American Institute of Chemical Engineers

STUDENT CONTEST PROBLEM

1981

345 East 47 Street • New York, New York 10017

CONTEST PROBLEM

1981

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS STUDENT CHAPTERS

Open Only to Undergraduates or Those
Without a Degree in Chemical Engineering

DEADLINE FOR MAILING

Solution must be postmarked not later than midnight, June 1, 1981.

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 readily available in handbooks and similar reference works. The use of textbooks, handbooks, journal articles, and lecture notes is permitted. In cases where there is disagreement in the data reported in the literature, the values given in the statement of the problem have been chosen as being most nearly applicable.

The problem is not to be discussed with any person whatever until June 1, 1981. This is particularly important in cases where neighboring institutions may not begin the problem until after its completion by another chapter. Submission of a solution for the competition implies adherence to the foregoing condition.

A period of not more than thirty consecutive days is allowed for completion of the solution. This period may be selected at the discretion of the individual counselor, but in order to be eligible for an award a solution must be postmarked not later than midnight, June 1, 1981.

The finished report should be submitted to the chapter counselor within the thirty-day period. There should not be any variation in form or content between the solution submitted to the chapter counselor and that sent to the AIChE Office. The report should be neat and legible, but no part need be typewritten.

The solution should be accompanied by a letter of transmittal giving only the contestant's name, school address, home address, and student chapter, lightly attached to the report. This letter will be retained for identification by the Secretary of the Institute. The solution itself must bear no reference to the student's name or institution by which it might be identified. In this connection, graph paper bearing the name of the institution should be avoided.

Each counselor should select the best solution or solutions, not to exceed two, from his chapter and send these by registered mail to

J. C. Forman, Secretary
American Institute of Chemical Engineers
345 East 47 Street
New York, New York 10017

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AIChE STUDENT CONTEST PROBLEM
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Dicyanobutene Reactor System

INTRODUCTION

Nylon 66 is produced by the condensation polymerization of adipic acid, $HOOC(CH_2)_4COOH$, and hexamethylenediamine, $H_2N(CH_2)_6NH_2$. Both monomers are produced by multistep syntheses with a high overall yield. We will be concerned with one of the steps in making hexamethylenediamine (HMD), namely, the cyanation of dichlorobutene (DCB) to dicyanobutene (DNB).

The reactions in the synthesis of HMD follow:

$C_4H_6 + Cl_2 \rightarrow C_4H_6Cl_2$ (1)
dichlorobutene (DCB)

$C_4H_6Cl_2 + 2NaCN \rightarrow C_4H_6(CN)_2 + 2\ NaCl$ (2)
dicyanobutene (DNB)

$C_4H_6(CN)_2 + H_2 \rightarrow C_4H_8(CN)_2$ (3)
adiponitrile (ADN)

$C_4H_8(CN)_2 + 4H_2 \rightarrow NH_2(CH_2)_6NH_2$ (4)
hexamethylenediamine (HMD)

The cyanation reaction (2) is carried out in an aqueous medium using a copper cyanide complex catalyst. Pilot plant studies have shown that control of pH and temperature is crucial.

Also, materials of construction are important; only glass-lined steel or Hastelloy C appears to be adequate. Since both the raw materials and materials of construction are expensive, it will be necessary to carry out a thorough evaluation of alternate designs to find the economic optimum.

STATEMENT OF PROBLEM

You are an engineer in a chemical engineering consulting, design, and construction company. Your recent work has been in nylon intermediates processes. A client has delivered basic data from a pilot plant study of the cyanation reaction. He would like your company to provide him with the design of a reactor system based on these data; all results should be shown in SI units.

The client's basic data contain information on the rate of reaction, materials of construction, investment and operating costs, and physical properties. Although the client normally supplies a complete data package, your company has usually found that it must use additional sources of information. A recommended list of references is attached. The client insists that you document fully any use of these references, and recommends the use of Guthrie (3) for total cost of the installed facility.

It will be your job to design a continuous reactor system to convert dichlorobutene (DCB) to dicyanobutene (DNB). You must provide a flow sheet which includes heat and material balances, a conceptual design of the optimum reactor system, including number, size and arrangement of the reactor(s), and a detailed estimate of investment and operating costs. You will also have to discuss alternate designs and show why the design you selected is the optimum.

REFERENCES

1. Levenspiel, O., "Chemical Reaction Engineering", 2nd Ed. John Wiley & Sons, 1972.
2. Perry & Chilton, eds., "Chemical Engineers Handbook", 5th Ed., McGraw Hill, 1972.
3. Guthrie, K., "Capital Cost Estimation", Chemical Engineering, March 24, 1969. 114-142 (also reprint #62).

MAGIC MONOMERS, INC.
Corporateville, U.S.A.

April 15, 1980

Mr. J. Q. Engineer
DOALL Chemical Engineering Co.
Richtown, Texas 98765

Dear Mr. Engineer:

To increase our nylon intermediates capacity, we are planning to install a facility for producing dicyanobutene (DNB) from dichlorobutene (DCB). The process (see attached block diagram) involves cyanation of DCB with aqueous sodium cyanide in the presence of a soluble copper cyanide complex catalyst.

Our Technical Division will design the feed preparation, product recovery, refining and catayst recovery areas of the process, and the supporting services. We request your services in designing a continuous reactor system. The annual production of crude DNB (100% DNB basis) shall be 96,000 metric tons, based on 8,000 operating hours per year.

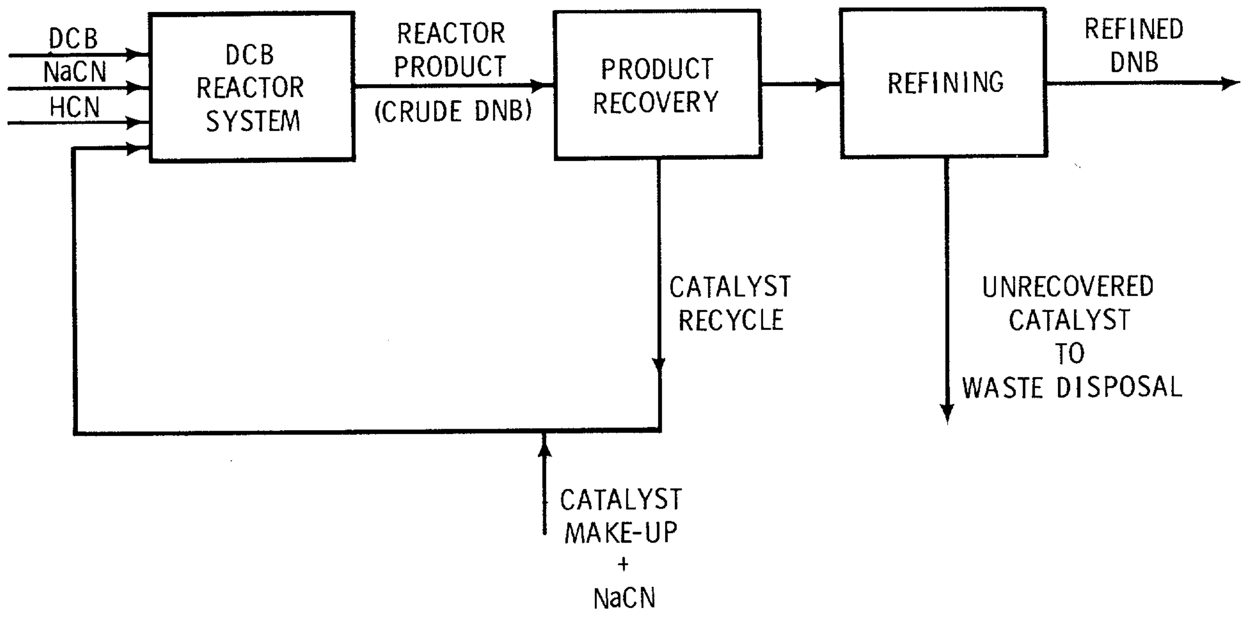
The high cost of the raw materials and materials of construction requires that you provide an optimum economic design. Our Economics Division will provide a guide for optimizing in accord with our internal evaluation practices. We plan to begin construction in 1982. The expected mid-point of construction should be in 1983, with startup in 1984. The proof year in which the project economics will be evaluated is 1987.

Very truly yours,

John D. Manager

John D. Manager
Magic Monomers, Inc.

DNB SYNTHESIS



MAGIC MONOMERS, INC.
Corporateville, U.S.A.

BASIC DATA REPORT

Process for the Manufacture of Dicyanobutene from Dichlorobutene by Aqueous Cyanation

Report Prepared By

Elmer B. Basic

February 29, 1980

INTRODUCTION

During the past two years, the Research and Technical Divisions of Magic Monomers, Inc. have made extensive studies on alternate routes for making dicyanobutene, an intermediate in manufacturing polyamide resins. Special circumstances related to supply and production of other Company products show that cyanation of dichlorobutene with aqueous sodium cyanide offers the most favorable economics.

The process chemistry has been worked out in considerable detail, and processing problems including corrosion have been studied in the pilot plant. The results are recorded in several reports filed under the general title, "Dicyanobutene from Dichlorobutene". This report provides only the basic data for developing reactor designs and economic evaluations.

PHYSICAL PROPERTIES

The physical properties of the feed and product streams are presented in Table BD I.

The DCB feed and the DNB produced are mixtures of isomers; however, these mixtures can be treated as single entities with the average properties given in Table BD I. A number of by-products are formed, but these can be treated as inerts. For sizing the reactor, use the average reactor mixture properties.

OVERALL REACTION

The cyanation of dichlorobutene (DCB) is carried out by reacting DCB with aqueous sodium cyanide in the presence of a soluble copper cyanide complex:

$$\underset{(DCB)}{C_4H_6Cl_2} + 2NaCN \xrightarrow[Cu(CN)_x]{} \underset{(DNB)}{C_4H_6(CN)_2} + 2NaCl$$

The kinetics of this reaction show an interesting behavior. The catalyst is soluble only in the aqueous phase; therefore the reaction proceeds only in that phase. Since, DCB is only slightly soluble in the aqueous phase the reaction starts out slowly. However, the DNB produced enhances the solubility of the DCB and as soon as the DNB begins to form, the reaction rate increases until the solubility of both DCB and DNB are at a maximum. When the reaction is run by the batch or semi-batch method, the reaction starts slowly, increases to a maximum, and finally, when the DCB feed is depleted, the rate falls off and the reaction stops.

PILOT PLANT OPERATION

General

A schematic flowsheet of the pilot plant operation is shown in Figure 1.

The reactor, a 25 liter, jacketed, glass-lined vessel with an agitator was operated in a semi-batch manner. The reactor was charged initially with DCB and catalyst solution, and brought to temperature. Sodium cyanide solution was then fed at a rate that held the pH in the range of 5.0-5.5. An aqueous solution of HCN was added continuously to neutralize excess alkali (NaOH, NH_3, and Na_2CO_3) in the NaCN feed. Exothermic reaction heat was removed by circulating cooling water through the jacket.

The reactor effluent was decanted. The crude DNB (organic phase) was sent to product recovery, and the heavier aqueous phase was sent to catalyst recovery.

The instrumentation needs are also shown in Table BD IV. Again, because of the corrosive material, installed spare instrument loops are needed for the pH and millivolt control.

The heat transfer specifications are in Table BD V. Included are the heat transfer coefficients measured in the pilot plant. We have also included the formulas for estimating coil and jacket areas in a vessel.

Possible designs include jacketed vessels, internal coils, and/or external heat exchangers with pumped recirculation. The pilot plant had serious pump maintenance and heat exchanger fouling problems with an external loop. Any external pumping and heat exchange system must have an installed duplicate system.

TABLE BD I. PHYSICAL PROPERTIES

REFINED DCB

COMPONENT	WT. %	MOL WT.
DCB	99.25	125
Misc Organics	0.50	125
H_2O	0.25	18

Heat capacity (liq)	1.5×10^3 J/kg · K (0.36 Btu/lb °F)
Density (liq)	1.16×10^3 kg/m^3 (72.3 lb/ft^3)
Viscosity (liq)	0.65×10^{-3} Pa · s (0.65 centipoise)

CATALYST SOLUTION (Combination of recycle and make-up)

COMPONENT	WT. %	MOL WT.
NaCu $(CN)_2$	6.5	138.6
Na CN	17.3	49.0
H_2O	76.2	18.0

Heat capacity (liq)	3.8×10^3 J/kg · K (0.91 Btu/lb °F)
Density (liq)	1.15×10^3 kg/m^3 (71.7 lb/ft^3)
Viscosity (liq)	1.5×10^{-3} Pa · s (1.5 centipoise)

SODIUM CYANIDE SOLUTION

COMPONENT	WT. %	MOL WT.
NaCN	26.0	49
Na_2CO_3	1.0	106
NH_3	0.3	17
NaOH	0.2	40
H_2O	72.5	18

Heat capacity (liq)	4.0×10^3 J/kg · K (0.96 Btu/lb °F)
Density (liq)	1.13×10^3 kg/m^3 (70.5 lb/ft^3)
Viscosity (liq)	1.5×10^{-3} Pa · s (1.5 centipoise)

HYDROGEN CYANIDE SOLUTION

COMPONENT	WT. %	MOL. WT.
HCN	9.0	27
H_2O	91.0	18

Heat capacity (liq)	4.0×10^3 J/kg · K (0.96 Btu/lb °F)
Density (liq)	1.00×10^3 kg/m^3 (62.4 lb/ft^3)
Viscosity (liq)	1.0×10^{-3} Pa · s (1.0 centipoise)

AVERAGE REACTOR MIXTURE

Heat capacity (liq)	3.4×10^3 J/kg · K (0.82 Btu/lb °F)
Density (liq)	1.13×10^3 kg/m^3 (70.5 lb/ft^3)
Viscosity (liq)	1.3×10^{-3} Pa · s (1.3 centipoise)

TABLE BD II. DCB REACTION KINETICS—PILOT PLANT DATA

TIME (MI)	DCB % CONVERSION
0	0.00
10	6.21
20	13.33
30	21.48
40	30.82
50	41.52
60	53.78
70	67.82
71	69.33
72	70.86
73	72.42
74	73.99
75	75.59
76	77.21
77	78.85
78.0	80.52
79.0	82.21
80.0	83.77
82.5	87.38
85.0	90.26
87.5	92.54
90.0	94.31
92.5	95.68
95.0	96.73
97.5	97.53
100.0	98.14
102.5	98.60
105.0	98.95
107.5	99.21
110.0	99.41
112.5	99.56
115.0	99.67

Catalyst ratio	0.038 kg Cu per kg DCB in initial charge
Reaction Temperature	80°C ± 2
Cyanide Consumption	8% of the CN^- in the catalyst stream is consumed in the reaction. 100% of CN^- added in sodium cyanide and hydrogen cyanide streams reacts.

TABLE BD III. DESIGN CONDITIONS

Operating temperature 80° C ± 2
Design Pressure 3.45×10^5 Pa gauge (50 psig)
Feed Temperatures

Refined DCB 60°C
Catalyst Solution 60°C
Sodium Cyanide Solution 40°C
Hydrogen Cyanide Solution 40°C

REACTION—The heat of reaction for the DCB to DNB reaction was determined experimentally at the reaction temperature of 80°C, and found to be -1.023×10^8 J/mol DCB consumed. (−44,000 Btu/lb-mol DCB).

YIELD—The yield loss of DCB to by-products in the reactor is 6% regardless of conversion when the reaction is carried out at 80°C ± 2. Any unconverted DCB constitutes an additional yield loss.

CATALYST—The catalyst is composed mainly of recycled material. The catalyst to DCB ratio should be the same as for the pilot plant tests. Catalyst loss is 0.5% through the reactor system.

TABLE BD IV. REACTOR DESIGN SPECIFICATIONS

INSTRUMENTATION—

- o pH control for NaCN addition to reactor (provide duplicate installation)
- o millivolt control for HCN addition to reactor (provide duplicate installation)
- o temperature control for cooling water to any coils, jackets, and heat exchangers
- o flow rate control for maintaining the proper catalyst/DCB ratio in the feed

AGITATION—Agitators and drives supplied on the glass-lined steel vessels (Table FD2) are considered adequate in terms of HP requirements

MATERIALS OF CONSTRUCTION—

Reactor vessels may be glass-lined steel or Hastelloy C. Piping must be Hastelloy C.

See Table BD V for materials for heat transfer equipment.

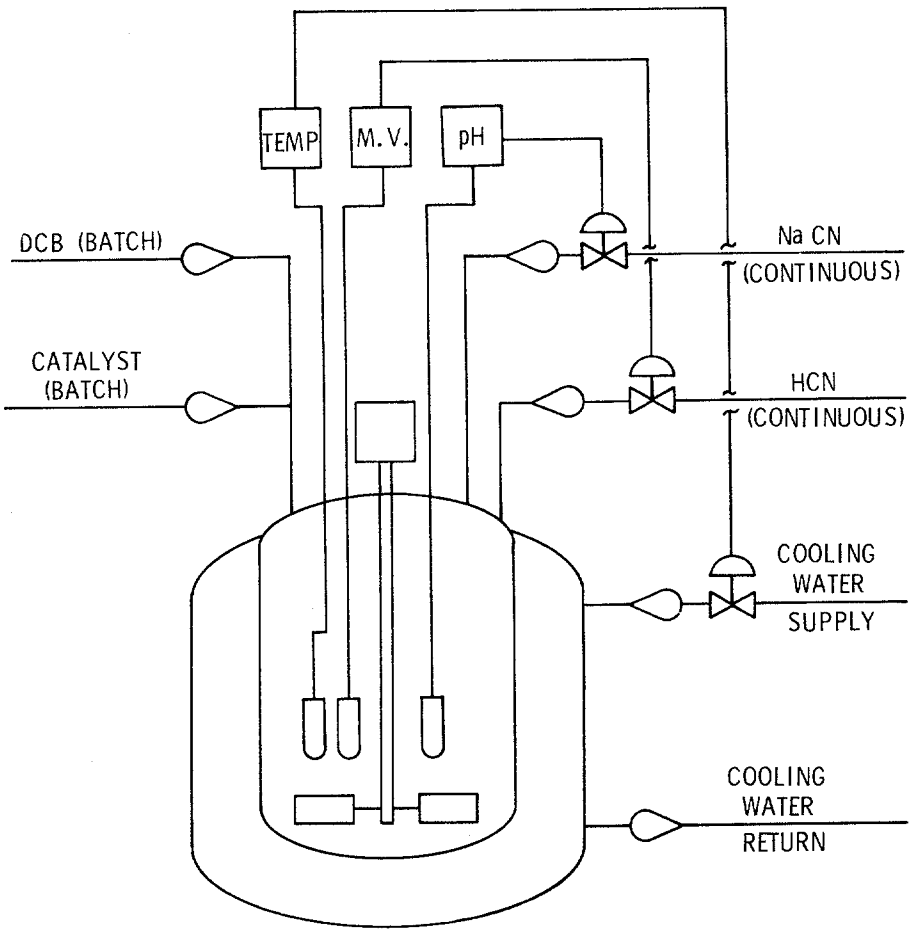


Figure 1. Pilot plant semi-batch reactor.

pH Control

Control of pH was found to be most important. It governs the concentration of the active catalyst species, and must be held within the range of 5.0-5.5. If the pH drops to 4.5, or increases to 6.0, the reaction rate drops by an order of magnitude. Since the NaCN feed is controlled by pH measurement, it is necessary to neutralize small amounts of NaOH, NH_3, and Na_2CO_3 contaminants present in the NaCN. This excess alkali is not consumed in the reaction, and if not neutralized by addition of aqueous HCN, it would interfere with control of the NaCN addition. The HCN addition can be controlled accurately with a millivolt readout from a special electrode system. The cyanide salts formed in the neutralization react with the DCB.

Catalyst

The optimum catalyst ratio was found to be 0.038 kg Cu per kg DCB in feed.

Temperature Control

Temperature control is also important. The preferred temperature is 80 ± 2°C. At higher temperatures, yield loss increases from hydrolysis and irreversible polymerization of the DCB. At lower temperatures the reaction rate slows appreciably; and at 76°C the DNB starts to crystallize on the heat transfer surfaces.

Agitation

Tests to determine the degree of agitation needed showed that the rate of reaction increased with increasing agitation, but became constant at a power input of 3 Hp/1000 gals. The data suggested that only enough agitation was required to disperse the organic and aqueous phases to the extent that the aqueous phase was always saturated with DCB.

Summary of Experimental Results

Numerous runs were made in the pilot plant reactor. The results are summarized in the Research and Technical Division reports cited above. For convenience, the results of several runs under the most favorable conditions are summarized, along with the conditions, in Table BD II. The results are expressed as percent conversion of DCB versus time from the start of sodium cyanide addition.

In a reaction of this type the overall rate is a complex relationship between the concentration of reactants (DCB, cyanide, and catalyst) in the aqueous phase. Since the DCB is only slightly soluble in the aqueous phase, the overall rate involves the mass transfer of the DCB into the aqueous phase. The rate for design purposes can be determined directly from the conversion data in Table BD II.

REACTOR DESIGN SPECIFICATION

The reactor conditions and specifications are summarized in Tables BD III and BD IV. Note that the reaction fluid is severely corrosive. Only glass-lined steel or Hastelloy C was satisfactory. Glass-lined piping is unacceptable because it is prone to leak and more expensive to maintain.

Table FD 1. Construction Cost Indexes— Engineering News Record (ENR)

ANNUAL AVERAGE INDEX	
1967	100
1968	108
1969	119
1970	129
1971	148
1972	164
1973	177
1974	189
1975	206
1976	223
1977	240
1978	259
1979	279
1980	307

FORECASTED	
1981	335
1982	365
1983	395
1984	425
1985	460
1986	495
1987	535

Table FD 2. Standard Jacketed Glass-Lined Steel Vessels—Purchased Cost -1980 (Including Motor, Gear Reducer, Seal, Impeller and Shaft)

WORKING CAPACITY M-GALLONS	DRIVE HP	COST $M
0.50	5	30
0.75	7.5	36
1.0	10	40
1.5	10	47
2.0	15	51
3.0	20	66
4.0	25	73
5.0	30	108
6.0	40	132
8	50	157
10	60	204
12.5	75	230
15	100	260
24	150	390

*Deduct 10% for vessels without jackets

Table FD 3. Hastelloy C Coils—Purchased Cost—1980

2" Sch. 10—$207/linear ft.

Hastelloy C Agitators—Purchased Cost—1980

(Includes Motor, Gear Reducer, Seal, Shaft, and Impeller)
All Wetted Parts Hastelloy C

HP	PURCHASED COST—$M
5	14.7
7.5	14.7
10	19.3
15	19.6
20	26.5
25	34.0
30	34.0
40	47.0
50	47.5
60	50.4
75	61.7
100	85.3
125	103
150	121

Hastelloy C Tanks, Piping, and Heat Exchangers

The materials factor for Hastelloy C tanks, piping, and heat exchangers is the same as for titanium, [Guthrie (3)].

Table FD 4. Instrumentation—Costs

Direct cost for each control loop will be $7000, including equipment, material and labor.

Table FD 5. Operating Costs

	1987 COSTS	ALLOCATED INVESTMENT DIRECT LABOR & MATERIALS COST ENR = 307
Electricity	$0.082/Kw-hr	$110/KVA
Cooling Tower Water	$0.11/M Gal	$ 70/GPM
Depreciation	8% of original investment	
Maintanence	7% of original investment	
Property Taxes & Insurance	1% of original investment	
Cost of Raw Materials	DCB Solution	$ 0.62/kg
	Catalyst Solution	$ 0.30/kg
	NaCN Solution	$ 0.082/kg
	HCN Solution	$ 0.0192/kg

Effective Income Tax Rate (federal plus state) 50%

Note: Assume that operating labor, operating supervision and overheads will not vary with the size of the process equipment in this area.

Raw Materials Inventory	– 1 month
Product Inventory	– 1 month cost of sales
Cash	– 1/4 month cost of sales
Accounts Receivable	– 1-1/2 months sales income
Selling Cost	– 10% of Sales Income

TABLE BD V. HEAT TRANSFER SPECIFICATIONS

Heat of reaction must be removed by one or more of the following:

- o jacket on glass-lined steel vessel
- o Internal helical coils of Hastelloy C using (50.8mm) 2″ Sch 10 tubing
- o External heat exchanger system, including pump, piping, and heat exchanger

HEAT TRANSFER AREA—STANDARD REACTOR VESSEL

Jackets—Area of Jacket is related to the working volume of reactor according to:

$$A = 3.7\ V^{2/3}$$

where A = jacket area (m^2)
V = reactor working volume (m^3)

COILS—Maximum area of the coil is related to working volume of reactor according to:

$$A = 4.6\ V^{2/3}$$

where A = coil area (m^2)
V = reactor working volume (m^3)

EXTERNAL HEAT EXCHANGER

There are no restrictions on the area that can be supplied in an external loop.

HEAT TRANSFER COEFFICIENTS

The overall heat transfer coefficient, U_0, for the various modes outlined above are:

TYPE	U_0
JacketedGlass-Lined Steel	80 W/m^2·K (14.1 Btu/hr·ft^2·°F)
International Hastelloy C Coils	120 W/m^2·K (21.1 Btu/hr·ft^2·°F)
External Heat Exchanger Hastelloy	150 W/m^2·K (26.4 Btu/hr·ft^2·°F)

COOLING WATER

Cooling water is available at 30°C. Assume a maximum rise of 10°C.

MAGIC MONOMERS, INC.
Corporateville, U.S.A.

Mr. J. Q. Engineer
DOALL Chemical Engineering Co.
Richtown, Texas

Dear Mr. Engineer:

Magic Monomers Dicyanobutene Project Economic Evaluation

Reference: Letter—John D. Manager to J. Q. Engineer, dated April 15, 1980

At Mr. Manager's request, I am providing the accompanying material to aid you in developing an optimum design for a continuous reactor system to produce dicyanobutene (DNB) by the cyanation of dichlorobutene (DCB).

The method for optimizing process equipment design is consistent with our internal evaluation practice.

The cost data in Tables FD1 to FD5 provide the information for use in your evaluations.

Very truly yours,

I. B. N. Accountant

I.B.N. Accountant, Manager
Finance Division

MAGIC MONOMERS, INC.
Method for Optimizing Process Equipment

Magic Monomers, Inc.'s Management has agreed that net return on original investment (NROI) is an adequate basis for optimizing the design or process equipment. The proof year should be the third year of operation.

In this method, the increase in net earning that would result by increasing the size of the process equipment is compared with the additional investment needed to obtain this net earnings change. If this exceeds our criterion of 15% net-return-on-original-investment, the extra increment of process investment should be installed. A formula for the method follows:

$$\mathrm{NROI} = \frac{(\mathrm{NE})_{n+1} - (\mathrm{NE})_n}{(\mathrm{TI})_{n+1} - (\mathrm{TI})_n}$$

n,n+1	Alternatives n and n+1
NROI	Net return on original investment
NE	Net Earnings, (S-COS) × (1 − ITX)
S	Sales
COS	Cost of Sales, RMC + OL + OSV + MT + UTL + DEPN + PTI + OH + SC
ITX	Effective Income tax rate (Federal plus State)
RMC	Raw Material Costs
OL	Operating Labor, including employee benefits
OSV	Operating Supervision, including employee benefits
MT	Maintenance cost including labor, materials, supervision, and employee benefits
UTL	Utilities costs
DEPN	Depreciation
PTI	Property taxes and insurance
OH	All company overheads
SC	Selling costs
TI	Total Investment, PI + WC
PI	Permanent Investment
WC	Working Capital, RMI + PDI + CASH + ACR
RMI	Raw Material Inventories
PDI	Product Inventories
CASH	Cash on hand less accounts payable
ACR	Accounts Receivable