



CHAPTER IV

MONOISOPROPYLAMINE PROCESS

4.1 Introduction

Monoisopropylamine is one of most important manufacturing in pharmaceutical industries. The mono-isopropylamine process contains of multi-unit operations; heat exchanger, vaporizer, flash tank, heater, cooler, adiabatic plug flow reactors and three distillation columns. Fresh feed streams of isopropyl alcohol and ammonia are introduced into the process. The desired products are MIPA and water.

4.2 Reaction Kinetics

Monoisopropylamine is usually produced from reaction of isopropyl alcohol (IPA) with ammonia. The reaction is endothermic vapor-phase, which required to high dew point temperature.

The main reaction:



(Isopropyl alcohol) (Ammonia) (Monoisopropylamine) (Water)

There is also a sequential reaction of MIPA and IPA to form di-isopropylamine (DIPA):



(Isopropyl alcohol) (Monoisopropylamine) (Di-isopropylamine) (Water)

An additional reversible reaction is:



(Diisopropylamine) (Ammonia) (Monoisopropylamine)

Model formulation this research, kinetic parameters for monoisopropylamine following as Table 4.1

Table 4.1: Reaction Kinetics (Luyben, 2009)

Reaction	k	E(Btu/lbmol)	Concentration terms(kmol/m ³)
4.1	2.533×10^{13}	54000	$C_{IPA}C_{NH_3}$
4.2	1.086×10^{16}	67500	$C_{IPA}C_{MIPA}$
4.3 forward	8.530×10^{15}	67500	$C_{NH_3}C_{DIPA}$
4.3 reverse	8.530×10^{15}	67500	$(C_{MIPA})^2$

Overall reaction rates have units of $\text{kmol} \cdot \text{s}^{-1} \cdot \text{m}^{-3}$

4.3 Process Description

The monoisopropylamine process comprises of a tubular reactor and three distillation columns. There are both gas and liquid recycles. The liquid recycles are leaved ammonia distillation column and DIPA distillation column. Fresh feed streams of isopropyl alcohol and ammonia are introduced into the process. The desired products are MIPA and water byproduct. An undesirable byproduct of diisopropylamine (DIPA) is also produced and recycled to disappearance since its formation reaction is reversible. An excess of ammonia in the reactor restrain the DIPA reaction, so ammonia is also recycled in the reactor.

The mixture is fed to a heat exchanger (FEHE) that restore some energy from the hot reactor effluent stream, which result in a heat-transfer area of 1375 ft² to transfer $4.94 \times 10^6 \text{ Btu} \cdot \text{h}^{-1}$. The preheated streams is fed to a vaporizer along with two gas recycle stream, which two gas recycles consist gas recycle from flash tank and vent gas from ammonia distillation column. The vaporizer operates at 345 psia and produce vapor at its dew point and before fed to a reactor preheat to 158.3 °C using heater. The reactor is exothermic. With an inlet temperature of 158.3 °C, the exit temperature T_{out} is 174.3 °C

The reactor effluent is cooled and partially condensed in the FEHE before going to a condenser in which it is cooled to 60 °C using cooling water. The two-phase stream from the heat exchanger is fed to a flash tank. In the flash tank, vapor

flow is feedback to reactor and liquid flow is fed into the ammonia distillation column. The ammonia column (C1) has 12 stages and is fed on stage 6, the operating pressure is 300 psia and design condenser temperature is 60 °C. The ammonia column (C1), vent rate is 3.72 kgmole/hr., bottom flow is fed to MIPA product column (C2). The MIPA product column (C2) has 22 stages and is fed on stage 10, the operating pressure is 30 psia and design condenser temperature is 62.3 °C. The monoisopropylamine product is removed as the distillate product (C2) and base column DIPA is sent to the DIPA recycle column (C3). The distillate from ammonia column (C1) is recycling back to reaction section and mixed with fresh feed ammonia. This vent from ammonia column recycles backs to mix with gas recycle from flash tank. The bottom column (C1), heavy key component (MIPA, water and DIPA) is fed to MIPA product column (C2). The bottom column (C2) is fed to the DIPA recycle column C3. This column C3 is removes the light key components (DIPA and IPA); the distillate is recycled back to the reaction section. The bottom column is used to remove the heavy key component (water) by-product.

4.4 Phase Equilibrium

The Three columns are required the removal of ammonia at column 1, water at column 2 and MIPA product at column 2. The NRTL physical property package is used in this study. The normal boiling point of ammonia, MIPA, IPA, DIPA and water are -14.0, 44.5, 54.0, 91.5 and 105.9 °C respectively. The components that must be separate in the system are relatively easy to separates by the distillation columns. Note that the boiling point of IPA and DIPA are very close to the IPA recycles entering the reactor with recycle DIPA in the column 3.

4.5 Flow Sheet

Figure1. Shows the flow sheet of the MIPA process with the equipment sizes and condition that are the economic optimum, as discussed in the next section. The fresh feed of IPA is set 45.36 kgmole/hr. and feed ammonia 45.31 kgmole/hr..

4.6 Reaction and column

The fresh feed (ammonia and IPA) to pre-heat in a vaporizer is fed to reactor a vapor phase. Inlet temperature reactor is 158.3 °C, the exit temperature T_{out} is 174.3 °C. The reactor is gas-phase tubular reactor operation adiabatic, spec reactor is aspect ratio $L/D = 10$. The resulting reactor size is not unreasonably large (2458 ft². with a diameter of 6.8 ft.). The reactor is exothermic.

Column 1, ammonia recycle column (C1): The column has 12 stages and fed on stages 6, which is the optimum feed stages to minimize reboiler heat input. The operation pressure is 300 psia. A partial condenser is used with a small vent stream. The Reflux ratio (RR) is 0.347. The design specification in the condenser is a temperature of 60 °C, so cooling water can be used in the condenser. The distillate is mostly ammonia and MIPA that are in the liquid from the flash drum. The basecase show in Figure1 is the optimum economic design, which corresponds to a total ammonia flowrates 300 lbmole/hr. The design specification is to keep ammonia from dropping out the bottom and distillate of the downstream column. Since the specified MIPA purity 99%, a very small ammonia composition in the bottom 0.0005 is required and distillate 99%mol ammonia. The column diameter is 2.79 ft., and the reboiler heat input (QR1) is 4.785×10^6 Btu/hr. Both of these increase if more ammonia recycle is used.

Column 2, MIPA product column (C2): This column has 22 stages and fed on stage 10. The operation pressure is 30 psia. It is composition 99 %mole monoisopropylamine (MIPA) with small amounts of IPA and a temperature 63.0 °C. The reflux ratio (RR) is 1.6. Energy consumption QR2 is 0.994×10^6 Btu/hr., and the column diameter is 2.47 ft. The design specification is to attain high-purity MIPA in the distillate and minimize the loss of MIPA in the bottom, 0.1 %mole MIPA impurity in the bottom.

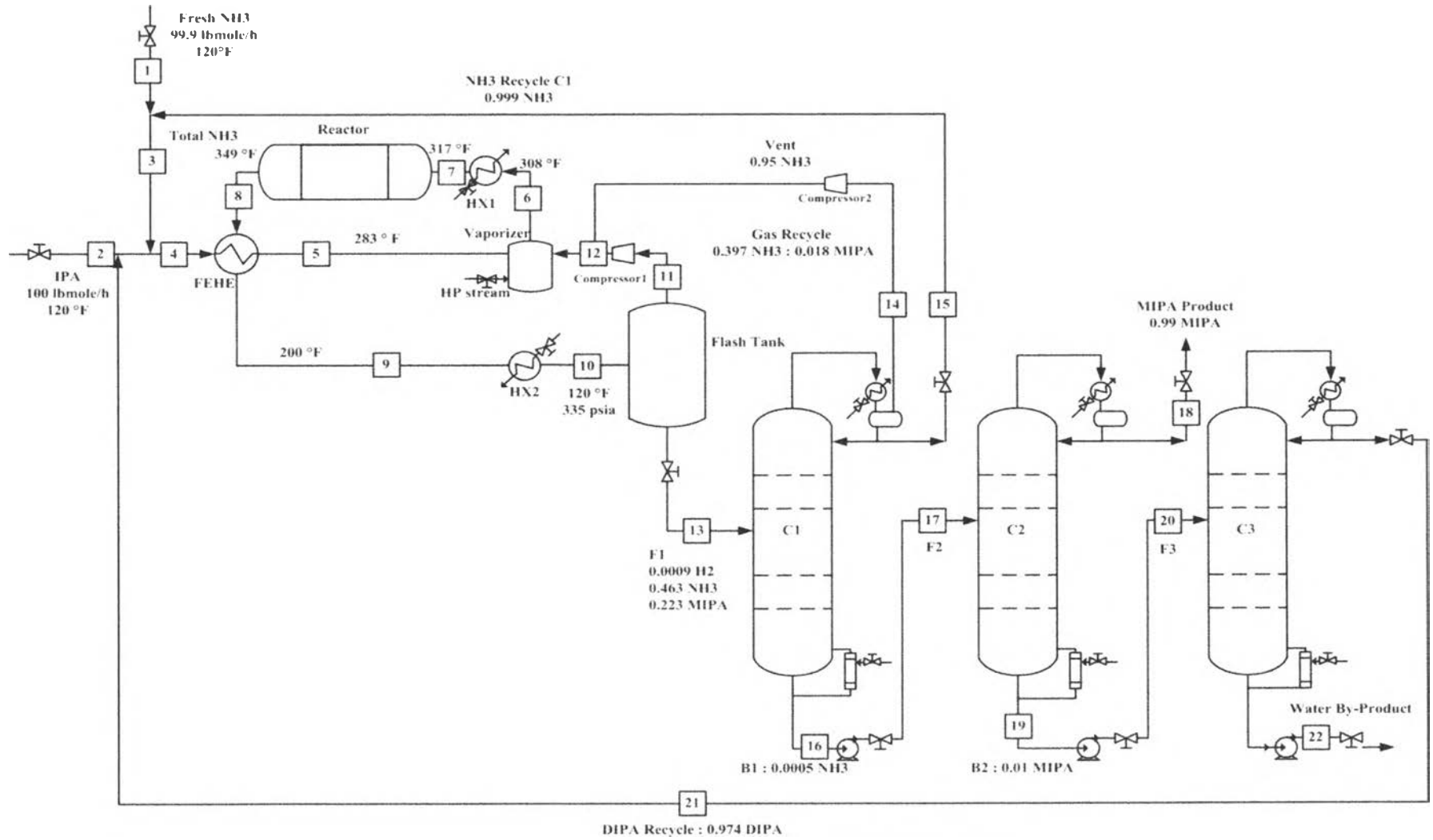


Figure 4.1: Flow sheet for monoisopropylamine process (Base Case),Luyben,2009

Column 3, DIPA product column (C3): This column has 52 stages and fed on stage 12. The operation pressure is 5 psia, which gives a reflux-drum temperature 62.0 °C. The reflux ratio (RR) is 4.88. Energy consumption QR2 is 0.994×10^6 Btu/hr. and the column diameter is 4.25 ft. The design specification 1 %mole water impurity in the distillate and 0.1 %mole DIPA impurity in the bottom. Notice that the column is operating under vacuum to maximize relative volatilities. Theoretical trays are assumed in all distillation columns, and capital costs are not adjusted for tray efficiencies.

4.7 Steady State Simulation of monoisopropylamine Process

The steady state simulation model is performed by using HYSYS with information and data collected from Luyben (2009). Appendix A provides the data and conditions for the unit operations which are involved in the process. The NRTL physical property package is used in the HYSYS simulations for its low pressure region which is suitable for monoisopropylamine process.

New control structures design procedure, Wongsri 2012

The design procedure is carried out in eight steps as follow:

Step 1: Gather relevant plant information and control objective including constraints for control. Before initiating work on the control structure design, is it necessary to obtain all information relevant to process control. The process objectives and constraints will determine the lower/upper bounds on the control variables as well as set points on quality variables.

Step 2: List manipulated variables (control degree of freedom, CDOF).

The CDOF can be obtained using the guideline given in table 4.2 and the guideline for pairing the controlled variables with the manipulated variables.

Table 4.2 Degree of freedom for simple units

Unit	DOF / unit
Independent stream	1
Heater, cooler, pump, and compressor	1
Heat exchanger with a by-pass stream	1
Adiabatic plug flow reactor	0
Non-adiabatic plug flow reactor	1
Adiabatic flash separator	2
Simple distillation column	5

Step 3: Establish fixture plant.

The principal idea of establishing a fixture plant is first to have an entire plant fluid-filled and a material-balanced. This idea is similar to creating *hydraulic* control structure proposed by Buckley [7]. It does not by all mean that all material balances control is managed at this step. Only the control loops conforming component balances are designed. In this step, we provide handles to regulate material flows and therefore eliminating the snowball effect or material accumulation. By establishing a fixture plant we mean creating a material-balanced process plant:

(3.1) Keep the materials entered and reentered fixed.

$$q_i(t) + q_r(t) = \text{constant} \quad (1)$$

This leaves the recycle streams free to adjust; one degree of freedom is added to the process.

If the composition of the recycle streams differ from the fresh feed stream significantly, each stream are separately controlled:

$$q_i(t) = \text{constant} \quad (2)$$

$$q_r(t) = \text{constant} \quad (3)$$

In this settlement, the flow of recycle stream cannot be used to regulate, e.g., the level of the reflux drum.

(3.2) Adjust the flow of exit material streams (products, by-products, and inert) according to their accumulations.

$$q_o(t) = q_i(t) - dq/dt \quad (4)$$

(3.3) Locate the quantifiers; i.e. the indicators of the representative accumulation, for the rest of the components and design the control loops to regulate their inventories in the plant. The quantifier can be volume (mass), pressure, or flow rate.

$$q_p(t) = -dq/dt \quad (5)$$

$$q_p(t) = \text{constant} \quad (6)$$

In retrospect, the material balances are checked in this step, since the control loops generated accomplish the plantwide material balances. Therefore, it is guaranteed the plantwide inventory will be regulated.

Step 4: Handling the disturbances.

In this step, the disturbances are handled by configuring the control loops employing the principle of disturbances management:

(4.1) Heat Disturbances

The Heat disturbance is divided into 2 categories. Heat Disturbance Category 1 (HDC1) is the heat disturbance that does not directly effect on product qualities. The heat disturbance in a process stream is usually rejected at a point before a reactor or separator by a heater or a cooler to maintain the stream temperature at its desired value. Heat Disturbance Category 2 (HDC2) is the heat disturbance that will affect the product qualities, such as heat disturbance in a process stream toward to a reactor or a separator. The disturbance is manipulated to regulate the composition.

(4.1.1) Direct the thermal disturbances that are not directly related to quality to the environment via the next and nearest exit points, usually heaters or coolers, to

(4.1.1) Direct the thermal disturbances that are not directly related to quality to the environment via the next and nearest exit points, usually heaters or coolers, to keep the thermal conditions of process stream fixed. The thermal condition of process stream is changed along the process plant, usually by heater or cooler of process to process heat exchanger.

(4.1.2) Manage the thermal disturbance that related to quality in order to maintain the product specification constraints.

(4.2) Material disturbances

The configuration of the control loops depend on the desired material pathways. The pathways can be obtained by analyzing the results of the material disturbance tests. The test is suggested to be done on the changing of composition, total flow, and component flow. The material disturbances can be generated at reactors and separators, besides coming with feeds and recycle streams. So if the feeds and recycle streams are fixed, the only places that alter the material (total or component) flow rates are the reactors and the separators. At reactor, its inlet temperature is adjusted in order to keep the reactor component flow rate or its composition in outlet stream. The decision of whether how to choose to control the component flow or the composition or not to control is based on the profit maximization or the smooth operation policies.

Since the distillation columns, usually the one-point control is common. To control top or bottom temperatures, depend on the material disturbance rejection policy.

Step 5: Design the control loops for the remaining control variables and/or adding enhanced controls, i.e. cascade, feed forward controls.

Step 6: Energy management via heat exchanger networks.

If potential heat exchanger networks or alternative heat integrated processes (HIPs) exist, list additional control variables and manipulated variables.

Step 7: Optimize economics and/or improve control performance. For example, the controls scheme/structure of the reactor (e.g. temperature/composition sensor location), the control scheme of the distillation column (e.g. reflux to feed ratio control), the optimal operating temperatures of the reactors, the recycle flow rates, the sequence of separation, etc. If the opportunity of optimization exists, we might backtrack to the previous step as dictated.

Step 8: Validate the designed control structures by rigorous dynamic simulation. The measures can be costs, raw material and energy consumptions, control performances of the total plant or some selected loops, etc.