PRODUCTION OF ETHYLBENZENE BY LIQUID-PHASE BENZENE ALKYLATION

A Thesis

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CERTIFICATE

This is to certify that the thesis entitled, **“production of ethylbenzene by liquid-phase benzene alkylation**” submitted by **prasanna kumar sahoo** for the requirements for the award of Bachelor of Technology in Chemical Engineering at National Institute of Technology Rourkela, is an authentic work carried out by him under my supervision and guidance.

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ABSTRACT

The work deals with optimization of the process of production of ethylbenzene by liquid-phase benzene alkylation. This process involves the reaction of benzene with ethylene to form ethylbenzene. Ethylene reacts with ethylbenzene to form undesired product di-ethyl benzene, if the temperatures of reactor or concentrations of ethylene are high. Di-ethyl benzene reacts with benzene to form ethylbenzene. Di-ethyl benzene is the highest-boiling component in the system; it comes out the bottom of two distillation columns. The recycling benzene is more expensive. The economic optimum steady-state design is developed that minimizes total annual cost. Thus it provides a classic example of an engineering design and optimization of a process. The purpose of this project is to develop an optimum design for the ethylbenzene process considering reactor size, benzene recycled.

Keywords: design, distillation, control, process control

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CHAPTER 1

INTRODUCTION

1. INTRODUCTION

Ethylbenzene is an organic compound with the formula $C_6H_5CH_2CH_3$. The aromatic hydrocarbon is important in the petrochemical industry and as an intermediate in the production of styrene, which is used for making polystyrene, it is a common plastic material. Also present in small amounts in crude oil, ethylbenzene is produced by combining benzene and ethylene in an acid-catalysed chemical reaction.

It is used as a solvent for aluminium bromide in anhydrous electro deposition of aluminium. Ethylbenzene is an ingredient in some paints and solvent grade xylene is nearly always contaminated with a few per cent of ethylbenzene. [8]

1.1 Industrial Uses of Ethylbenzene

Which industries used this chemical?	How is it used in this industry?
Machinery Mfg. and Repair	Solvents - Machinery Manufacture and Repair
Rubber Manufacture	Solvents - Rubber Manufacture
Paint Manufacture	Hydrocarbon Solvents
Wood Stains and Varnishes	Varnish Solvent
Paper Coating	Solvents
Electroplating	Electroplating - Vapours Degreasing Solvents

1.2 Properties of Ethylbenzene

- Appearance : Clear, colourless liquid
- Molecular formula : C_8H_{10}
- Molar mass : 106.17 g mol^{-1}
- Density : 0.8665 g/mL
- Melting point : -95 °C, 178 K, -139 °F
- Boiling point : 136 °C, 409 K, 277 °F
- Solubility in water : 0.015 g/100 mL (20 °C). [8]

CHAPTER 2

LITERATURE REVIEW

2. LITERATURE REVIEW

2.1 Process

In this process we used two reactors in series, two distillation columns and two liquid recycle streams. It is a nice example of a multiunit complex process that is typical of many chemical plants found in industry.

The ethylbenzene process involves gaseous ethylene into the liquid phase of the first of two CSTR reactors in series. Both the reactors operate at high pressure to maintain liquid in the reactor at high temperatures required for reasonable reaction rates. A large liquid benzene stream is fed to the first reactor. The heat of exothermic reaction is removed by generating steam in this reactor.

Effluent from first reactor is fed into second reactor along with recycle stream of Di-ethyl benzene. This reactor is adiabatic. Effluent from second reactor is fed to a distillation column that produces a distillate that is mostly benzene, which is recycled to first reactor along with fresh feed of make-up benzene. Bottom stream is a mixture of ethylbenzene and Di-ethyl benzene. It is fed to a second distillation column that produces ethylbenzene distillate and Di-ethyl benzene bottoms, which is recycled back to second reactor.

Process Flow sheet

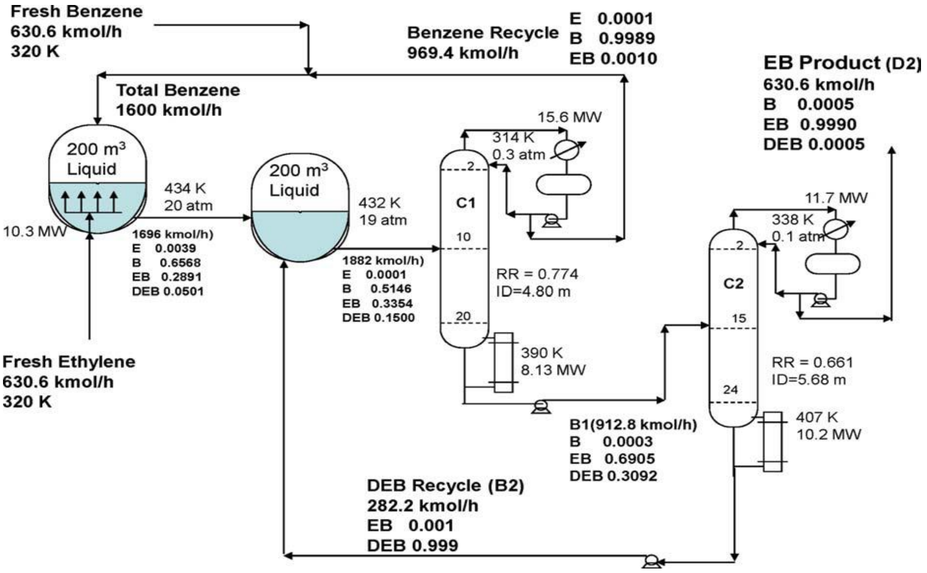

Figure 2.1 Ethyl benzene flow sheet. [Luyben, 2010]

2.2 Reaction Mechanism and kinetics

Production of ethylbenzene involves the liquid-phase reaction of ethylene with benzene

$$C_2H_4 + C_6H_6 \longrightarrow C_8H_{10}$$

$K = 1.528 \times 10^6$

E (Cal/mole) = 17,000

Concentration terms (kmol/m^3)= $C_E C_B$

Undesirable reaction occurred by the formation of Di-ethyl benzene from reaction of ethylbenzene with ethylene.

$$C_8H_{10} + C_2H_4 \longrightarrow C_{10}H_{14}$$

$K = 2.778 \times 10^7$

E (Cal/mole) = 20,000

Concentration terms (kmol/m^3) = $C_E C_{EB}$

A third reaction also occurs, in which Di-ethyl benzene reacts with benzene to form ethylbenzene.

$$C_{10}H_{14} + C_6H_6 \longrightarrow 2C_8H_{10}$$

K = 1000

E (Cal/mole) = 15,000

Concentration terms (kmol/m^3) = $C_B C_{DEB}$

2.3 Process Design Basics

Process design is a very important aspect before any project implementation; a proper Design during the initial stages can save costs to a great extent. The cost involved in designing a project is very less compared to construction cost and it can be greatly helpful in maximizing profits of the plant as well as providing a safe environment.

The following points need to be taken care for a proper process design.

- .Raw material cost reduction. Selectivity of reaction is increased by proper use of catalysts. Increasing selectivity can reduce separation and recycle costs.
- Capital-cost reduction. Better flow sheeting can reduce capital costs effectively
- Energy use reduction. Pinch point analysis is used for energy saving.
- Increased process flexibility. Process plant should be able to handle a range of feed compositions.
- Increased process safety. Nonlinear analysis can be done to make the process safer.
- Increased attention to quality. Reduction of by products and the effective use of process control equipment can lead to process safety.
- Better environmental performance. Minimization of harmful wastes to the environment. [Dimian, 2003]

CHAPTER 3

DESIGN: PROCEDURE, RESULT & DISCUSSION

3. DESIGN: PROCEDURE, RESULT AND DISCUSSION

3.1 Procedure

In this process reactors of equal size are assumed. Reactors containing 200 m^3 of liquid and a total benzene stream of 1700 kmol/h. Total benzene stream is distillate from first column is 999.6 kmol/h and fresh benzene feed. Two fresh feeds ethylene & benzene are each of 700.4 kmol/h. All of the ethylene and benzene reactant leave as ethylbenzene product in distillate-2 from second column. First reactor operates at 436 K and 20 atm. 82.5 kmol/h of Di-ethyl benzene generated in first reactor with 466.6 kmol/h of ethylbenzene, 7.3 kmol/h of unreacted ethylene leaving.

Temperature of the saturated steam is 415 K ,a reactor temperature of 435 K. Effluent from first reactor is fed into second reactor. Recycled Di-ethyl benzene comes from bottom of the second column is fed into the second reactor at 283.2 kmol/h. Di-ethyl benzene leaving in the effluent of second reactor is also same as 283.2 kmol/h. Second reactor convert all the Di-ethyl benzene formed in the first reactor back to ethylbenzene.

Effluent from second reactor is at high pressure and high temperature. It is fed into first distillation column. First column has 21 stages and a reflux ratio of 0.784. It operates at 0.3 atm, it gives a reflux-drum temperature of 315 K and it permits the uses of cooling water in condenser. Base temperature is 392 K; it permits the uses of low-pressure steam (435 K, 4 atm) in reboiler. Distillate is mostly benzene, which is mix with the fresh benzene and recycled to the first reactor.

Second column has 25 stages and a reflux ratio of 0.672. Which is operates under low vacuum at 0.1 atm, it gives a reflux-drum temperature of 336 K and permit the use of cooling water in condenser. Base temperature is 409 K; it permits the uses of low-pressure steam in reboiler. Distillate is high-purity ethylbenzene. The bottoms Di-ethyl benzene is recycled to the second reactor.

3.2Design of Distillation Columns

For optimizing the design of a distillation column is to determine values of the design optimization variables that minimize the total annual cost. The design optimization variables include pressure, total number of trays, and feed tray location.

- Column diameter: Aspen Tray using double-pass trays Sizing.
- Column length: total number of stages trays with 2 ft spacing plus 20% extra length.

Reactors:

- Aspect ratio = 1
- Half full of liquid

Reboilers:

- Differential temperature = Steam temperature – Base temperature
- Heat-transfer coefficient = 0.588 kW/K m2

Condensers:

- Differential temperature = Reflux drum temperature − 310 K
- Heat-transfer coefficient = 0.872 kW/K m2

Energy cost:

- LP steam (433 K) = Rs350.1 per GJ
- MP steam (457 K) =Rs369.9 per GJ
- HP steam (537 K) = Rs442.3per GJ

Value of steam generated in reactor;

LP steam (410 K) = Rs270 per GJ

Total annual cost = (capital cost/payback Period) +Energy Cost

Payback period = 3 years

3.2.1 Column Pressure Selection:

In column-1(C1):

Table 3.1 Column Pressure Selection in C1

Pressure(atm)	0.1	0.3	0.4	0.5	1
base temperature(K)	288	315	323	330	352
Reactor temperature (K)	374	393	399	406	427
column diameter (m)	6.5	4.8	4.44	4.17	3.62
steam	LP	LP	LP	LP	HP
reboiler duty (10^6 cal/s)	1.68	1.82	2.23	2.29	2.67
condenser duty (10^6 cal/s)	3.77	3.70	3.67	3.64	3.61
reboiler area (m^2)	-	344	441	571	636
condenser area (m^2)	-	3038	1294	856	416
Capital cost (Rs45*10^6)	-	2.42	1.88	1.74	1.33
Energy cost (Rs45*10^6/year)	-	1.95	2.15	2.21	2.90
total annual cost (Rs45*10^6/year)	-	2.69	2.75	2.92	3.45

In column-2(C2):

Table 3.2 Column Pressure Selection in C2

Pressure(atm)	0.1	0.3	0.5	0.7	-
base temperature(K)	336	368	385	396	-
Reactor temperature (K)	404	425	439	450	-
column diameter (m)	5.76	4.43	4.16	4.12	-
steam	MP	MP	MP	HP	-
reboiler duty (10^6 cal/s)	2.33	2.64	3.08	3.28	-
condenser duty (10^6 cal/s)	2.87	2.94	3.07	3.15	-
reboiler area (m^2)	323	646	257	326	-
condenser area (m^2)	506	243	194	174	-
Capital cost (Rs45*10^6)	1.70	1.43	1.18	1.20	-
Energy cost (Rs45*10^6/year)	2.47	2.95	3.97	4.30	-
total annual cost (Rs45*10^6/year)	3.10	3.33	4.23	4.69	-

The pressure selected for Column-1(C1) is 0.3 atm and for Column-2(C2) is 0.1 atm.

3.3 Number of column trays

Using more trays reduces the reboiler heat input, which reduces the column diameter and heat exchanger area. But using more trays increases the height of column, which increases capital cost.

Table 3.3&3.4 gives results for both columns C1 & C2 over a range of tray numbers. The pressure in C1 is 0.3 atm. The pressure in C2 is 0.1 atm. Increasing number of trays reduces the energy cost and capital cost of heat exchanger.

Column Tray Number Optimization:

For column-1 (C1)

Pressure = 0.3 atm

Table3.3 Column Tray Number Optimization for C1

total number of stages	17	21	27
feed stage	8	10	13
column diameter (m)	5.16	4.84	4.73
reboiler duty (10^6 cal/s)	2.20	1.94	1.91
condenser duty (10^6 cal/s)	4.03	3.76	3.62
shell (Rs45*10^6)	0.657	0.773	0.926
heat exchangers(Rs45*10^6)	1.75	1.64	1.61
total capital cost (Rs45*10^6)	2.41	2.44	2.56
Energy cost (Rs45*10^6/year)	2.32	2.03	2
total annual cost(Rs45*10^6/year)	3.23	2.85	2.89

For column-2(C2)

Pressure = 0.1 atm

Table 3.4 Column Tray Number Optimization for C2

total number of stages	21	25	31
feed stage	13	15	18
column diameter (m)	5.85	5.74	5.60
reboiler duty (10^6 cal/s)	2.54	2.41	2.45
condenser duty (10^6 cal/s)	2.90	2.82	2.74
shell (Rs45*10^6)	0.99	1.12	1.30
heat exchangers(Rs45*10^6)	0.75	0.73	0.73
total capital cost (Rs45*10^6)	1.76	1.87	2.07
Energy cost (Rs45*10^6/year)	2.79	2.68	2.67
total annual cost(Rs45*10^6/year)	3.37	3.25	3.39

3.4 Economic Optimization of Process

Design optimization variables in this process are reactor size and benzene recycle flow rate. Ethylene conversion in the first reactor is fixed at 99%. Increasing reactor size means lower the reactor temperature, ethylbenzene selectivity is better, and lower Di-ethyl benzene recycle flow rates. Increasing benzene recycle give better ethylbenzene selectivity and lower Di-ethyl benzene recycle, but separation cost is increase. Di-ethyl benzene recycles and comes out bottom of both distillation columns.

Effects of Reactor Size and Recycle

Volume of reactor =150 m^3

Table 3.5 Effects of Reactor Size and Recycle for150 m^3

total benzene(kmol/h)	1600	1700	1800
DEB recycle (kmol/h)	524.9	316.3	257
reactor temperature 1 (K)	440	442	442
column diameter 1 (m)	4.97	5.05	5.17
reboiler duty 1 (10^6 cal/s)	2.07	2.04	2.06
condenser duty 1 (10^6 cal/s)	4.04	4.07	4.28
column diameter 2 (m)	6.0	5.76	5.68
reboiler duty 2 (10^6 cal/s)	2.85	2.47	2.47
condenser duty 2 (10^6 cal/s)	3.23	2.85	2.78
total energy cost (Rs45*10^6/year)	0.944	0.845	0.869
total capital cost (Rs45*10^6)	4.67	4.58	4.89
total annual cost (Rs45*10^6/year)	2.53	2.34	2.44

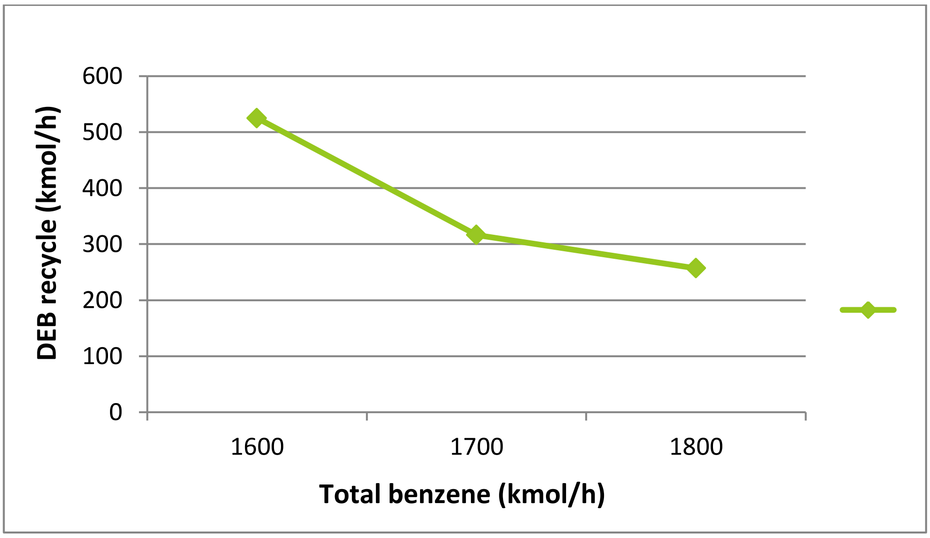

Figure 3.1 Effect of benzene recycles and reactor size on Di-ethylbenzene recycle

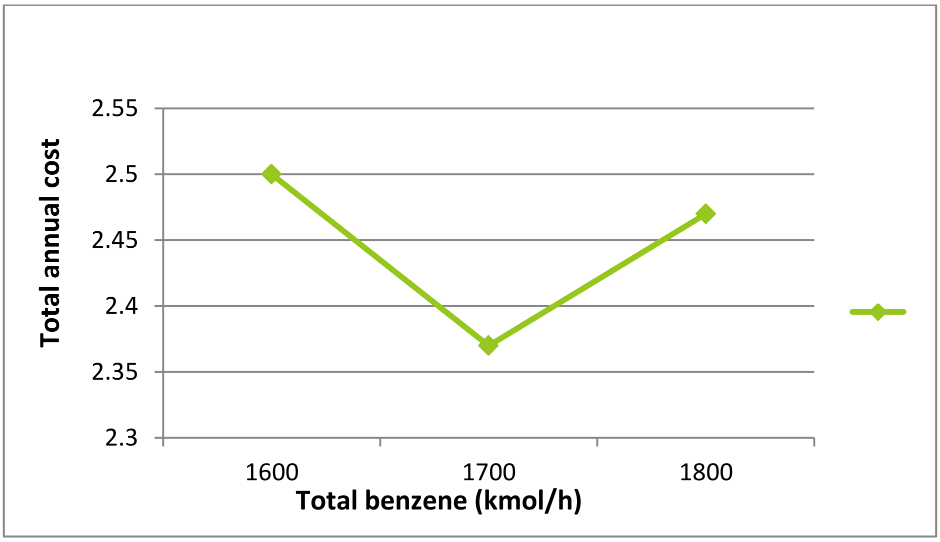

Figure 3.2 Effect of benzene recycles and reactor size on total annual cost.

Volume of reactor =200 m^3

Table3.6. Effects of Reactor Size and Recycle for 200 m^3

total benzene(kmol/h)	1500	1600	1700
DEB recycle (kmol/h)	388.6	281.2	232.3
reactor temperature 1 (K)	433	434	434
column diameter 1 (m)	4.72	4.83	4.94
reboiler duty 1 (10^6 cal/s)	1.90	1.93	2.02
condenser duty 1 (10^6 cal/s)	3.56	3.76	3.96
column diameter 2 (m)	5.87	5.69	5.62
reboiler duty 2 (10^6 cal/s)	2.61	2.45	2.35
condenser duty 2 (10^6 cal/s)	2.96	2.81	2.74
total energy cost (Rs45*10^6/year)	0.763	0.721	0.776
total capital cost (Rs45*10^6)	4.77	4.75	4.81
total annual cost (Rs45*10^6/year)	2.37	2.34	2.39

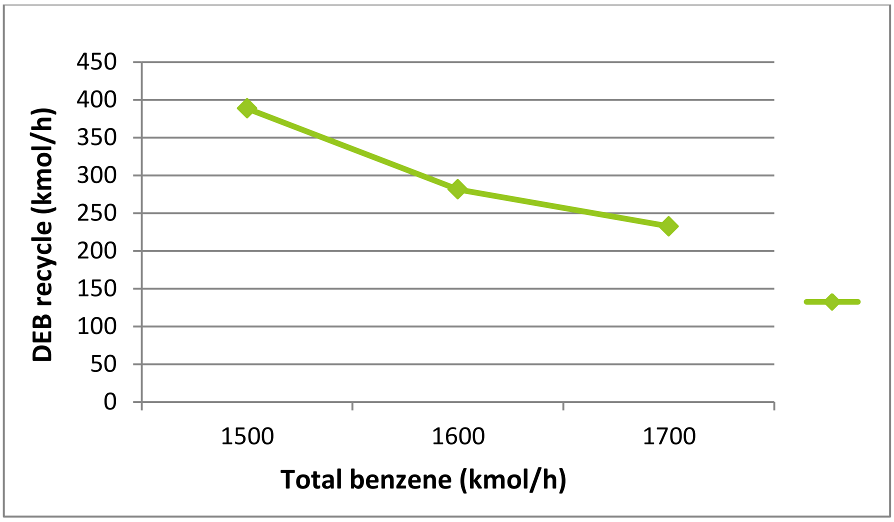

Figure3.3 Effect of benzene recycles and reactor size on Di-ethylbenzene recycle

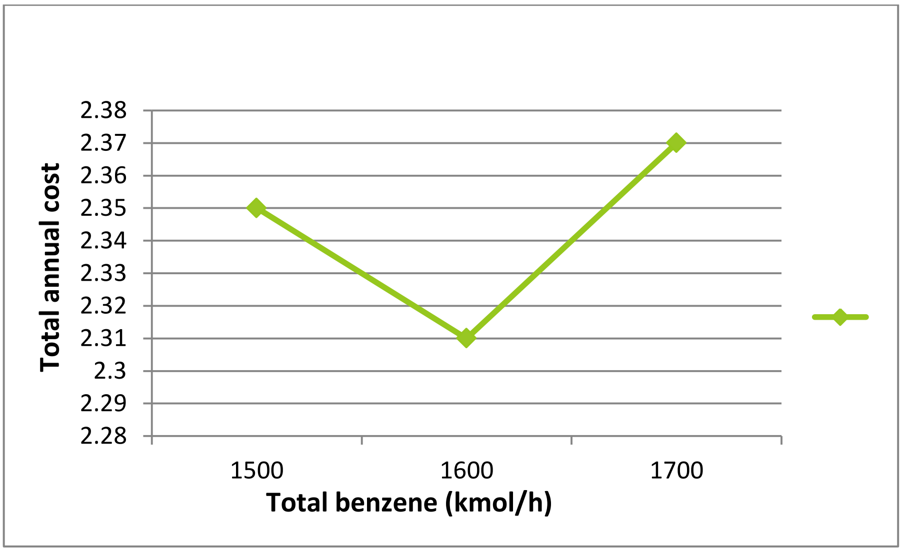

Figure 3.4 Effect of benzene recycles and reactor size on total annual cost.

Volume of reactor =250 m^3

Table 3.7 Effects of Reactor Size and Recycle for 250 m^3

total benzene(kmol/h)	1400	1450	1500
DEB recycle (kmol/h)	392.1	318	275.9
reactor temperature 1 (K)	426	426	427
column diameter 1 (m)	4.51	4.53	4.61
reboiler duty 1 (10^6 cal/s)	1.84	1.85	1.86
condenser duty 1 (10^6 cal/s)	3.29	3.36	3.44
column diameter 2 (m)	5.86	5.78	5.69
reboiler duty 2 (10^6 cal/s)	2.63	2.51	2.45
condenser duty 2 (10^6 cal/s)	2.99	2.87	2.80
total energy cost (Rs45*10^6/year)	0.695	0.674	0.767
total capital cost (Rs45*10^6)	4.97	4.95	4.95
total annual cost (Rs45*10^6/year)	2.39	2.36	2.45

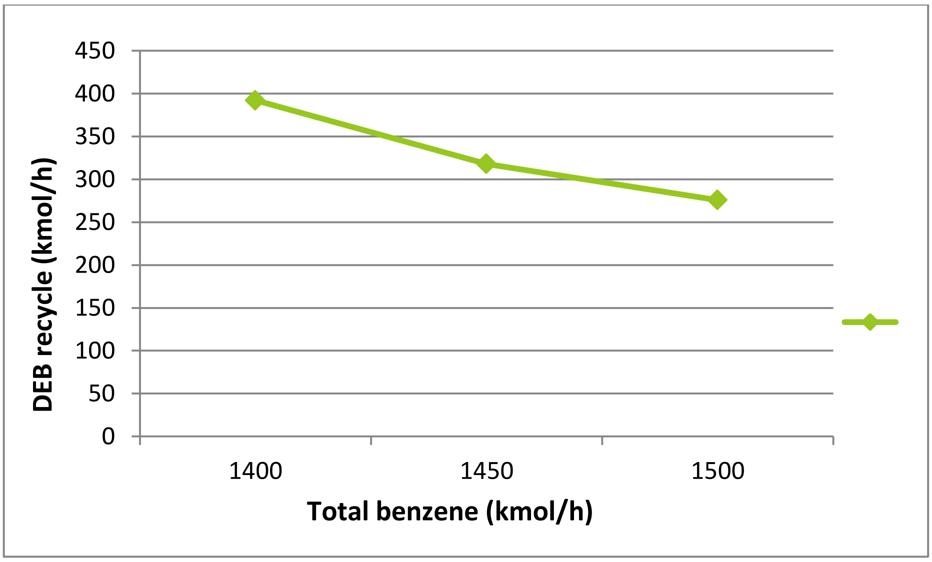

Figure 3.5 Effect of benzene recycles and reactor size on Di-ethylbenzene recycle

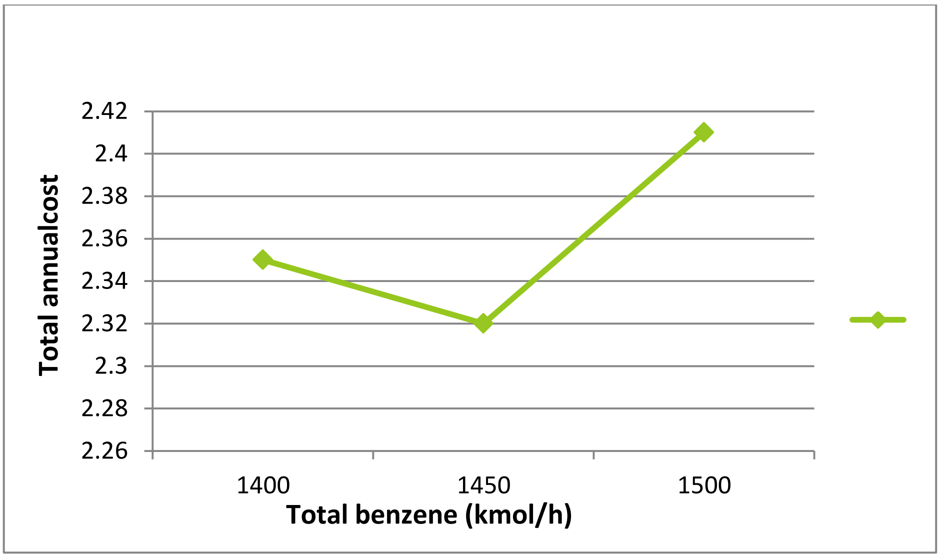

Figure 3.6 Effect of benzene recycles and reactor size on total annual cost.

CHAPTER 4

CONCLUSIONS

4. CONCLUSIONS

In the optimization process, the main emphasis was given on saving cost of raw materials rather than saving energy and capital costs. The ethylbenzene process exhibits an interesting design feature in terms of the engineering trade-offs. The basic components of the ethylbenzene process are the reactor and the distillation column. Optimization in the reactor section was conducted and it was found that increase in the reactor size lower reactor temperatures, better EB selectivity, and lower DEB recycle flow rates. Increasing benzene recycle give better ethylbenzene selectivity and lower Di-ethyl benzene recycle, but separation cost is increase. Therefore depending on the requirement of a particular industry it could be modified to provide the desired result.

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