, most important industrial processes in the world. A by-product of this process is a stream containing a mixture of heavy paraffins, olefins, diolefins, and aromatic compounds. Most of the material is C_5 and heavier, though C_4's are often present. This stream is usually catalytically hydrogenated, then returned to the cracking furnaces as feed or blended into the motor-gasoline pool.

Separation and utilization of these by-products is becoming an alternative to such outlets. You are to consider recovery of a component from this by-product for use as a feedstock to another process. As the design engineer, you are to maximize the economic production of high purity dicyclopentadiene (DCPD) from a 55,000 lb/hr naphtha cracking by-product. The commercial unit is to be brought on-line January 1, 2002. Your design *must* be optimized and include the items listed in the order and format specified below.

Your report *must* be formatted as specified below, containing each item listed.

Report Table of Contents Format:

A. Title Page

B. Table of Contents

C. Executive summary - A summary (maximum of two-pages), highlighting important findings, including the nature of the process and results of the economic analysis.

D. Introduction - Complete problem statement, including project background and design objectives.

E. Process Discussion - Provide a detailed description of the process, the function of major equipment, stream connectivity, cost savings, safety, control and other design features. Include a discussion of alternative processes that were considered, and the advantages and disadvantages of each. Provide results, using figures, tables, and graphs to support claims proposed. *Results and support calculations must be in the following units (kg, kmol, °C, kJ, kPa, m, and hr).*

F. Process flow diagram (PFD) - Include a flow scheme showing all major process equipment. Each process stream should be numbered. Show the basic control instrumentation, including measurement points for temperature, pressure, and flow rate, and the associated control devices.

G. Premises List - provide a numbered list of premises made and justifications for applying those premises. Clearly indicate where each premise was used in the development of the process design.

H. Assumptions List - provide a numbered list of the assumptions made and justifications for making those assumptions. Clearly indicate where these assumptions were applied in the development of the process design.

I. Economic Summary - Include a summary and discussion of the economic methods and analysis employed. Include appropriate cash flow tables. Also include a summary of the economic optimization work performed.

J. Conclusions/Recommendations - Provide your conclusions and recommendations for the process design. Recommendations should address (a) future research needs, and (b) additional definition needed to complete optimization of the project.

K. References - Listed and formatted in a standard, science citation notation.

Appendices Format

A1. Mass/energy balance - Describe each stream on the PFD. Report stream number, weight fraction, temperature, pressure, and flow rate (component and overall) for each stream.

A2. Economic Analysis - Provide a complete documentation of the economic analysis performed and summarized in the main body of the report. Include spreadsheet calculations showing formulae, sample calculations, and sources of methods used. The economic optimization work must be fully documented (e.g., if distillation optimization is one of the 2-3 top economic optimizations, then it must be documented in this appendix).

A3. Utilities summary - Include a table showing duty, consumption, and cost of utilities for each major equipment piece. Show the total consumption and cost for each major utility category. These totals should be appropriately included and cited in the economic analysis provided in the main body of the report.

A4. Equipment Specifications List - provide a list of all the equipment used in the process, including type, description, function, materials of construction, size, operating conditions, purchase cost, and all important specifications.

A5. Safety, health, and environmental Regulations - Address regulatory issues, process and material hazards, and safety issues associated with the process. Discuss the implications of the federal regulation 29 CFR 1910.119 if appropriate.

A6. Computer process simulators and other programs - the use of generally available process simulators (Aspen®, Hysim®, Chemcad®, Provision®, etc.) together with spreadsheets and student developed computer programs is acceptable. All process simulation programs must be fully documented as to their design and simulation use. Complete input files and output reports for the economically optimum alternatives must be included. A process simulator flowsheet, which shows the connectivity between blocks of the simulation, must be included. Each stream number on this simulator flowsheet must have a one-to-one correspondence with a stream number on the Process Flow Diagram.

A7. Back-up/support data and calculations - provide documentation for calculations made by hand at least on a sample basis, but preferably include all hand calculations made in completing the design. Include flow charts, input files, and output reports from programs and simulators. Explain computer model(s), nomenclature, and relevant information to familiarize the reader with the capability and acceptability of the program. All special purpose computer programs (i.e., Fortran, TK Solver, Mathematica, MathCad, Excel cash flow spreadsheets etc.) must be documented by including output and coding files. This means cell formula printouts must be included for spreadsheet programs.

II. PROCESS DESCRIPTION

You are assigned the task of determining the economic feasibility of using one of the components in the steam-cracked naphtha by-product stream as a feedstock to another process. The company contracting your services is particularly interested in recovering dicyclopentadiene (DCPD) from this by-product stream. The stream also contains significant amounts of the cyclopentadiene (CPD), which reversibly dimerizes to DCPD as shown in Figure 1. In the economic optimization of DCPD recovery, forward *and* reverse reactions must be considered.

Figure 1. Reversible dimerization of CPD

CPD and DCPD can be isolated from the C_5 fraction by leveraging the dimerization in multiple fractional distillations. The by-product stream(s) may be returned as a discounted naphtha stream or if economically feasible, may be hydrogenated over a suitable Pd catalyst and returned as full-value naphtha. Waste vent streams are to be valued at fuel value.

In order to evaluate this feedstock, there must be economic incentive to process this stream as compared to buying an equivalent quantity of DCPD on the open market. High purity DCPD (>97%) cost has varied between $0.27 and $0.38 over the past ten years.

You must provide a complete plant design and economic analysis for a process capable of economically recovering high purity DCPD and a diolefin-rich isoprene by-product stream from the specified feed.

An additional economic optimization variable that must be considered is the total hydrogenation of the diolefin-rich isoprene by-product. Total hydrogenation of the diolefin-rich by-product can be performed to boost the economic value of the stream. The preferred reaction style is using a trickle-bed reactor.

A minimum 15% discounted-cash flow return on investment (DCFROI) must be achievable for the project.

III. PROCESS DESIGN / ECONOMIC ANALYSIS DATA &GUIDELINES

A Feed Specifications

Temperature - 68.0°F; Pressure - 100.0 psig; Flowrate - 55,000 lb/hr

B CPD/DCPD Reaction and Kinetic Data

CPD reversibly dimerizes to DCPD according to the reactions and rate equations below (*note: Activation energies are in kcal/mole*):

Forward Reaction: $r_f = k_f[CPD]^2$

$k_f = 1.2 \times 10^6\, e^{(-16.7/RT)}$ (L kgmol^{-1} s^{-1})

Reverse Reaction: $r_r = k_r[DCPD]$

$k_r = 6.0 \times 10^{12}\, e^{(-34/RT)}$ (s^{-1})

C Feedstock and Product Analysis

- An analysis of the feed is provided in Table 1 on page 7.
- Two products are to be recovered: (1) a high-purity (≥97%wt) DCPD product, and (2) a diolefin-rich by-product (hydrogenated or untreated).
- The Reid Vapor Pressure (ASTM D-323-58) of the diolefin-rich by-product must not exceed 15.8 psia.
- 99.5wt% of the 1-pentene in the feed must be recovered in this stream.

D Flowsheet Considerations

- The dimerization reaction occurs everywhere DCPD or CPD exist, and cannot be limited to occur solely in an assigned "reaction vessel."
- A starting point for the process flow diagram is provided below, though this scheme is neither required nor optimized for the final design.

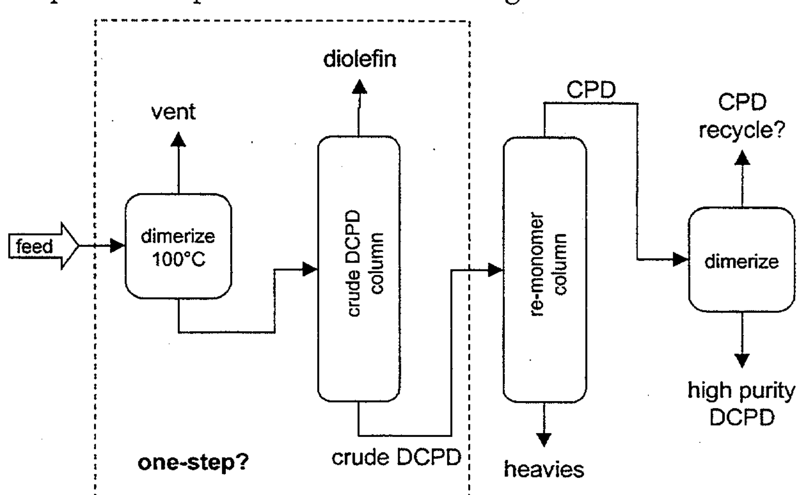


Figure 2. Potential Flowsheet for DCPD Isolation

E Miscellaneous Design Requirements

- *Inventory* - Provide 24 hour surge capacity for all isolated streams entering or leaving the process. More capacity should be provided where a higher risk to on-line time is an issue.
- *Materials of Construction (MOC)* - Determine acceptable MOC for this process, and clearly state what MOC you are using in your cost basis.
- *Equipment Ratings* - maximum allowable working pressure (MAWP) for pressure vessels must be specified, including overprotection systems.
- *Process Structure* - Document the overall size and cost of the process structure needed to safely support the process, and list any applicable assumptions used (e.g. cost per square meter of structure area).
- *Safety and Environmental* Regs for the U.S. and State of Texas must be followed. Wastes are to be handled in a manner that meets all State of Texas and Federal regulations. Hydrocarbon emissions to both air and water will be closely monitored and reported to the proper authorities after normal, day-to-day operation is attained after start-up.

F Technical Data

- *Physical properties* can be retrieved from available reference sources such as Perry's Chemical Engineer's Handbook, CRC Handbook of Chemistry & Physics, and from the AICHE DIPPR Pure Component Property Database.
- The default VLE methods included in the mainline process simulators (ASPEN, et al.) are expected to reflect the AICHE DIPPR data bank with sufficient accuracy to be used for the design work on this project.
- *Vapor-Liquid Equilibria* are described using the Redlich-Kwong-Soave EOS.

G Hydrogenation Reactor Design Specifications

The hydrogenation reactor will be over-designed to handle fluctuations in the concentration of unsaturates in the feed. Design specifications to be used for this purpose are explicitly provided below. The temperature of the reactor shall not exceed 265°F. Hydrogen partial pressure in the reactor should be such as to suppress vaporization of the hydrocarbon. All reaction occurs in the liquid phase.

• conversion	99.9%+
• catalyst	0.3% supported Pd (bulk density = 55.6 lb/ft^3)
• liquid mass velocity	5000 $lb/lb\text{-}ft^2$ (mass velocity of liquid feed / reactor cross sectional area)
• liquid hourly space velocity	3 ft^3/ft^3-hr (volumetric flow of the liquid feed / catalyst bed bulk volume)
• hydrogen	2 mole % excess

H Raw Material, Product, and Utility Values

- Market value of Naphtha can be assumed to be $263/ton.
- Feedstock is valued at the price of Naphtha plus $8/ton, delivered.
- High Purity DCPD is valued at tech-grade market value, or $0.28/lb.
- Unhydrogenated diolefin-rich by-product is valued at Naphtha less $35/ton.
- Hydrogenated diolefin-rich by-product is valued at the price of Naphtha.
- The waste vent stream is burned at fuel value of $2.50 per million BTU.
- Available utilities and their usage costs are:

600 psig saturated steam	$6.00/Klb
160 psig saturated steam	$4.00/Klb
30 psig saturated steam	$2.75/Klb
Cooling tower water (98°F supply, 120°F return)	$0.400/Kgal
Electricity	$0.070/kwh
Hydrogen (99.999wt%)	$3.00/1000 scf
Palladium	$295/Troy oz
Catalyst support	$0

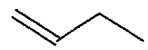
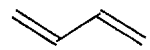
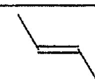
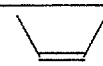
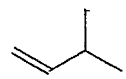
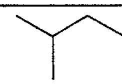
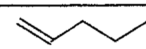
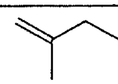
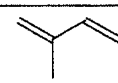
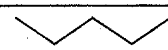
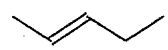
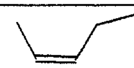
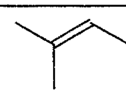
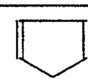
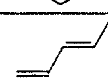
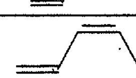
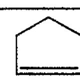
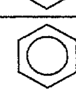
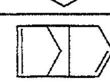
I Economic Analysis Guidelines

- *Purchased Equipment Cost* may be estimated by methods in Peters & Timmerhaus, simulator data, or any generally acceptable and documented source. Cost factors are to be based on Texas Gulf Coast delivery.
- *Capital Estimate* may be made using (1) methods from Peters and Timmerhaus, (2) process simulators, or (3) any generally acceptable and documented method.
- *Working Capital and other Economic Factors* - may be estimated using the cost factors given in Peters & Timmerhaus.
- *Discounted Cash Flow Analysis* is to be done as described in Peters & Timmerhaus. Assume: (1) ten year project life, (2) 1Q 2002 startup, (3) MACRS depreciation, (4) tax rates are 34% Federal and 6% State.

IV. REFERENCES

- Peters, M.S., and K.D. Timmerhaus, Plant Design and Economics for Chemical Engineers, 4th Edition, McGraw-Hill, 1990.
- ASTM D-323-58, "Standard Method of Test for Vapor Pressure of Petroleum Products (Reid Method)."
- C.N. Satterfield, "Trickle Bed Reactors," *AICHE Journal*, **21**(2), 1975.
- G.C. Bond and A.F. Rawle, "Catalytic hydrogenation in the liquid phase. Part 1. Hydrogenation of isoprene catalysed by palladium, palladium-gold, and palladium-silver catalysts," *Journal of Molecular Catalysis A: Chemical*, **109**, p. 261-271, 1996.

Table 1. Analysis of Process Feedstock

Component	*Acronym*	*Structure*	*Normal BP (°C)*	*mass fraction*
1-butene	1-C4		20.8	0.002
1,3-butadiene	1,3-BD		24.1	0.006
trans-2-butene	T-2-C4		33.6	0.002
cis-2-butene	C-2-C4=		38.7	0.003
3-methyl-1-butene	3MB1		68.1	0.008
i-pentane	iC5		82.1	0.152
1-pentene	1-C5=		85.9	0.038
2-methyl-1-butene	2MB1		88.1	0.048
isoprene	IP		93.3	0.150
n-pentane	nC5		96.9	0.197
trans-2-pentene	T-2-C5=		97.4	0.041
cis-2-pentene	C-2-C5=		98.5	0.019
2-methyl-2-butene	2MB2		101.4	0.024
cyclopentadiene	CPD		106.7	0.106
1,3-trans-pentadiene	T-PIP		107.6	0.062
1,3-cis-pentadiene	C-PIP		111.3	0.038
cyclopentene	CPE		111.6	0.022
cyclopentane	CPA		120.7	0.011
benzene	BENZENE		176.2	0.027
dicyclopentadiene	DCPD		unknown	0.044