CHAPTER IV

HDA PROCESS

4.1 Process Description

The hydrodealkylation HDA of toluene process (Alternative1) by Douglas (1988) on conceptual design as in Figure 4.1 contain nine basic unit operations: reactor, furnace, vapor-liquid separator, recycle compressor, two heat exchangers, and three distillation columns. Two raw materials, hydrogen, and toluene, are converted into the benzene product, with methane and diphenyl produced as by-products. The two vapor-phase reactions are

$$\text{Toluene} + H_2 \rightarrow \text{benzene} + CH_4$$

$$2\ \text{Benzene} \leftrightarrow \text{diphenyl} + H_2$$

The kinetic rate expressions are functions of the partial pressure (in psia) of toluene p_T, hydrogen p_H, benzene p_B, and diphenyl p_D, with an Arrhenius temperature dependence. Zimmerman and York (1964) provide the following rate expression:

$$r_1 = 3.6858 \times 10^6 \exp(-25616/T)\ p_T\ p_H^{1/2}$$

$$r_2 = 5.987 \times 10^4 \exp(-25616/T)\ p_B^2 - 2.553 \times 10^5 \exp(-25616/T)\ p_D\ p_H$$

Where r_1 and r_2 have units of lb.mol/(min.ft^3) and T is the absolute temperature in Kelvin. The heats of reaction given by Douglas (1988) are –21500 Btu/lb.mol of toluene for r_1 and 0 Btu/lb.mol for r_2.

The effluent from the adiabatic reactor is quenched with liquid from the separator. This quenched stream is the hot-side feed to the process-to-process heat exchanger, where the cold stream is the reactor feed stream prior to the furnace. The reactor effluent is then cooled with cooling water and the vapor (hydrogen, methane) and liquid (benzene, toluene, diphenyl) are separated. The vapor stream from the separator is split and the remainder is sent to the compressor for recycle back to the reactor.

The liquid stream from the separator (after part is taken for the quench) is fed to the stabilizer column, which has a partial condenser component. The bottoms stream from the stabilizer is fed to the product column, where the distillate is the benzene product from the process and the bottoms is toluene and diphenyl fed to the recycle column. The distillate from the recycle column is toluene that is recycled back to the reactor and the bottom is the diphenyl byproduct.

Makeup toluene liquid and hydrogen gas are added to both the gas and toluene recycle streams. This combined stream is the cold-side feed to the process-to-process heat exchanger. The cold-side exit stream is then heated further up to the required reactor inlet temperature in the furnace, where heat is supplied via combustion of fuel.

Six alternatives HENs for the HDA process had been generated (Terril and Douglas, 1987). Alternative 1 has simply an enlarged FEHE (Tables 4.1 to 4.4 contain data for selected process streams, Table 4.5 presents equipment data and Table 4.6 compiles the heat transfer rates within process equipment). Alternative 2 is the same as Alternative1, expect the recycle column is pressure shifted to be above the pinch temperature, and the condenser for the recycle column is used to drive the product column reboiler. All of the other alternatives also include this pressure shifting. In Alternative 3, the reactor effluent is used to drive the stabilizer column reboiler, whereas in Alternative 4 the reactor effluent is used to drive the product column reboiler. For Alternative 5, the reactor effluent stream is used to drive both the stabilizer column reboiler and the product column reboiler consecutively. Alternative 6 is the most complex one, since it consists of three FEHEs and all the reboilers in the three columns are driven by the reactor effluent stream.

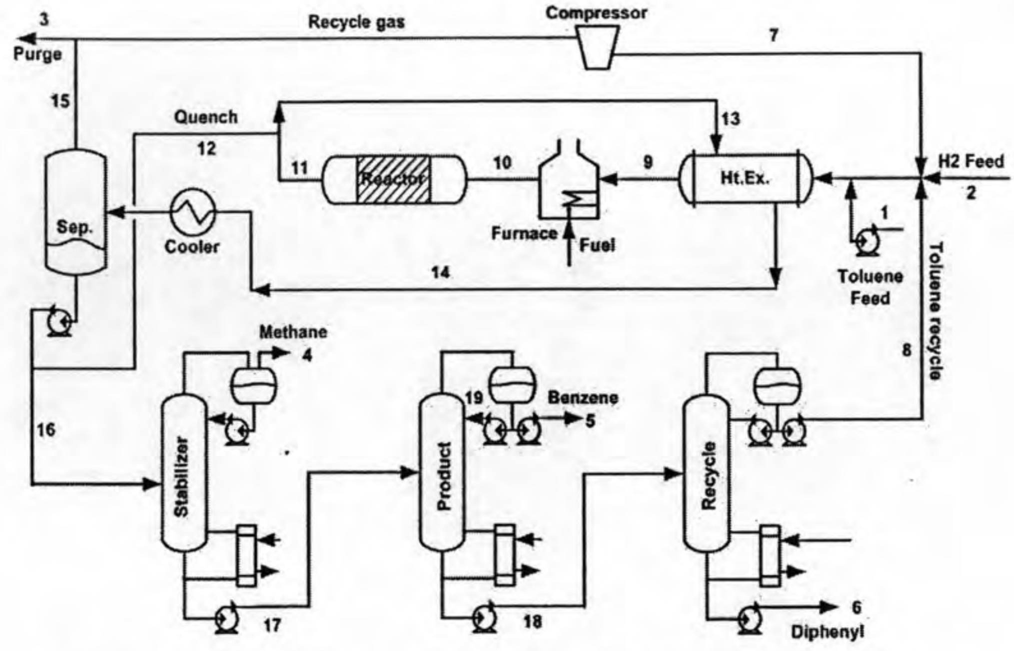

Figure 4.1: Hydrodealkylation of toluene process (alternative1)

The benefit obtained from energy integration with the base case flowrate for the six alternatives is given in Table 4.7. The energy saving from the energy integration fall between 29 and 43 %, but the cost saving are in the range from -1 to 5 %. The cost saving are not as dramatic the raw material costs dominate the process economics.

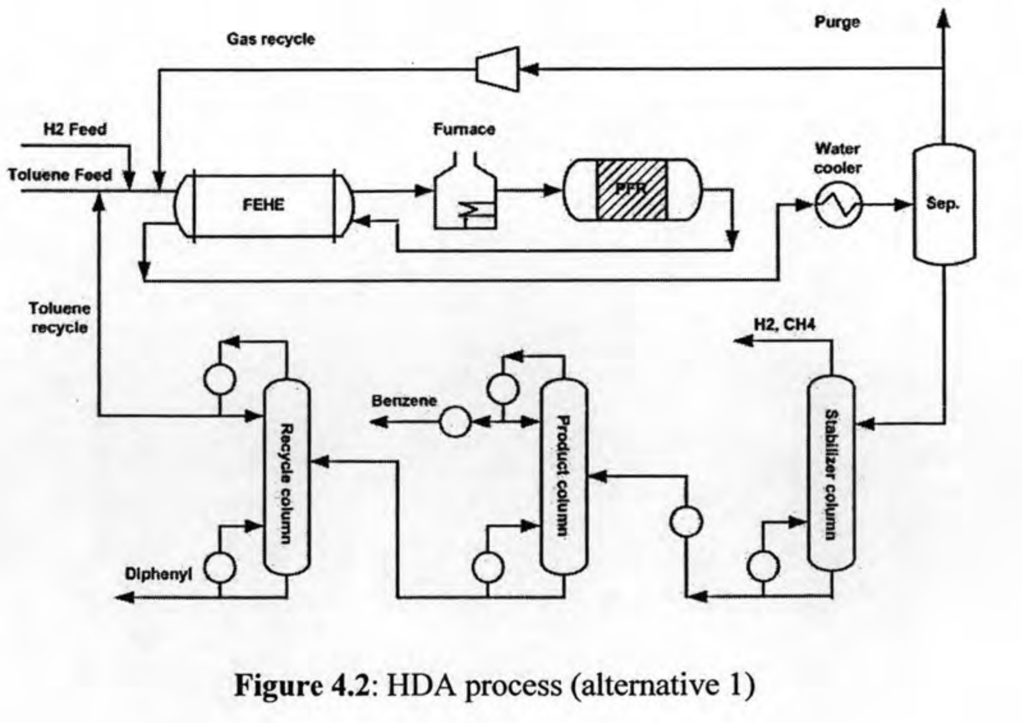

Figure 4.2: HDA process (alternative 1)

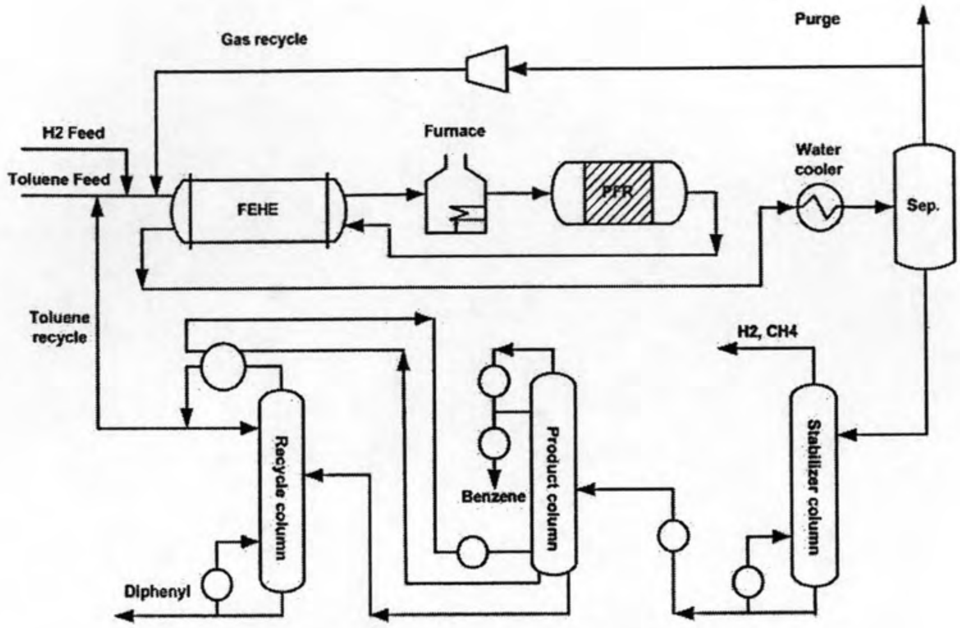

Figure 4.3: HDA process (alternative 2)

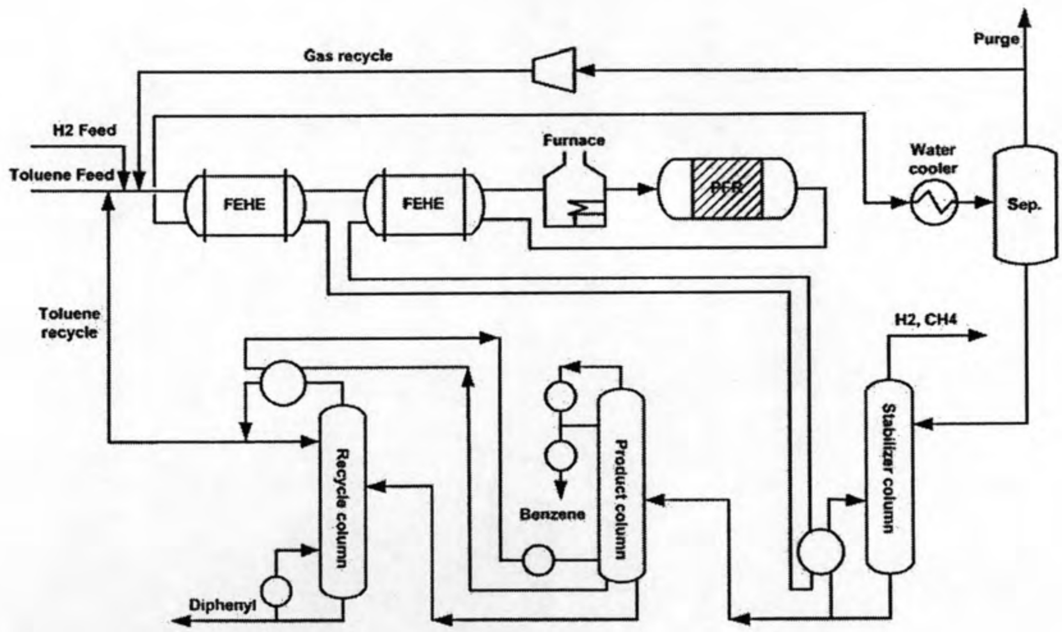

Figure 4.4: HDA process (alternative 3)

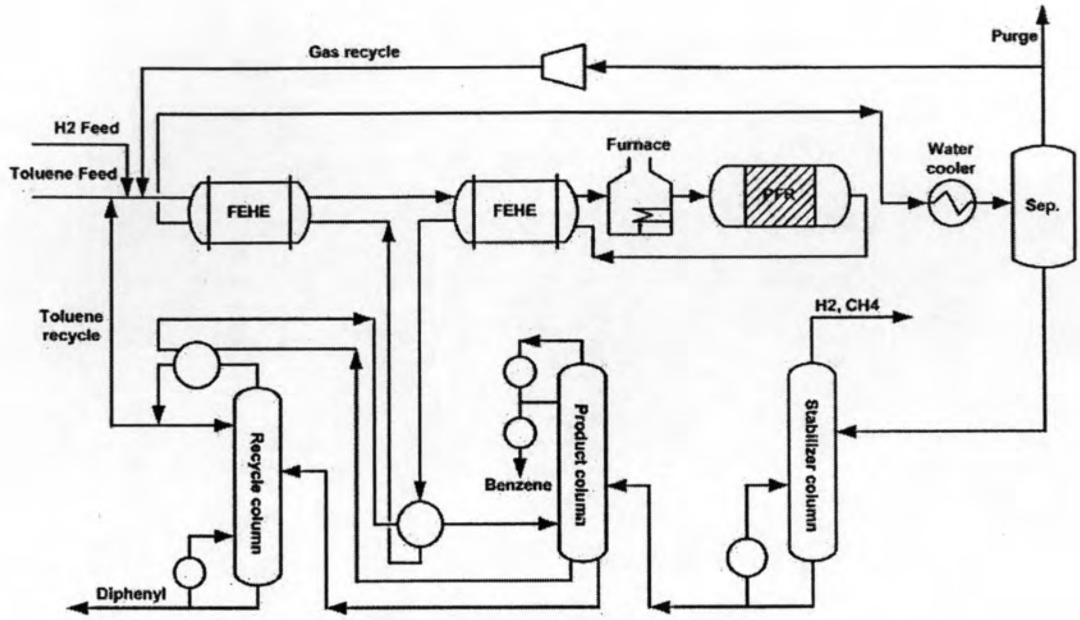

Figure 4.5: HDA process (alternative 4)

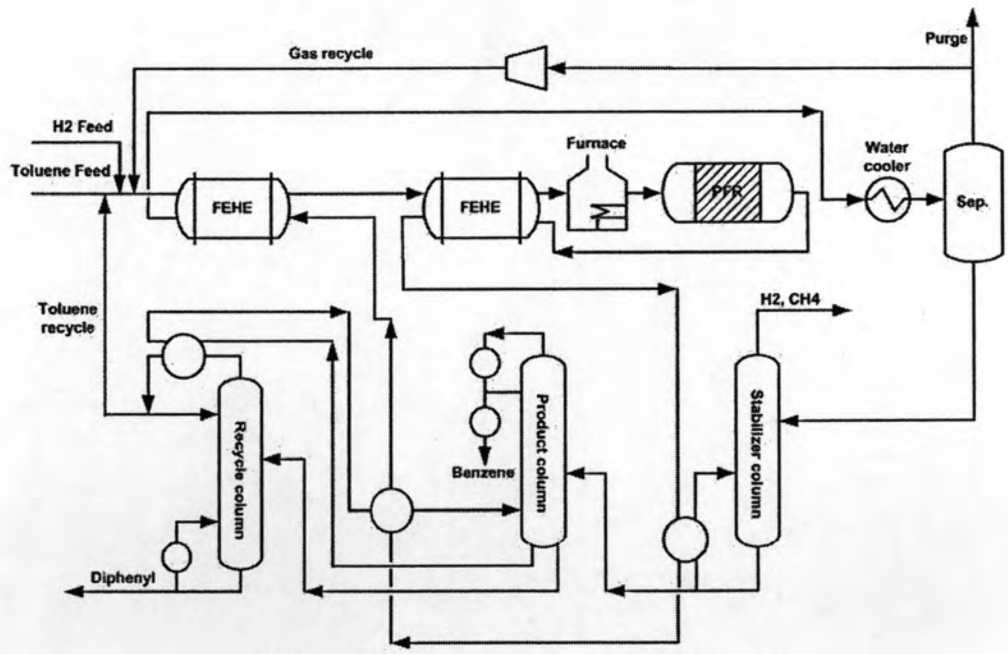

Figure 4.6: HDA process (alternative 5)

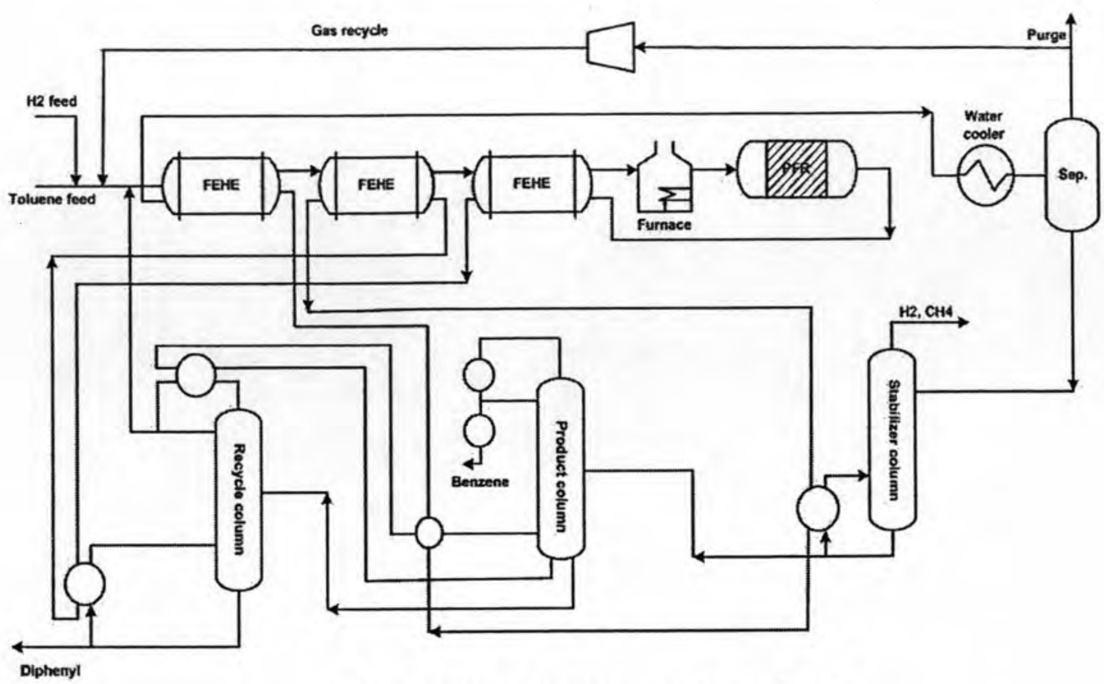

Figure 4.7: HDA process (alternative 6)

Table 4.1 Process stream data, part 1

	Fresh toluene	Fresh hydrogen	Purge gas	Stabilizer gas	Benzene product	Diphenyl Product
Stream number	1	2	3	4	5	6
Flow (lb.mol/h)	290.86	490.38	480.88	21.05	272.5	6.759
Temperature (^{o}F)	86	86	115	113	211	559
Pressure (psia)	575	575	480	480	30	31
H_2, mole fraction	0	0.97	0.3992	0	0	0
CH_4	0	0.03	0.5937	0.9349	0	0
C_6H_6	0	0	0.0065	0.0651	0.9997	0
C_7H_8	1	0	0.0006	0	0.0003	0.00026
$C_{12}H_{10}$	0	0	0	0	0	0.99974

Table 4.2 Process stream data, part 2

	Gas recycle	Toluene recycle	Furnace inlet	Reactor inlet	Reactor effluent	Quench
Stream number	7	8	9	10	11	12
Flow (lb.mol/h)	3519.2	82.14	4382.5	4382.5	4382.5	156.02
Temperature (^oF)	115	272	1106	1150	1263.2	113
Pressure (psia)	513	30	513	503	486	486
H_2, mole fraction	0.3992	0	0.4291	0.4291	0.3644	0
CH_4	0.5937	0	0.4800	0.4800	0.5463	0.0515
C_6H_6	0.0065	0.00061	0.0053	0.0053	0.0685	0.7159
C_7H_8	0.0006	0.00037	0.0856	0.0856	0.0193	0.2149
$C_{12}H_{10}$	0	0.00002	0	0	0.0015	0.0177

Table 4.3 Process stream data, part 3

	FEHE Hot in	FEHE Hot out	Separator Gas out	Stabilizer feed	Stabilizer bottoms	Product bottoms
Stream number	13	14	15	16	17	18
Flow (lb.mol/h)	4538.5	4538.5	4156	382.5	361.4	88.91
Temperature (^oF)	1150	337	113	113	200	283
Pressure (psia)	486	480	486	480	480	33
H_2, mole fraction	0.3518	0.3518	0.3992	0	0	0
CH_4	0.5294	0.5294	0.5397	0.0515	0	0
C_6H_6	0.0907	0.0907	0.0065	0.7159	0.7538	0.0006
C_7H_8	0.0260	0.0260	0.0006	0.2149	0.2275	0.9234
$C_{12}H_{10}$	0.0021	0.0021	0	0.0177	0.0187	0.0760

Table 4.4 Process stream data, part 4

	Product column reflux	Recycle column reflux
Stream number	19	20
Flow (lb.mol/h)	300	12
Temperature (^oF)	211	272
Pressure (psia)	30	30
H_2, mole fraction	0	0
CH_4	0	0
C_6H_6	0.9997	0.00061
C_7H_8	0.0003	0.99937
$C_{12}H_{10}$	0	0.00002

4.2 Plantwide control strategies

Step1. Establish Control Objectives

For this process, the essential is to produce pure benzene while minimizing yield losses of hydrogen and diphenyl. The reactor feed ratio of hydrogen to aromatics must be greater than 5:1. The reactor effluent gas must be quenched to 1150 °F

Step 2. Determine Control Degree of Freedom

There are 23 control degrees of freedom. They include; two fresh feed valves for hydrogen and toluene, purge valve, separator base and overhead valves, cooler cooling water valve, liquid quench valve, furnace fuel valve, stabilizer column steam, bottoms, reflux, cooling water, and vapor product valves; product column steam, bottoms, reflux, distillate, and cooling water valves; and recycle column steam, bottoms, reflux, distillate, and cooling water valves.

Step 3. Establish Energy management system

The product benzene is produced from the exothermic reaction between hydrogen and toluene at 1158 °F. The reactor operates adiabatically, so for a given

Table 4.5 Equipment data and specifications

Unit operation	Property	Size
Reactor	Diameter	9.53 ft
	Length	57 ft
FEHE	Area	30000 ft^2
	Shell volume	500 ft^3
	Tube volume	500 ft^3
Furnace	Tube volume	300 ft^3
Separator	Liquid volume	40 ft^3
Stabilizer column	Total theoretical trays	6
	Feed tray	3
	Diameter	4.3 ft
	Reflux drum liquid holdup	7 ft^3
	Column base liquid holdup	250 ft^3
Product column	Total theoretical trays	27
	Feed tray	15
	Diameter	5 ft
	Theoretical tray holdup	2.1 lb.mol
	Efficiency	50%
	Reflux drum liquid holdup	25 ft^3
	Column base liquid holdup	30 ft^3
Recycle column	Total theoretical trays	7
	Feed tray	5
	Diameter	3 ft
	Theoretical tray holdup	1 lb.mol
	Efficiency	30%
	Reflux drum liquid holdup	100 ft^3
	Column base liquid holdup	15 ft^3

Table 4.6 Heat transfer rates

Unit Operation	Power (MW)
FEHE	19.400
Furnace	0.984
Separator condenser	5.470
Product reboiler	2.180
Product condenser	2.050
Recycle reboiler	0.439
Recycle condenser	0.405
Reactor heat generation	1.830

Table 4.7 Energy integration for HDA process

	Base case	Alternatives					
		1	2	3	4	5	6
1. TAC ($\$10^6$/yr), base case flows	6.38	6.4	6.45	6.38	6.11	6.04	6.03
2. Utilities usage (MW), base case flows	12.7	9.06	7.68	7.34	7.30	7.30	7.30
3. Energy saving (%)		29	40	42	43	43	43
4. Cost saving (%)		-0.3	-1	0	4	5	5

reactor design the exit temperature depends upon the heat capacities of the reactor gases, reactor inlet temperature, and reactor conversion. Heat from the adiabatic reactor is carried in the effluent stream and is not removed from the process until it is dissipated to utility in the separator cooler.

Energy management of reaction section is handled by controlling the inlet and exit streams temperature of the reactor for preventing the benzene yield decreases from the side reaction. In the reference control structure, quenched stream is used for control temperature at the design value and for saving cost from the cooling utility. However, this method makes the path of disturbance propagation to the separation section, so the product purity control must be tighter because of component inventories changing. The alternative way is using of the heuristic laws; Montree (2000) introduces about the energy management that "Decreasing the effect of heat integration in the process can be done by remove the energy as much as possible". Therefore, the cooling utility should be used for controlling the reactor exit temperature and preventing the disturbance propagation to the separation section as the second control structure. Another energy control loop is using of the cooling utility for removing excess heat from the heat exchanger to reach the optimal temperature in the separator.

Step 4. Set Production Rate

There are not constrained to set production either by supply or demand, then the production rate can be set by benzene production. Considering of the kinetics equation is found that the three variables alter the reaction rate; pressure, temperature and toluene concentration which is the limiting agent.

- Pressure control of the compressor operates at maximum capacity for yield purposes.
- Reactor inlet temperature is controlled by specify the reactant fresh feed rate and reactant composition into the reactor. The reactor inlet temperature is constrained below 1300 °F for preventing the cracking reaction that produces undesired byproduct.
- Toluene inventory can be controlled in two ways. First, liquid level at the top of recycle column is measured to change toluene feed flow as the reference control structure. Second, toluene flow in the system is measured for control amount of toluene feed flow as the first control structure. The second way gives the less process time constant than the first, then the response of the first control structure faster than reference control structure.

Step 5. Control Product Quality and Handle Safety, Operational, and Environmental Constraints

Benzene purity must be maintained at 99.97% for this research. Any methane that leaves in the bottoms of the stabilizer column contaminates the benzene product. The separation in the stabilizer column prevents the problem by using a temperature to set column stream rate (boilup). Toluene in the overhead of the product column also affects benzene quality. Benzene purity can be controlled by manipulating the column steam rate (boilup) to maintain temperature in the column.

Step 6. Control Inventories and Fix a Flow in Every Recycle Loop

In most processes a flow control should be present in all recycle loops. This is a simple and effective way to prevent potentially large changes in recycle flows, while the process is perturbed by small disturbance. We call this high sensitivity of the recycle flowrates to small disturbances the "snowball effect". There are two recycle control loops in this research; reference control structure and the first control structure.

Four pressures and seven liquid levels must be controlled in this process. For the pressures, there are in the gas loop and in the three distillation columns. In the gas loop, the separator overhead valve is opened and run the compressor at maximum gas recycle rate to improve yield so the gas loop control is related to the purge stream and fresh hydrogen feed flow. In the stabilizer column, vapor product flow is used to control pressure. In the product and recycle columns, pressure control can be achieved by manipulating cooling water flow to regulate overhead condensation rate.

For liquid loops, there are a separator and two (base and overhead receiver) in each column. The most direct way to control separator level is with the liquid flow to the stabilizer column. The stabilizer column overhead level is controlled with cooling water flow and base level is controlled with bottoms flow. In the product column, distillate flow controls overhead receiver level and bottoms flow controls base level. In the recycle column, the first control structure the total toluene flow to control level, while the reference control structure use the fresh toluene feed flow to control level. The base level of recycle column is controlled by manipulating the column steam flow because it has much larger effect than bottoms flow.

Step 7. Check Component Balances

Component balances control loops consists of:

- Methane is purged from the gas recycle loop to prevent it from accumulating and its composition can be controlled with the purge flow.
- Diphenyl is removed in the bottoms stream from the recycle column, where steam flow controls base level.
- The inventory of benzene is accounted for by temperature and overhead receiver level control in the product column.
- Toluene inventory is accounted for by level control in the recycle column overhead receiver.
- Gas loop pressure control accounts for hydrogen inventory.

Step 8. Control Individual Unit Operations

The rest degrees of freedom are assigned for control loops within individual units. These include:

- Cooling water flow to the cooler controls process temperature to the separator.
- Refluxes to the stabilizer, product, and recycle columns are flow controlled.

Step 9. Optimize Economics or Improve Dynamic Controllability

The basic regulatory strategy has now been established. Some freedom is used to select several controller set points to optimize economics and plant performance. Such as, the set point for the methane composition controller in the gas recycle loop must balance the trade-off between yield loss and reactor performance. Reflux flows to the stabilizer, product, and recycle columns must be determined based upon column energy requirement and potential yield losses of benzene (in the overhead of the stabilizer and recycle columns) and toluene (in the base of the recycle column).

4.3 Steady-State Modeling

First, a steady-state model is built in HYSYS.PLANT, using the flowsheet and equipment design information, mainly taken from Douglas (1988) and Luyben et al. (1998) in above tables. For our simulation, Peng-Robinson model is selected for physical property calculation because of its reliability in predicting the properties of most hydrocarbon-based fluids over a wide range of operating conditions. The reaction kinetics of both reactions are modeled with standard Arrhenius kinetic expressions available in HYSYS.PLANT, and the kinetic data are taken from Luyben et al. (1998). Since there four material recycles, four RECYCLE operations are inserted in the streams, Hot-In, Gas-Recycle, Quench, and Stabilizer-Feed. Proper initial value should be chosen for these streams, otherwise the iterative calculations might converge to another steady-state due to the non-linearity and unstable characteristics of the process. When the columns are modeled in steady-state, besides the specification of inlet streams, pressure profiles, number of trays and feed tray, two specifications need to be given for columns with both reboiler and condenser. These could be the duties, reflux rate, draw stream rates, composition fractions, etc. We chose reflux ratio and overhead benzene mole fraction for the stabilizer column. For the remaining two columns, bottom and overhead composition mole fractions are specified to meet the required purity of products given in Douglas (1988). The tray sections of the columns are calculated using the tray sizing utility in HYSYS, which calculates tray diameters, based on Glitsch design parameters for valve trays. Though the tray diameter and spacing, and weir length and height are not required in steady-state modeling, they are required for dynamic simulation.